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Mining Meets Water – Conflicts and Solutions

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FOREWORD

The extraction of mineral resources is the foundation of a modern economy and society. Since the Middle Ages, mining has played an important role in the prosperity of Germany and Europe. However, this prosperity is not without consequences as mining has altered the natural conditions of both landscapes and environments.

Water resources have been significantly affected, for example, by acid mine drainage and by the release of pollutants from mine leachates. It is therefore important to protect the environment and the surrounding ground and surface waters from the effects of mining. Furthermore, where mining takes place in regions with limited water resources, optimizing water consumption is essential in order to reduce competition for drinking water and agriculture. As well as a resource, water can also represent a threat to the safety of miners and the public, e.g. underground leaks or groundwater re-rise, which affects the geotechnical stability of mined ground.

In contrast to the risks and problems, recent developments show that mine water management creates opportunities to add value. Through selective extraction by enhanced separation technologies, valuable elements can be recovered from mine water. Especially in times of resource efficiency and raw material shortages, this recovery becomes more and more significant. Another promising field is using mine waters as a possible source of geothermal energy.

The International Mine Water Association (IMWA) deals with all these topics. The aim is to develop and investigate all issues in connection with mine waters through scientific and technological research. For this purpose, the international exchange between universities, research institutions and the industry is of great importance. IMWA is the most important international platform for connecting institutions in the field of mine water management. During the annual meetings, experts from around the world come together and present their latest research results and project experiences. The meetings take place at a different location every year, so that the hosts have the opportunity to draw attention to specific topics in their region or their particular expertise. The annual rhythm allows a frequent introduction and discussion of new trends and results.

This year, the annual meeting of the IMWA is held in Germany for the third time. We thank the IMWA for the possibility to host an annual meeting in Leipzig in the heart of the central German mining areas. Our aim was to highlight the jointly achieved successes in creating sustainable mining and post-mining landscapes, and also to present current projects in our mining regions of central Germany and Lusatia. For 25 years remediation has been performed in the region, particularly by the restoration company Wismut (remediation of legacies of uranium mining in the federal states Saxony and Thuringia) and LMBV (Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft, remediation of lignite open pits, dumps and pit lakes). This has produced many interesting and valuable insights and experiences, but at the same time, many questions as to the further development of the affected mining areas in future still exist. In particular, partners from research, industry and the German government have focused on the regional water balance of active mining and remediation industries. The results of years of experience are of international interest and can serve as a basis for further discussion, development and knowledge transfer.

The host of IMWA2016 is the Chair of Surface Mining at the Institute of Mining and Special Civil Engineering at the Technical University Bergakademie Freiberg. Since the establishment of the institute, the scientific exchange through international conferences and colloquia has been encouraged. The TU Bergakademie Freiberg, as a mining and resource university, is a widely recognized institution among mining experts. The co-host is Wismut GmbH, who this year looks back on 25 years of successful remediation of uranium mining in Saxony and Thuringia.

The importance of collaboration with other research groups is already apparent in the organization of IMWA2016. In addition to the host and co-host, numerous institutes and companies from the field of mine water management in central Germany are involved in organizing the IMWA2016 Annual Conference and thus contribute to its successful outcome. On behalf of the hosts and organizers, we therefore warmly welcome you to Leipzig and wish everyone an interesting and successful conference.

Best regards and Glückauf!

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TU Bergakademie Freiberg

Michael Paul
Wismut GmbH

CHAPTER 0

KEYNOTES

Rehabilitation of Water Resources induced by Large Scale Mining in Germany

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Extended Abstract

Lignite extraction by open cast mining in the Lausitz and Leipzig mining area has had a high impact on surface and subsurface water resources. During mining in 150 years, the water withdrawal from the groundwater layer resulted in a deficit of more than 13 bil. m³. Furthermore, the water quality deteriorated due to oxidation of pyrites minerals in the overburden. Finally, the ground water rise causes a lot of problems due to construction work done in the meantime not respecting the final ground water level. The overall aim of rehabilitation is to restore a stable, mostly self-regulating water balance in the area, as well on quantities as well on qualities.

Fast flooding of more than 50 big open mine pits with water from nearby rivers and mines allows economic stabilisation of pit slopes as well as water quality. An integrated water management system had been installed on technical as well as organisational basis.This water management consists of a large number of controlled in- and outlets, weir, pipes and monitoring wells. An innovative controlling and steering entity (Flutungszentrale Lausitz) had been installed. Surplus waters from rainfall are diverted for flooding mining lakes in the catchment area of river Spree, Schwarze Elster and Neiße. Furthermore, sophisticated working tools to predict short and long term effects had been developed. Modeling long term water balance (WBalMo) is carried out to use water streams on a daily basis. This steering committee is supervised by water authorities of the Länder in order to fulfill the EU water frame directive.

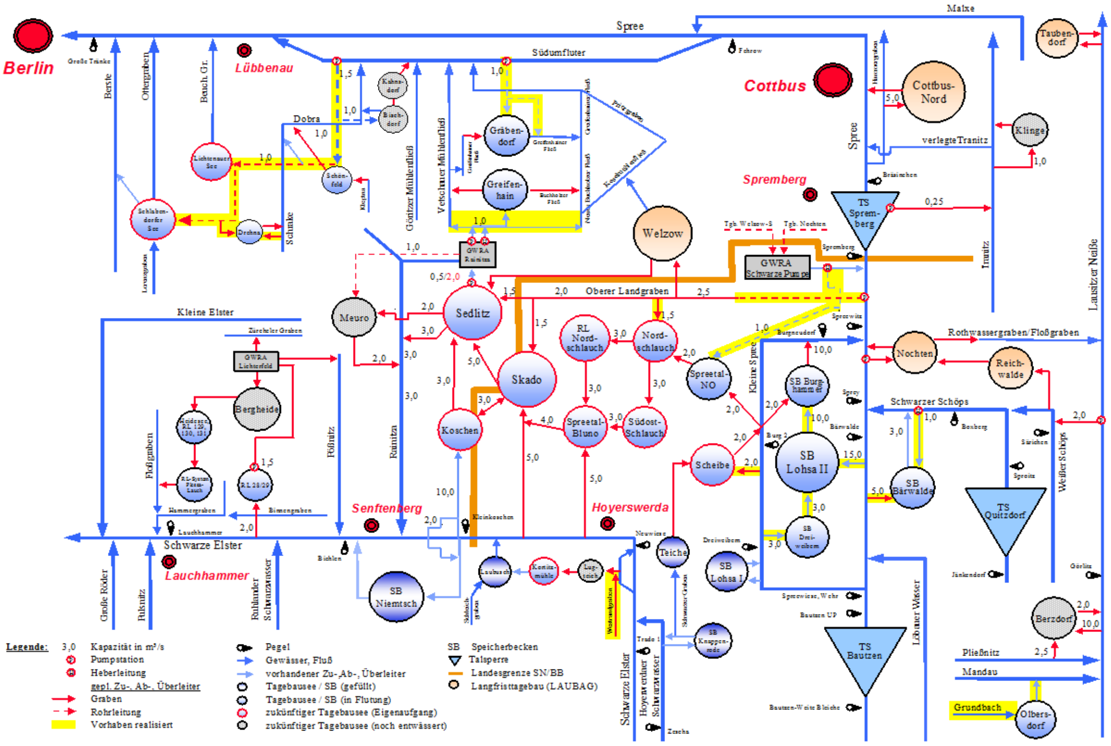

***Figure 1** Water management system in Lusatia*

Pit lakes and their run-off waters mostly do not meet the water quality requirement of discharge waters [1]. Hence, water treatment by chemical compensation as liming as well biological neutralization is carried out. Innovative liming technologies are developed with scientific support. A mobile treatment plant will treat the water by floating on the lake surface. Optimizing the liming process, the effectiveness on raw materials use has been pushed up. Further development work is carried out on test implementation with hydro carbonate buffering with CO_2 gas injection.

While mining on large scale ceased in this area, the ground water table rose in recent years. Water courses again are predominated by groundwater inflow. Large scale investigations have been carried out in order to detect the most important sources of iron contamination along the river Spree. Increased ferrous iron concentrations have been detected for example at highly permeable aquifers and the outflow of former bog areas. In order to remove iron from the Spree river water, various treatment units were designed and implemented. The concept for removing the iron followed the principles of simplicity in process, low cost design and minimal chemical additions. Water treatment plants are reused today as sedimentation ponds. Microbial treatment of groundwater shows good result significant by reducing iron and sulfate in the groundwater.

Key words: Water management system, iron hydroxides, sulfates, innovative treatment, removing iron techniques

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Progress and prospects of mine water management in the former East German Uranium Mining Province

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Extended Abstract

Uranium mining operations conducted from 1945 through 1990 in the East German uranium province had left behind mining legacies of unprecedented dimensions.

When designing holistic remediation concepts for five mine and two mill sites the mitigation of adverse impacts to downstream water courses was of key importance. Therefore, remedial work was focused on concentration, conditioning and encapsulation of solid mine waste to ensure the minimization of contaminant fluxes in the long run.

By the end of 2015 all mines have been decommissioned and chiefly flooded, while physical remedial work on mine dumps, tailings ponds and plant areas is to a large extent completed. Notwithstanding this, the operation of water treatment systems proved indispensable at six former production sites in the medium term to ensure compliance with protection goals for receiving streams and aquifers. During the period 2010-2015 total annual water treatment throughput amounted to approximately 20 million m^3.

Since long-term water management will continue to require the provision of considerable resources, optimisation of respective business procedures is one of Wismut’s key management tasks. Ongoing retrofitting of 1st generation treatment plants relies on changes in water quantity and quality, cost optimization, tightening of treatment standards, and advances in state-of-the-art technology. Projected adaptions in existing facilities are aimed first and foremost at improving uranium removal and optimizing residue disposal. Process combinations of ion exchange and fixed bed adsorption are under consideration as alternative technology to lime treatment. Smaller satellite plants are being operated by remote control and surveillance.

Geochemical long term processes, their prerequisites, boundary conditions and modes of action need further investigation across scales and levels in order to detect, harness and enhance potential NA-processes. In addition to uranium and Ra-226, the relevant spectrum of contaminants to be considered for long term mitigation primarily includes As, Fe and sulfate.

Waste or Resource? Extraction Potential from Acid Mine Drainage for Useful Resources

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Extended Abstract

Acid mine drainage could be a source of hydrogen, metals, and gypsum for energy and com-mercial products. For example, discharge from the Richmond Tunnel at Iron Mountain, California and the Reynolds adit at the Summitville mine, Colorado, each release between 30 and 200 metric tons per year of dissolved copper. For the period of 1994-2002, an estimated $6 million in copper and $14 million in iron was discharged from Iron Mountain. Instead of treating this drainage water with lime or limestone to produce an uneconomic sludge, the copper and other metals could be recovered and recycled into resources for commercial products. Currently a low-iron water near Breckenridge, Colorado, produces about 40,000 kg/yr of zinc by precipita-tion with sulfide and the insoluble material is shipped to a smelter to enrich the feed in zinc for better recovery. A demonstration plant removing high-purity gypsum from contaminated groundwater at a mining site in Arizona has been operating for more than 5 years. In China, removal of copper from an acid mine water by sulfide precipitation has also been found to be viable. The challenge is (1) to separate the valuable components from each other in a manner that is efficient and economically viable, (2) to stockpile components in an environmentally safe manner, and (3) to transport the separated components to an industry that can use them as source material for production. Every site must be assessed individually to ascertain what types of extraction, stockpiling, and transport are most appropriate.

Extraction techniques cover a wide variety including electrochemical, microbiological, evapora-tion, precipitation, solvent extraction, ion exchange, and reverse osmosis. Many of these techni-ques have been tried before with variable and usually limited success either from an economic or technical perspective. However, from the point of view of getting aqueous contaminants out of the environment and into recycled production, these technologies may be considered effecti-ve. With considerable emphasis on sustainable practices today, these techniques need to be evaluated and re-evaluated, improved, and further developed both alone and in combination for inactive and active mine sites.

Electrochemical techniques offer considerable versatility but can suffer from competing electro-de reactions and high energy demands depending on the type of cells used. Copper cementa-tion, which takes advantage of spontaneous electrochemical replacement of scrap iron by copper, is a very old, efficient, and inexpensive technique that could be used at Iron Mountain and Summitville and many other mine sites without applying electrical current. At many mine sites, tailings and/or waste-rock pile leachates could be run through a copper cementation or solvent extraction plant. With the application of current in specially designed electrochemical cells, hydrogen gas can be obtained as well as selective removal of metals depending on pH and composition of the solution. Fuel cells can be built based on iron oxidation and oxygen reduction.

Microbial bioreactors have been built for sulfate reduction to produce aqueous sulfide which can be used to precipitate metal sulfides. Recent investigations have shown that microbial sulfate reduction can be accomplished at relatively low pH (circa 3–4). The metal sulfides can then be transported to smelters for metal recovery. Bioreactors also oxidize dissolved ferrous iron and precipitate ferric iron. With careful control of pH, sulfate concentration, and ratios of ferrous to ferric iron, different iron phases can be precipitated that include schwertmannite, jarosite, goethite, and magnetite with variable recovery of other metals. In Canada, microbial degradation of thiocyanate and of the resulting ammonia and nitrate is working efficiently on a large scale to remove toxic components from gold extraction to meet regulatory discharge requirements.

New techniques combining electrochemistry and microbiology such as microbial electrolysis of water are opening up new avenues for potential application. This process of biocatalyzed electrolysis produces hydrogen at much lower applied voltages than normally required.

Every wastewater needs to be carefully considered with respect to the components that need to be removed, their marketability, and the energy and storage requirements. For each waste-water there may be an optimal sequence of extraction techniques that benefits the industry and the environmental concerns.

For inactive mines, the capital outlay for an optimal design could be expensive and difficult to fund but at least some return on the finances could be realized rather than the current situation of substantial remediation costs with no return of capital. However, for active or planned mines, resource-recovery techniques could be introduced earlier to decrease environmental contami-nation, provide an additional source of income, and reduce future liability.

Key words: Acid mine water, resource recovery, extraction

Mine water as a resource - Innovative solutions and concepts for the mine water management in modern mining and mineral exploration

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Extended Abstract

World's mining each year disposes or discharges into surface water billions of cubic meters of water derived from dewatering of mine sites. In Poland, the water inflow to both open pit and underground mine sites amounts to around 3.5 – 3.6 mln m^3 per day. 90 % of these water is discharged into surface water. In terms of quality, c.a. 75% of mine inflow water, which is around 2.5 – 2.6 mln m^3 daily, is of low mineralization, allowing for its direct use in economy. KGHM Polish Copper – the biggest Polish ore metal mining company – pumps out from the rock mass around 26 million cubic meters of water annually, of which around 23 million cubic meters are discharged into Odra river (www.kghm.com). Due to qualitative parameters, very often this water might be used for further application in agriculture or for drinking water supply. However, vast amount of mine water is of low-quality, is highly mineralized and enriched in a number of components classified as impurity.

The main issue of modern mining, not only in Poland, is an inflexible and old-fashioned model of water management. In this model, after pumping the water into the surface and its partial usage in technological processes, the mine water is treated as sewage. After simple treatment processes it is directed to the sewage system or to the surface water. This action very often causes a significant change in river's ecosystems.

An innovative approach to the mine water management relies on comprehensive analysis of hydrogeological conditions and physico-chemical parameters of groundwater. These analyses should be conducted during the ore exploration and mine planning stages. Furthermore, the current monitoring of inflow water during exploitation is also indispensable. Accurate quantitative and qualitative recognition of water coming from particular water-bearing horizons allows on precise planning of the production as well as on proper prior planning of effective excessive mine water management, along with maximization of useful compounds recovery, application for the purpose of geothermal energy production or with usage in different branches of industry. It also makes forecasting of processes connected with mine closure possible.

KGHM Polish Copper for the past 60 years has been extracting the copper ore deposit in three underground mines: Lubin Mine, Rudna Mine and Polkowice-Sieroszowice Mine, located at Fore-Sudetic Monocline in the South-Western Poland. The depth of extraction is diversified and it varies from 400 meters in the South to 1200 meters in the North of the deposit. In the initial mining phase, which covered the shallower, southern part of the deposit, the mineralization of inflow water amounted to 350 – 500 mg/L, whereas now it amounts to 1 g/L. After the pumping out from the mine, the water was almost entirely used in technological cycle, and its excessive amount was placed into water pond at tailings facility. After the clarification, the water was directed into Odra river. Currently, the inflow intensity in the southern area oscillates around 15-30 m^3 per minute, which constitutes to around 90% of the total inflow to all three mine sites. Over the years, the exploitation also covered the northern, deep parts of the deposit, where the inflow water is highly saline and mineralization amounts to 100-150 g/L. The inflow intensity in this area does not exceed 3 m^3 per minute and generates around 10% of inflow water volume. The waters derived from both areas are combined in the mine dewatering system, and in the form of saline water are being put into technological circulation at processing plant, then to tailing facility and later on are re-directed to the Odra river.

The newest concepts based on detailed examinations of mine inflow water and drillhole tests of water from the foreland of excavated area assume flexibility and optimization of mine dewatering system by, among others, selective water discharge. Low-mineralized water are to be used in technological processes, maximizing the cycle amount in the closed circuit. The best quality water are the potential source for the crops watering and as fire reserve for the forestry, while during the wintertime it might be discharged directly into the surface water without deterioration of its quality. Furthermore, the concept assumes several other optional scenarios of brines application, that except of high mineralization are also characterized by high temperature value (30 – 40 Celsius degrees) and are enriched in many useful compounds (e.g. B, Li, Ba). Collected selectively underground might be a material for cosmetic industry and for health resorts, a source of geothermal energy and a by-product in the useful compounds recovery process and production of fertilizers for agricultural purposes. Furthermore, the concept assumes purification of as large amounts of mine water as possible, including technological water. After the process of mineral components recovery, placing the mine water into absorptive parts of rock-mass will be conducted. These actions will make significant reduction of discharge of impurities into Odra river possible. As a result, the minimization of environmental royalties caused by the discharge will occur.

Key words: innovative mine water management, useful compounds recovery, mine water reuse, circular economy

Latest development in water management of Eastern-German lignite industry

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Abstract

About 25 years ago the lignite industry in Eastern Germany underwent major changes in conjunction with closing of many mines. In terms of water management rehabilitation this process has today enormous impact, in addition to the sharp rise in current requirements of environmental, water and mining law. In order for the various tasks can be mastered there was and still is the need for close cooperation between the active mining and remediation mining.

The tasks that have to be done here, refer to the creation of good quality rest lakes and their integration in the regional water balance and deal with minimization of impact from both active and abandoned mines to ground water and surface waters.

In the following article, the measures, tools and methods are described, which play an essential role in the water management of the East German lignite industry.

Key words: eastern German lignite industry, water management, water treatment, impact compensation

1. Introduction

Lignite mining in eastern Germany looks back on 200 years of history. It was and the extent of mining is steadily closely linked to the political and economic interests of the state and the governments.

Due to political changes in the late 80´s of the 20th century in the former GDR the traditional lignite mining areas in eastern Germany (around Leipzig and in Lusatia) underwent major changes. While alone in the area around Leipzig 1989 20 mines has been operated, the number decreased to 11 until 1991 and in 1995 has been 3 mines left. The extraction rate was lowered from around 100 Mio. t in 1989 (ca. 300 Mio. t in whole eastern Germany) to 19 Mio. t (81 Mio. t) in 2015. Because in one fell swoop around 85 % of the mines were shut down the mining industry faced enormous challenges concerning mine reclamation and water management. As this could not be handled by the remaining mining operations, which itself had been in economic transformation, the reclamation and water management of mines shut down between 1989 and 1994 became state task.

Therefore today we still find the following structure in eastern German lignite industry:

- Vattenfall Europe Mining AG:

  producing mines in Lusatian mining area (predominantly for power generation)
- MIBRAG mbH:

  producing mines in Leipzig mining area (predominantly for power generation)
- ROMONTA GmbH:

  producing mine in Leipzig mining area (predominantly for production of montan wax)
- LMBV mbH:

  reclamation and water management of abandoned mines, shut down between 1989 and 1994, state owned

2. Water Management in Leipzig and Lusatian mining area

Particularly for water management of abandoned mines and with it for water management of the whole mining areas the close cooperation of producing mining companies and mines in reclamation is essential.

The close cooperation can be illustrated focusing on Leipzig Mining area. South of Leipzig MIBRAG operates the Vereinigtes-Schleenhain-mine and Profen-mine while LMBV is responsible for reclamation of 7 abandoned mines (Profen-Nord/Werben, Zwenkau, Cospuden, Espenhain, Witznitz, Bockwitz, Haselbach). The mines are located within an area of about 1.500 km². As all mines belong to the same catchment basin (Weißelsterbecken), there are numerous water related dependencies and interferences between the several mines.

Started to set up already in the 80´s, after 1990 the overall hydrological model “HGMS”, which covers the whole mining area and includes all important mining related and other boundaries, became the basis for all water related planning and operation. One of the most important aspects on this has been the analysis of technological variants of flooding the abandoned mines. As there river water was not available due to quantitative and qualitative reasons flooding the mines with water from dewatering works in producing mines turned out to be the best available alternative. A pipeline with a length of 65 km, which connects the producing with the abandoned mines was erected and is co-operated by LMBV and MIBRAG. From 1998 to 2015 about 500 Mio. m³ mine water had been pumped from coal producing mines to abandoned mines. Thus helped all partners, coal producer MIBRAG in water management, mine reclaimer LMBV in realizing fast and cost-efficient mine reclamation and the region gaining reputation from new perspectives in economy, recreation and nature protection.

Today there are widely reclaimed landscape and coal production nearby.

Both earlier and much more today minimizing the engagement of lignite mining on the water balance is a mandatory requirement in order to be able to continue the operation of open pits in social consensus. Water protection and water treatment have top of the agenda – in Leipzig and in Lusatian mining area.

In the Leipzig mining area the progress in water related restoration resulted in reduction of pumping rate from operating mines to abandoned mines already in the last years and the rate will decrease further in future. Along with worse quality in mine water and higher legal requirements it was necessary to increase investments in water management in operated mines. These investments in Leipzig mining area relate to water treatment and impact compensation and are based on 2 points:

- Regular forecasts on mine dewatering and its impact
- Strategic planning for a sustainable provision of mine water for compensating measures during the complete mining period and during groundwater rise (f. e. well batteries, pipelines/pumping stations, local solutions) considering mine water treatment (Mine water treatment plants, natural attenuation)

So already in 2010 in Vereinigtes-Schleenhain-mine a mine water treatment plant (MWTP) was brought into operation with a deironising capacity of 60 m³/min. The iron content of the mine water of about 20-70 mg/l is reduced to less than 3 mg/l.

In the year 2017 another mine water treatment plant will be put into operation in Profen-mine. This MWTP will be able to handle mine water of about 120 m³/min, reducing iron content from 10-40 mg/l to less than 1,5 mg/l. A substantial portion of the total amount of water treated in this plant will be used for the most extensive compensating measures of MIBRAG (amongst a lot smaller measures) to equalize the influence of dewatering works of the Profen mine on Weiße Elster flood plain. About 25 m³/min will be brought separately to the river Weiße Elster upstream.

Facilities of the Lusatian mining area served as a model for the mine water treatment plants of MIBRAG. Due to different boundary conditions and local requirements Vattenfall continuously operated MWTP´s all the time in its operating mines. But also here investments in mine water management increased for several years – particularly with regard to compensating measures near the mines of Vattenfall.

For dewatering the Lusatian lignite mines in 2015 around 420 Mio. m^3 mine water had been pumped. Dewatering here just like in Leipzig mining area occurs preferably using vertical filter wells.

With respect to geological conditions in Lusatia mine dewatering forms a large drawdown cone. Therefore Vattenfall tries increasingly to contain the groundwater lowering by constructing deep sealing walls. Due to the history of mining in Lusatia and due to the duration of dewatering measures the effects on groundwater are still significantly.

As a result of groundwater lowering a potential for conflict can arise, where is both the need for mine dewatering and on the other hand the requirement to maintain surface water and water use. In order to avoid the deterioration of condition of surface waters, also here compensating measures are necessary, such as supporting the river flow by discharging purified water in it (s. c. eco-water, water purified in MWTP which is used e. g. for waterbound ecosystmes). Against this background the mine operator takes measures to water treatment, water supply and impact minimization. This measures usually focuses on the same points as in Leipzig mining area, supplemented by the following:

- Planning and construction of tie line for eco-water – impact compensation
- Planning and construction of sealing walls – impact minimization

21% of the pumped water is directly returned to bodies of surface water in order to be immediately distributed and to contribute to a stable water balance. This water is of good quality and without elevated ferric content. The remaining 79% is routed onwards to mine water treatment facilities (MWTP). This water is distributed onwards as follows; 48% is discharged into the Spree River and Neisse River, with a small share of this amount being discharged into the ecosystem; 31% is used in the lignite-fired power plants as cooling water and service water. This pit water is required to operate the power plants. 90% of the water used in the three power plants originates from the sump dewatering performed in the opencast mines.

Vattenfall Europe Ming AG operates six mine water treatment facilities (MWTP), while Vattenfall Europe Generation AG operates one such facility at the Jänschwalde power plant in order to treat and distribute the extracted pit water. Each year, these facilities retain 15.900t of iron, which is in the form of alkaline water containing ferric hydroxide with a solids ratio of 2%. In a facility located at the interior dump of the opencast mine Nochten (Tzschelln GWBA), the alkaline iron-hydroxide water (AEW) is dehydrated by a third-party enterprise not belonging to the Vattenfall corporation, the solid matter is then collected to manufacture iron granules serving water and flue gas purification purposes and put on the market.

The hydraulic barriers/ Sealing Walls Vattenfall has constructed are already taking effect in countering an exacerbation of the dewatering indicated problems. They are a unique differentiator of the mining region of Lusatia as compared to other mining regions. As a consequence of the hydraulic barriers, less water needs to be extracted, so that the region's water balance is impacted less and, what is likewise significant, less peripheral ferric oxide is laid dry. The hydraulic barriers are made of water-impermeable clay; at present, they can be installed down to a maximum depth of 110 to 150m. To date, VE-M has constructed approximately 25km of hydraulic barriers. A further 16km are in construction.

3. Conclusions

As stated previously, mine water management is one of the most important topics for eastern German lignite mining companies. Thereby the coexistence of old mining and mines in operation plays an important role for all water related planning, problems and problem solving. Water protection and water treatment have top of the agenda – in Leipzig and in Lusatian mining area.

Simulating mining-related reactive transport processes across multiple length and time-scales

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Extended Abstract

Accounting simultaneously for both subsurface fluid flow and biogeochemical processes through reactive transport modeling has become an essential tool for interpreting observed hydrochemical data and to understand the processes controlling natural and contaminated subsurface systems.

Spatial scales of interest range from the pore scale to the regional scale and time scales of interest for reactive transport problems may vary from minutes to 1000’s of years. Depending on data availability to constrain model development and applications the chemical complexity addressed by the reactive transport simulations often varies widely and typically decreases with increasing spatial scale.

This presentation will discuss several mining-related reactive transport modelling studies across scales to illustrate current capabilities and the application of data-driven modelling approaches. The illustrative examples will include laboratory-scale modelling underpinning the development of a novel arsenic remediation technique, model investigations on improved uranium in situ leaching strategies, predictive modelling for uranium mine closure scenarios and model predictions of the diffuse sulphate emissions from a former mining district.

Stable isotope tools for assessing flow dynamics and contaminant degradation in mining landscapes

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Extended Abstract

The extraction of mineral resources and solid fossil fuels and the impact of the various extraction technologies on the natural hydrogeochemical environment may result in a widespread diffuse contamination of vast landscapes. Major symptoms of this contamination type are acidification and extremely high mineralization of the (sub-) surface water with sulfate, iron and/or heavy metals. In some cases, technological measures are successfully applied for an active remediation of the environmental impact, in many other cases, however, the only appropriate way to manage such vast diffuse contamination sources is the implementation of the natural attenuation concept.

Independently of the applied concept, successful remediation always depends (i) on a precise determination of hydrogeological boundary conditions, (ii) on a suitable monitoring approach for controlling the effectiveness of the measures and (iii) on a reliable prediction of future scenarios for sustainability. In that context, stable isotope signatures are a very powerful tool for assessing the dynamics that control the flow of water through the contaminated system and its hydrological interaction with the surroundings. Also, stable isotopes are successfully applied for the identification and quantification of biogeochemical transformation processes leading to a degradation of the contaminants.

Besides basic concepts of stable isotope applications, two examples are presented that give insight into the successful application of isotope tools for scientific governance of remediation measures. The first example refers to an isotope based decision support related to the covering of a heavy-metal emitting slag heap in a former copper mining region with an impermeable barrier. The second example shows how isotope signatures can be used to predict the natural attenuation potential in a lignite mining dump.

Key words: stable isotope signatures, flow dynamics, biogeochemical processes, natural attenuation

CHAPTER 1

Mine Water Regulation and General Aspects

Mine water discharge quality – a review of classification frameworks

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Abstract

Mining activities are commonly associated with impacts on water resources. Water protection, management and treatment is considered to be one of the most complex and costly issues of mining activities. Water classification in general has become an important tool for assessment and management of surface water bodies and several recognised systems exist for characterisation and classification of water quality. A prominent example is the EU Water Framework Directive (2000/60/EC), which was designed to classify surface waters according to ecological and chemical status. However, most water classification systems are impractical for mine water assessment.

A review of specific mine water classification systems showed that the number is limited, frameworks are predominantly geared towards Acid- and Metalliferous Mine Drainage (AMD/MMD) and classification is mostly based on geochemical parameters. This approach could be called historical as sulphide mineral oxidation has been the dominating water contamination process in mining for decades. Consequently, other types of mining induced water contamination, such as salinity, are neglected in both mine water classification and regulation. Non-metalliferous types of mine discharge/effluent are often handled and regulated on a case-by-case basis or not at all, leading to uncertainty for key stakeholders and in some cases to unnecessary deterioration of water quality.

A new mine water classification framework linked with water treatment is necessary if mine water issues are to be addressed at a more comprehensive and consistent basis for multiple issues around the globe. Successful application of interdisciplinary or impact-based systems has been demonstrated on a regulatory level and the lessons-learned could be used for broader implementation. Based on a review of existing frameworks the most important aspects and advantages as well as suitable classification parameters were compiled. We then lay the foundation of a revised mine water classification framework that would contribute to the improvement of mine water management.

Key words: Mine water, classification, Acid Mine Drainage, salinity, framework

Introduction

In the years to come the mining industry will face the challenge of adopting more integral and sustainable practices all over the life-cycle of resource projects. Mine effluent in particular is a common community and environmental concern, as it can have serious impacts on water quality, aquatic life, ecosystems and drinking water resources. Because of decreasing ore grades and increasing scale of mining activities, rock exposure to atmospheric conditions due to excavation, blasting, drilling and subsidence as well as the sheer mass of waste rock, tailings and overburden is increasing over time. As a result, water contamination, especially Acid Mine/Rock Drainage (AMD/ARD), has become the number one problem associated with modern mining activities (Franks et al. 2014, Pokhrel & Dubey 2013). In this context, mine water management on a local, regional and national scale is one of the key aspects of mining operation and regulation (IIED 2002). Differing international practices in assessment, classification and regulation of mine water can be a limiting factor for the mining industry, impeding transnational investment and at times denying downstream water resource users adequate pollution protection.

Classification of mine water can help avoid uncertainty amongst stakeholders and consequential adverse effects on water resources by categorising mine effluent and providing information on typical contamination processes, hazards, risks and suitable mitigation or treatment options (Wildeman & Schmiermund 2004). Over time a number of classification systems have developed and been proposed, reported or discussed in the literature (e.g. Younger 1995). The objective of this paper is to provide a literature based review of the current status of mine effluent classifications and to make recommendations with regard to future improvements and the development of a suitable framework for more widespread application. It is noted that the terms mine discharge, effluent and drainage are used interchangeably throughout the paper.

Mine Water Contamination

Contamination of mine water is usually the result of a number of different interrelated factors, including but not limited to geological background, climate, geochemistry, biochemistry, commodity, mine type and processing method. However, a number of prevalent processes are commonly associated with mining activities. For decades attention of regulators, industry, research and communities has predominantly been focused on AMD as archetypal mine water pollution. AMD is commonly associated with low pH (1 – 5), low dissolved oxygen and high concentrations of toxic metals, metalloids and sulphate (Morin & Hutt 1997). Beyond that, non-acidic Metalliferous Mine Drainage (MMD), also known as Neutral Mine Drainage (NMD), has been distinguished and acknowledged as an independent type of mine effluent in recent decades. MMD is commonly associated with circum-neutral pH (6 – 8), low dissolved oxygen and medium to high concentrations of sulphate and metals that are soluble (e.g. Cu, Zn, Cd) or insoluble (Fe, Al, Mn) under aerobic conditions. Even slightly enhanced iron content in surface waters, not yet considered metalliferous, can lead to distinctive staining of creek-, stream- or riverbeds due to ochre formation (Belmer et al. 2014, Gray 1996a).

Mine effluent or process water from non-sulphidic lithologies or low-sulphur coal and lignite mines can be highly saline due to major cations and anions without containing elevated metal concentrations. Because of the substantial change in water chemistry, this type of mine water must be considered as contaminated, albeit being neither AMD nor MMD (Lincoln-Smith 2010, Palmer et al. 2010, Wildeman & Schmiermund 2004, Wright 2011). In the literature this type of mine water is sometimes referred to as Saline (Mine) Drainage (SD). SD is generally considered to be non-toxic to humans and ecosystems (at least short-term), however, it can have serious long-term impacts on water quality, aquatic life and the aesthetics of surface waters (Bernhardt & Palmer 2011, Cañedo-Argüelles et al. 2013, Hall & Anderson 1995, Lincoln-Smith 2010, van Dam et al. 2014). In general, water salinity is deemed insignificant compared to AMD, as both perceived threat and visible effects are by far less prominent. For this reason, it is much less frequently dealt with or described in studies and often no consistent regulations exist, mandating mitigation or treatment (Wildeman & Schmiermund 2004, Wright 2011). This grey area needs to be addressed by regulators to provide consistent protection of water resources on the one hand and facilitate straightforward water management for mine operators on the other hand.

Mine Water Classification Schemes

Mine water classification approaches are usually tailored for a specific type of drainage, commonest AMD/ARD as it is the worst and most prominent type of mine water pollution. The most important classification frameworks and some minor ones specifically designed for mine water assessment are described below.

Physico-chemical Classification

Classification of mine water is predominantly focused on water chemistry. Consequently, most classification systems use physico-chemical parameters to distinguish between different types of mine water. The most prominent example of such a system can be found in the Global Acid Rock Drainage (GARD) Guide, an online-based open-source compilation of methods and technologies for the prediction, prevention, mitigation, management and monitoring of mine water contamination with a focus on AMD generation as a result of sulphide mineral oxidation (INAP 2009). The GARD Guide classification framework is kept very simple and it should be noted, that the terms and characterisations have been present in literature long before the GARD Guide. Mine water is categorised in three classes that are roughly outlined and defined by max. four parameters only (cp. Table 1). The lack of more quantitative definitions is acknowledged by the authors.

Table 1 *The GARD Guide mine water classification (INAP 2009)*

GARD Guide classification	Class description	Thresholds
Acid Rock Drainage / Acid and Metalliferous Mine Drainage	• Acidic pH • Moderate to elevated metals • Elevated sulphate	• pH < 6
Neutral Mine Drainage (NMD)	• Near-neutral to alkaline pH • Low to moderate metals • Low to moderate sulphate	• pH > 6 • Sulphate < 1,000 mg/L • TDS < 1,000 mg/L
Saline Drainage (SD)	• Neutral to alkaline pH • Low metals (only moderate Fe) • Moderate sulphate, Mg and Ca	• pH > 6 • Sulphate > 1,000 mg/L • TDS > 1,000 mg/L

Other mine effluents not deriving from sulphide mineral oxidation can be assessed as well, but as the system is focused on dissolving and leaching of acid generating or neutralising minerals and salts, other waters are categorised almost exclusively according to their sulphate content. In most cases this would lead to SD or NMD classification, however, if little sulphate is present, saline mine water containing vast amounts of major cations and anions could even be classified as freshwater.

The two to four-pronged GARD Guide classification approach (usually AMD/ARD – MMD/NMD – SD – Freshwater) can be found in several other systems and definitions, such as the Canadian Mine Environment Neutral Drainage program (e.g. MEND reports 1.16.1b, 1.20.1 and 10.1) and a number of mine water classifications in international literature (e.g. AUS DITR 2007, Glover 1975, Hedin et al. 1994, Hill 1968, Morin & Hutt 1997, Wildeman & Schmiermund 2004). These physico-chemical classifications are predominantly defined by pH, metal and sulphate content, which limits the framework to AMD-related water pollution. Morin & Hutt (1997) tried to solve the problem by adding a fourth class labelled “Other” to account for mine drainage from non-metal mines that is not primarily characterised by pH or metal concentrations. A different, more itemised rating is provided by the Irish Acid Mine Drainage Index (ARDI) and subsequent modifications (Gray 1996b, Kuma et al. 2011). Another framework primarily concerned with pyrite oxidation and AMD formation was developed to compare mine water of various origins by using a diagram with sulphate concentration on the abscissa and neutralisation potential, as a cumulative parameter for acidic or buffering species, on the ordinate (Schoepke & Preuss 2012). This system was developed with regard to groundwater seepage and pit lakes from lignite mining and the applicability to other commodities is limited.

A more holistic approach was prepared by the Minerals Council of Australia (MCA) as part of the Water Accounting Framework (WAF) for the minerals industry. The framework features three categories according to water quality and treatment requirements for classification of water input and output of mining operations and facilities (cp. Table 2). Assessment is primarily based on chemical parameters such as pH, TDS and harmful or toxic constituents, and secondarily on biochemical constituents such as coliforms or pesticides/herbicides. A level of treatment is assigned that would be necessary to achieve human consumption standards as described in recognised drinking water standards (MCA 2014, Timms & Holley 2016).

Table 2 *The WAF mine water classification (MCA 2014)*

WAF classification	Class description	Thresholds
Category 1 **High water quality**	Minimal effort necessary to achieve drinking water quality	• pH = 6 – 8.5, TDS < 1,000 mg/L • No turbidity after sedimentation, no/traces of pesticides/herbicides or harmful constituents • Coliforms < 100 cfu/100ml
Category 2 **Medium water quality**	Moderate treatment necessary for individual constituents	• pH = 4 – 10, TDS = 1,000 – 5,000 • Coliforms > 100 cfu/100ml
Category 3 **Low water quality**	Significant treatment necessary to achieve satisfactory water quality	• pH < 4 or > 10, TDS > 5,000 mg/L

Both the GARD Guide and WAF classifications use pH and TDS as a primary water quality indicator. However, whereas the GARD Guide is focused on sulphate concentration as the system is adapted for sulphide mineral oxidation and AMD, the WAF classification uses a number of parameters that are harmful to human health and provides a decision tree for simple categorisation. The WAF system provides wide-ranging applicability, but as it was designed specifically for the minerals industry, the decision tree lacks a component to account for AMD (e.g. sulphate). The WAF classification could form the basis for mining related discharges to be accounted for in the Global Sustainability Reporting Initiative (GRI). As discussed by Leong et al. (2015) and Mudd (2008), the EN22 indicator of the GRI is to report the total volume of discharge by destination and water quality, so to understand the potential for environmental impacts. However, there are no specific guidelines provided beyond these principles, for which the WAF could provide a way forward.

Table 3 *Mine drainage pollution classes (Hill 1968)*

Hill (1968)	**Class description**	**Thresholds** (Ac=Acidity [mg/L $CaCO_3$])		
Class I	Acid drainage	• pH = 2.0 – 4.5 • Ac = 1,000 – 15,000	• Fe^{2+} = 500 – 10,000 mg/L • Fe^{3+} = 0 mg/L	• SO_4 = 1,000 – 20,000 mg/L • Al = 0 – 2,000 mg/L
Class II	Partially oxidised and/or neutralised	• pH = 3.5 – 6.6 • Ac = 0 – 1,000	• Fe^{2+} = 0 – 500 mg/L • Fe^{3+} = 0 – 1,000 mg/L	• SO_4 = 500 – 10,000 mg/L • Al = 0 – 20 mg/L
Class III	Oxidised and neutralised/alkaline	• pH = 6.5 – 8.5 • Acidity = 0	• Fe^{2+} = 0 mg/L • Fe^{3+} = 0 mg/L	• SO_4 = 500 – 10,000 mg/L • Al = 0 mg/L
Class IV	Neutral and not oxidised	• pH = 6.5 – 8.5 • Ac = 0	• Fe^{2+} = 0 – 500 mg/L • Fe^{3+} = 0 mg/L	• SO_4 = 500 – 10,000 mg/L • Al = 0 – 2,000 mg/L

An older framework can be found in Hill (1968), where classification is based on mine water chemistry related to distance from pollutant formation (cp. Table 3). The categorisation proposed by Hill (1968) is primarily focused on (natural) thermodynamic processes taking place with increasing distance from the pollution source. Class III mine water could be considered as the natural equilibrium after incremental oxidation and neutralisation, comparable to actively or passively treated mine water. Apart from the outdated focus on point sources the system is very similar to current classification schemes and therefore displays the same limitations. This clearly shows, that approaching mine water classification with a rather one-dimensional focus on sulphide mineral oxidation has not changed significantly in the past 50 years.

Deposit Based Classification

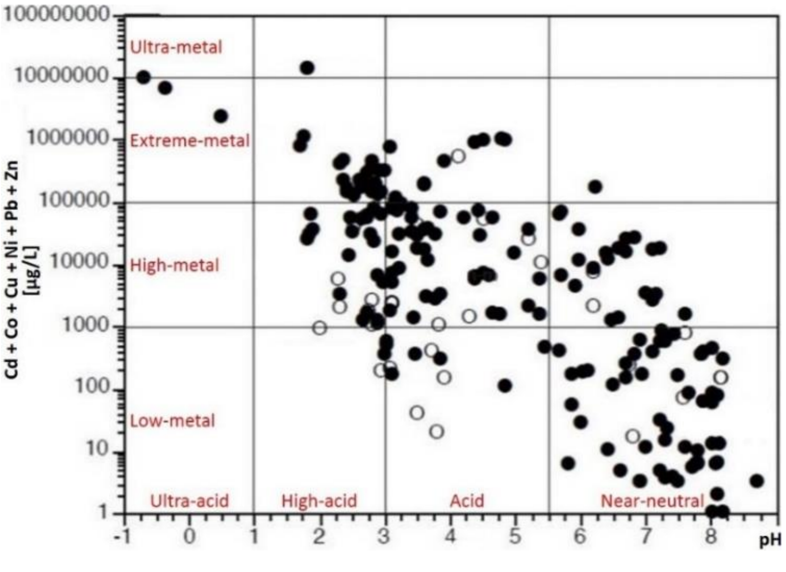


Figure 1 *Ficklin diagram of natural waters (open circles) and mine waters (closed circles) draining diverse mineral-deposit types (modified, cp. Plumlee et al. 1992, 1999)*

The USGS developed an empirical system postulating that similar mineral deposit geologies produce similar drainage water (Plumlee et al. 1999, Seal & Foley 2002). Databases were used to create the necessary geoenvironmental models of mineral deposits and results can be plotted in a classification diagram. In these so-called "Ficklin diagrams" drainage pH is plotted against the sum of six dissolved heavy metals (Cd, Co, Cu, Ni, Pb, Zn) typical for acid generating environments (cp. Figure 1). Classification is based on these two indicators and combines one out of four pH-dependent attributes (near-neutral to ultra-acid) with one out of four metal-content-dependent attributes (low to ultra-metal) to form the respective category (Ficklin et al. 1992, Plumlee et al. 1992, 1999).

The diagrams are based on the assumption that effluent quality is largely dependent on geology and climate, which is why the plots and diagrams can be used for AMD and MMD as well as for naturally occurring ARD. As the system is based on deposit geology, the most important metals of sulphide mineral oxidation (Fe, Al, Mn) are excluded, as their omnipresence would obliterate the connection between background geology and effluent composition (Kuma et al. 2011, Plumlee et al. 1999). Obviously, the system is unsuitable for saline mine effluent, as major cations and anions are disregarded except for sulphate. The system is, however, highly applicable and meaningful for metal mines and can be used to link deposit paragenesis and mine water pollution (Kauppila & Räisänen 2015, Seal & Foley 2002).

Chemical-ecological Classification

An environmental impact assessment (EIA) derived by the UK National Rivers Authority (now: Environment Agency) estimates the impact of mine discharge on surface waters by assessing six different chemical, ecological and visual impact categories (cp. Table 4). For each category four subcategories (A = high; B = medium; C = low; D = none) are outlined with physicochemical impacts specifications (Davies et al. 1997, Jarvis & Younger 2000, UK Environmental Agency 1996):

Table 4 *UK classification of mine water impacts on surface waters (Jarvis & younger 2000)*

Physicochemical parameter (in decreasing order of importance)	**Impact on receiving waters**			
	A – High	**B – Medium**	**C – Low**	**D – None**
Area affected [m^2]	A1: > 10,000 A2: 2,500 – 10,000	B1: 1,000 – 2,500 B2: 10 – 1,000	< 10	0
Length affected [km]	> 0.50	0.01 – 0.50	< 0.01	0
Substrate quality for salmonid reproduction	Rocks / stones / gravel	Bedrock / boulders / rocks	artificial channel / sand / silt	–
Iron deposition (visual)	High	Medium	Low	None
Total iron [mg/L]	> 3.0	2.0 – 3.0	< 2.0	0
pH, DO [%], total Al [mg/L]	3 failures*	2 failures	1 failure	No failures

***Failures:** pH < 7; DO (dissolved oxygen saturation) < 70%; total Al > 1.0 mg/L

The classification system was successfully used to rank mine effluents and surface waters in the UK according to severity of impact (Davies et al. 1997). In a second phase additional impact assessments on benthic macroinvertebrates and fisheries' potential of the respective surface waters were used to determine an environmental quality index (EQI), which indicated sites with the most urgent need for action (Banks & Banks 2001, Jarvis & Younger 2000). The system proved to be effective and highlighted the benefits of a good classification system. Moreover, chemical and ecological aspects were innovatively combined in a more holistic approach (Jarvis & Younger 2000). Although especially visual and biological components make the application more difficult in terms of everyday use, the system is nonetheless very useful from a rehabilitators and regulators point of view.

A simple, descriptive index for the assessment of biological impacts of mine effluent was developed by Gray (1996a) with a focus on river bed substrate as the most important habitat for macroinvertebrates, fish and macrophytes in lotic systems. The index is based on visual assessment of AMD precipitates (ochre or yellowboy) in receiving watercourses and a qualitative indication of the severity is provided. The system is very simple and inexpensive, but at the same time very limited, as only seeable iron flocculation and precipitation and the consequential impact on substrate and biota are taken into account.

Environmental Pressure Based Classification

A different approach for assessment and classification of mine water was developed and published by Puura & D'Alessandro (2005) by relating environmental pressures to mine water discharge. The system uses water flow and quality to classify mine water discharge and to subsequently develop a ranking of polluted mine sites. Effluent characterisation is based on "the number of times any environmental standard (maximum permissible concentration, MPC) is exceeded" (Puura & D'Alessandro 2005). The system comprises five categories, incrementally representing the number of MPC exceedances (A = >1,000; B = 100 – 1,000; C = 10 – 100; D = 1 – 10; E = 0). Results can be plotted in a graph with metal emissions on the ordinate and MPC exceedance on the abscissa (cp. Figure 2). Ultimately, a pressure factor (PF) is calculated (PF = log(MPC-exceedance) + log(flow rate)), which can be directly related to the potentially polluted volume of clean water per day ($V_{polluted} = 10^{PF}$).

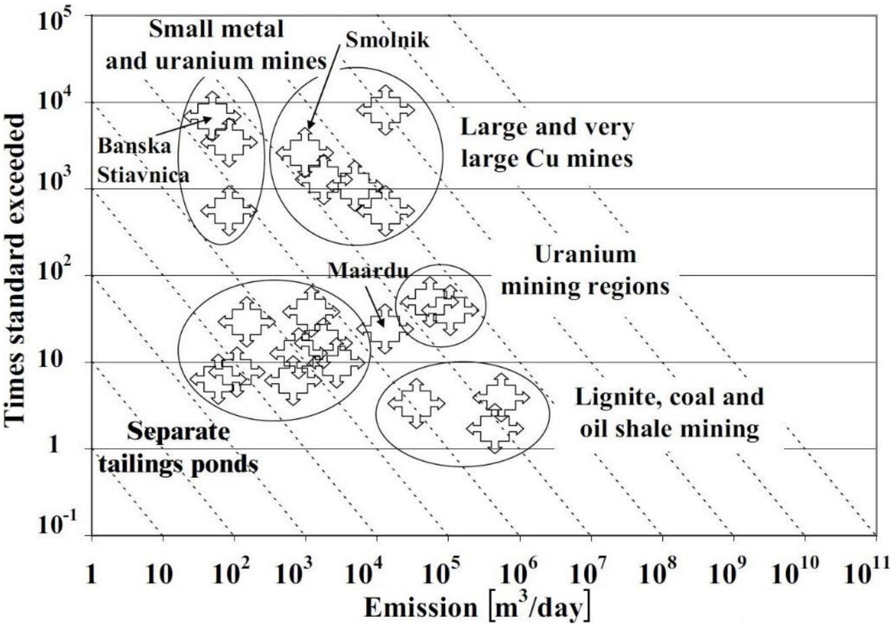


Figure 2 *Metal emissions plotted against MPC exceedance (cp. Puura & D'Alessandro 2005)*

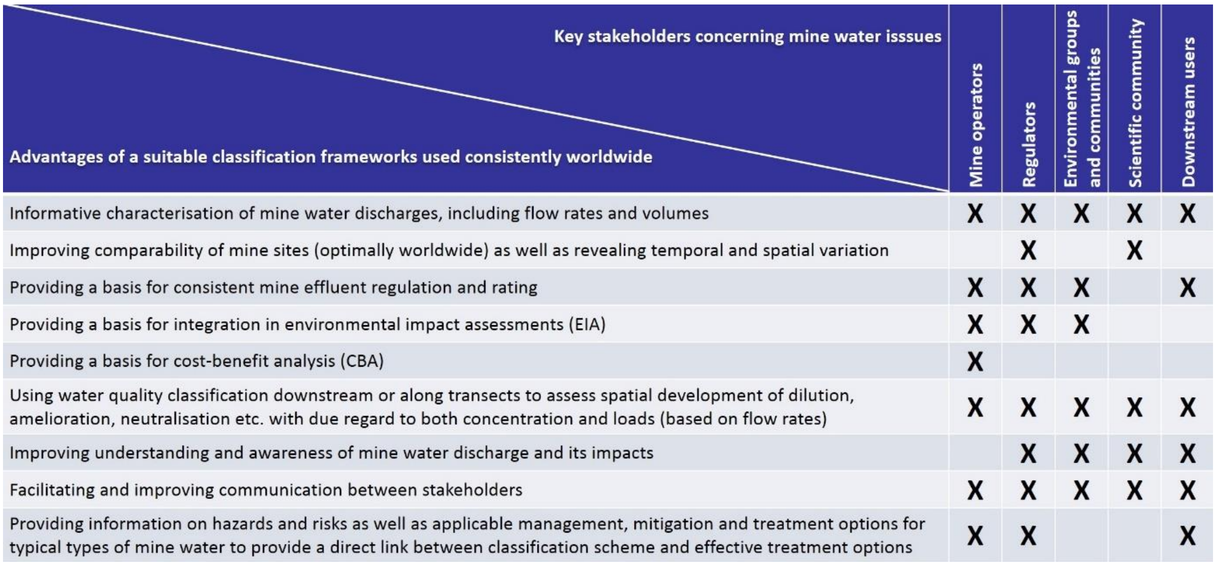
The system is very versatile and can be adapted for different situations and purposes, including individual and multiple contaminants as well as different mine sites, as long as respective environmental standards are in place. Nevertheless, it did not receive much attention in literature.

A somewhat similar approach is described by Mullinger (2004), where the impact of mine discharge on surface waters was ranked by incrementally scoring transgression of water quality standards for metal loads (Cd, Cu, Pb, Zn) and ecological impacts. On this basis an environmental quality standard (EQS) failure score can be determined for classification and ranking of different mine sites (Mullinger 2004).

Mine water classification and regulation in practice

As of yet, none of the mine water classification schemes described above is being used or referenced as a standard classification system on a regular basis and transregional scale. The reason for this is that the vast majority of studies related to mine water deal with AMD or MMD, where the category is obvious and classification efforts would be redundant. Whilst strict regulations are in place for AMD and MMD, most regulations fail to identify or classify other contaminants including turbidity and salinity. In cases where limitations or trigger values are in place (e.g. for sulphate, sodium, EC, TDS etc.), these are often ignored or discounted with reference to dilution (Belmer et al. 2014, Cañedo-Argüelles et al. 2013, Palmer et al. 2010, Wildeman & Schmiermund 2004, Wright 2011). A current guideline for mine water discharge quality in Western Australia allows for variations of +/–10% on natural seasonal background water quality indicators (e.g. EC, TSS, DO, radionuclides) (WA 2000). These guidelines may be difficult to practically achieve with limited baseline data for projects in environments with substantial seasonal variation. At some mine sites in Australia (e.g. NSW OEH 2012), site specific triggers are developed based on eco-toxicity studies of local invertebrates, a more expensive but more effective approach than adopting default national water quality limits for freshwaters as outlined in the ANZECC 2000.

Discharge limits are mostly determined on a case-by-case basis during the licensing procedure, varying significantly from country to country (Puura & D'Alessandro 2005). Although this makes sense in terms of site specific background (especially catchment geology and climate), the environment and downstream users of water resources (communities, agriculture, drinking water production etc.) are usually the ones to live with the consequences of degraded water quality (Cañedo-Argüelles et al. 2013, Wright 2011). A large number of methods, tools and systems for characterisation and classification of mine wastes can be found in the literature. However, mine water classification is lacking comprehensive frameworks that are widely adopted in practice. This is surprising, as classification systems such as the Richter scale, Köppen climate classification, USDA soil taxonomy etc. are used in most natural sciences to simplify the scientific dialogue and numerous studies exist for AMD/ARD prediction. A limiting factor might have been the complexity of water pollution by mining activities. Classification systems in general need to be straightforward, coherent and as comprehensible and simple in application as possible (Horton 1965). A suitable classification framework specially tailored for mine effluent could be beneficial in many different ways to the key stakeholders of mining activities (cp. Figure 3).



Key stakeholders concerning mine water isssues Advantages of a suitable classification frameworks used consistently worldwide	Mine operators	Regulators	Environmental groups and communities	Scientific community	Downstream users
Informative characterisation of mine water discharges, including flow rates and volumes	X	X	X	X	X
Improving comparability of mine sites (optimally worldwide) as well as revealing temporal and spatial variation		X		X	
Providing a basis for consistent mine effluent regulation and rating	X	X	X		X
Providing a basis for integration in environmental impact assessments (EIA)	X	X	X		
Providing a basis for cost-benefit analysis (CBA)	X				
Using water quality classification downstream or along transects to assess spatial development of dilution, amelioration, neutralisation etc. with due regard to both concentration and loads (based on flow rates)	X	X	X	X	X
Improving understanding and awareness of mine water discharge and its impacts		X	X	X	X
Facilitating and improving communication between stakeholders	X	X	X	X	X
Providing information on hazards and risks as well as applicable management, mitigation and treatment options for typical types of mine water to provide a direct link between classification scheme and effective treatment options	X	X			X

Figure 3 *Benefits and beneficiaries of a suitable classification framework*

Another shortcoming of current mine water quality classification schemes is the lack of consideration of water quality mitigation or treatment options. There are few independent guides available for first-pass consideration of the suitability and limitations of treatment options (e.g. PIRAMID Guidelines or US EPA Reference Guide 542-R-14-001). It is possible that classification schemes could be adjusted to reflect options for treatment technologies (e.g. threshold TSS that reduces AMD treatment). However, separate studies are therefore often required for consideration of technically feasible and cost effective solutions to water quality issues through mitigation, active and/or passive treatment. Technologies for water quality treatment are developing in part as a response to the rapidly growing market for mine water treatment (Bluefield Research 2014).

Summary

This review of mine water classification systems reveals a long established focus on AMD and MMD. For both mining regulators and operators acidity and metal toxicity are the major concerns, as the worst impacts on water quality can be expected and strict regulations apply. For this reason it is not surprising that almost all classification systems use pH and metal concentration as key characteristics for the segregation of categories. However, this does not address emerging awareness of broader water quality issues. Current systems are very vague in terms of mine water salinity, and sulphate is the only major ion that can be found in multiple schemes as it correlates strongly with sulphide oxidation (Plumlee et al. 1999).The importance of salinity and other characteristics (e.g. turbidity, toxicity) with regard to water quality and impact on aquatic ecosystems is increasing worldwide and should find entrance into existing mine water classification systems to attract the attention of regulators and industry (Belmer et al. 2014; Cañedo-Argüelles et al. 2013). As of yet, none of the mine water classification schemes described above is being used or referenced as a standard classification system on a regular basis.

It is challenging for one water classification framework to incorporate a broader range of relevant factors and processes, yet remain practical for application (Horton 1965). However, assessment and subsequent ranking of mine sites in the UK and Ireland using straightforward mine water classification has proven effective and demonstrated the benefits and utility of such a system (Jarvis & Younger 2000). The same can be said about application of the WAF framework by 90 % of mine sites in the Australian Hunter Valley coalfield (Timms & Holley 2016). An improved and extended mine water classification framework could be a valuable tool to help regulators close the remaining gap in water and mining policies.

Conclusions / Recommendations

A revised mine water classification framework could play a major role in addressing mine water issues on a larger scale and on a catchment, national and international basis. As water impacts are investigated by numerous (local) experts from different disciplines and countries, it is recommended that the revised framework be straightforward and based upon unambiguous, standard characteristics. A combination of chemical, ecological and other key parameters (cp. Figure 4) is advisable as well as depending on the water resource in question (mine discharge, surface water, groundwater). In addition, the classification system should be applicable to any mining activity regardless of mine-type or commodity and describe typical formation, occurrence, properties, hazards, management, mitigation, treatment and monitoring options for defined types of mine water, as well as providing appropriate references.

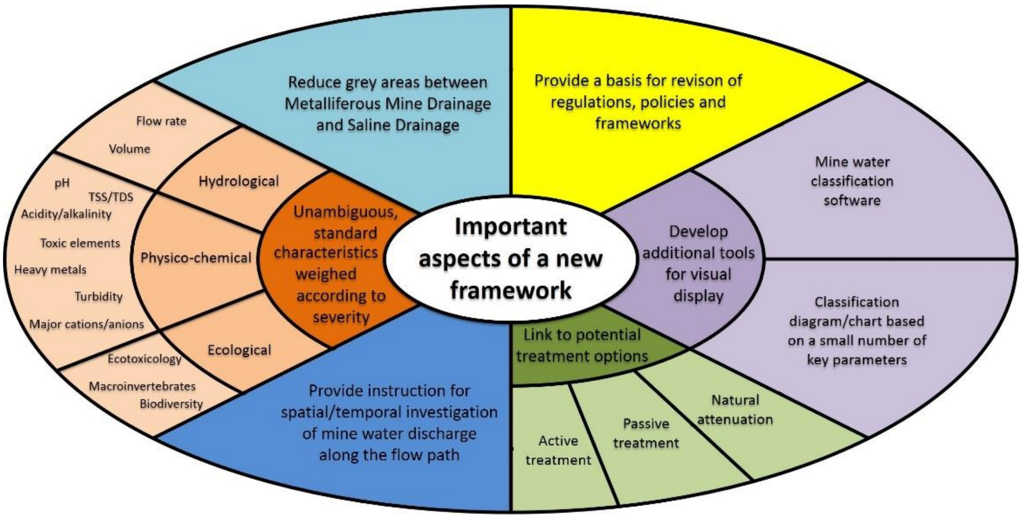


Figure 4 *Recommendations for a new classification framework*

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Pulling together mine water management across site & business for performance: principles, business role & inclusive governance, strategic & practice framework

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Abstract

A new, benchmark approach for mine water management across a site & business is presented. Developed as a framework style to incorporate governance, strategy & operational guidance, the system identifies key components required for water performance linked across business functions & project stages as an inclusive & encompassing map for effective & influential water management.

The framework is presented as a series of schematics & guidelines, covering:

- Business role of water & activity styles across a project pipeline & mine life cycle;
- Principles of approach for definition, design & outcomes of water in mining;
- Milestone requirements by project stages for water;
- Water management strategy map, where each component outlines core plans, critical information & skills across three key areas, including:
  - Governance: Risk, standards, criteria & metrics;
  - System knowledge & dynamics: Key tools & knowledge;
  - Monitoring & response: Capacity to detect & act.

Implementation of this new style of water management approach for an international resource group achieved impact & success beyond expectations, delivering significant step change water reliability & risk management, cost effectiveness, performance & culture across each business with integration across all sites & studies.

As an innovation potentially significant to an industry working in highly complex environments & settings, the approach is open & transferable to any mine site, commodity or mining method and is shared to promote discussion & action in evolving mine water management across the global extraction industry.

Key words: Mine water management, water performance, water framework, water innovation, water futures

Introduction

Water performance is a growing requirement for the mining industry. Increased expectations for production reliability & safety, environment & social alignment, legacy value & risk management is shifting regulation & operational requirements towards greater controls & more stringent constraints, often in parallel with increased project complexity and resource competition. Water management features as a key risk across the industry currently (BMI 2013; Deloitte 2016; EYGM 2015), and looking to the future, it is likely as trends continue that deep transformation to current practices will be required to enable successful development and operation of mining projects.

Responding to increased pressure, risk & requirements faces challenges at both a structural & functional level with common current practices for water. Water management in mining could be described as often the product of the sum of many parts, where water capacity & responsibility is nested across business functions such as environment, sustainability, mining, technical services, assets and processing, with gaps generally supported with external expertise where detected or required. And whilst water flows between or across multiple domains on a site by nature, management of water across those domains is separated by departments, creating gaps & inconsistencies. There are often mismatches in responsibilities and in-house knowledge, with varying levels of coordination and collaboration between groups across a site or business. And whilst the immediate suggestion may be to hire water specialty in house for resolution, the challenge is hampered both by the structural differences in various types of water expertise from training (such as surface water, groundwater or infrastructure), and the business model being able to support additional roles.

In recognition and response to changing business needs & operating environment, a new to industry system & service innovation for water management was designed, developed & implemented across an international mining group. Designed as a framework-style for use & adaptation, the approach essentially looks to manage water as an overall system, and provides a roadmap with operating guide for mine water management across the mining cycle from exploration to legacy.

An initial prototype of a holistic approach with an international mining group delivered significant value outcomes in performance, production & risk management – linking across all operations, sustainability, studies (SEIA, Concept/PFS/FS) & infrastructure. A culture of holistic water management was established, with common language & understandings across multi-disciplinary groups, in-house ownership & capacity to deliver against objectives for water performance. Technical & strategic advice integrated groundwater, surface water, dewatering & water diversions, risk, water supply, hydropower/geothermal, regulation & compliance, storm water, drainage, sediment control & AMD, containment & discharge, tailings, water chemistry, closure & community, & water handling infrastructure like dams or river diversions.

Given the originality & benchmark significance of the water management framework for industry & working success (with learnings), an overview of the approach is shared with the mine water community to generate discussion & provide a viable mechanism to assist in strategic water management elsewhere as a broader application. An overview of the design approach, strategy development & prototype mine water management strategy frameworks are presented in the interest of contributing to the evolving practice of mine water & to meet the challenge of change to come.

Strategy development

Design approach

A series of key questions opens up the strategy and critical thinking space for how water management might be configured for greater impact as a core business role. Questions such as:

- What or who defines “good” water management & performance for a site or business?
- What is the direct business role of water management for mining throughout a project life?
- How might we integrate water into a mining business?
- What aspects of mine water are important to have managed & to what level?
- How might mine water management play a greater role in driving resilience & performance across the life of projects?
- How might water play a role in shaping greater outcomes/relationships for communities & environment from exploration through to legacy?

Defining the frame of designing for water performance is the multiple views of how people see water. From a birds’ eye view as shown in Figure 1, for any given site or business there are at least four key perspectives across a water system for a mine with different senses of water value, expectations, power & stakes. Host communities, international markets & investors, regulators & governments & mine operators each hold different perspectives & influence on water performance either as a contributor, or from the external view in judgement. Notably, each group is significant to project & operation viability, and for all except the mine operators, site water management is held to overall performance as a measure of fit and responsibility. The design requirements of incorporating each key perspective extends the frame of who the system is being designed for, and inures the fundamental need for holistic water management to deliver successful mine water performance.

Setting direction

In starting out a reformed water management, the intention was to deliver to four key directives:

- Provide a holistic, system approach to managing water across a site or business;
- Integrate & position water into business processes, & match guidance/service required by stage to support outcomes;
- Link science to application to pragmatic problem solving & decision making;
- Bring leadership & guidance across the water arena (all water/hydro disciplines) to suit business need, increase decision rigour for investment strength & build in-house capacity.

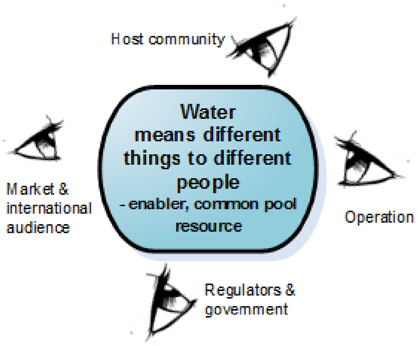


***Figure 1** A representation of the different views of water.*

Mapping the territory

To capture the extents, nature & basis of water as a whole for an overarching view, a generalised global schema map of water in mining was developed as presented in Figure 2. The map lists technical and project development components of water to represent the structure by which project level water knowledge & tools is built (such as a feasibility study), along with interactions and touchpoints with other key disciplines such as closure, community, tailings & geohazards, Linkages between the wide ranging components of water in mining reveal the critical network of overall water performance.

Finding the role

Often it is difficult to place where all of water fits in the traditional structure of organisations – somewhere in & between operations, studies, innovation, environmental & assets. As a means to focus to the role of water without markers & allow a new way of seeing, a map of the practical role of water throughout the life cycle of projects was created as shown in Figure 3. Activity types & level of knowledge are mapped from exploration through studies to operations to legacy, with leadership & strategic management needs across all stages. The business role of mine water is mapped in business function, without department – the role exists as an entity and also between groups.

Establish definition logic & tangible objectives

A working definition of water performance is then adopted as:

1. Suitability of design, investment & operations to surrounding environment & setting across foreseeable life of assets, scales & legacy;
2. Safe operation & water control – inrush/dewatering, drainage, wall stability & potable to sanitary systems;
3. Water security - access to water share/rights as an initial & ongoing enabler of operation;
4. Effective water balance management – particularly rainfall variability & water availability, directly influencing mine production & water supply reliability at wet and dry extremes;
5. Containment of impact sources & any waters contacted – including managed releases or discharge to external environments to agreed targets;
6. Stewardship of water resources & landscapes- respect to existing & future water uses & value to host communities & environments, particularly vulnerability to scarcity or change;
7. Efficiency in the water-power nexus – power demand for water supply, pumping (movement) & treatment technology, dependent to method of power generation for cost & sustainability.

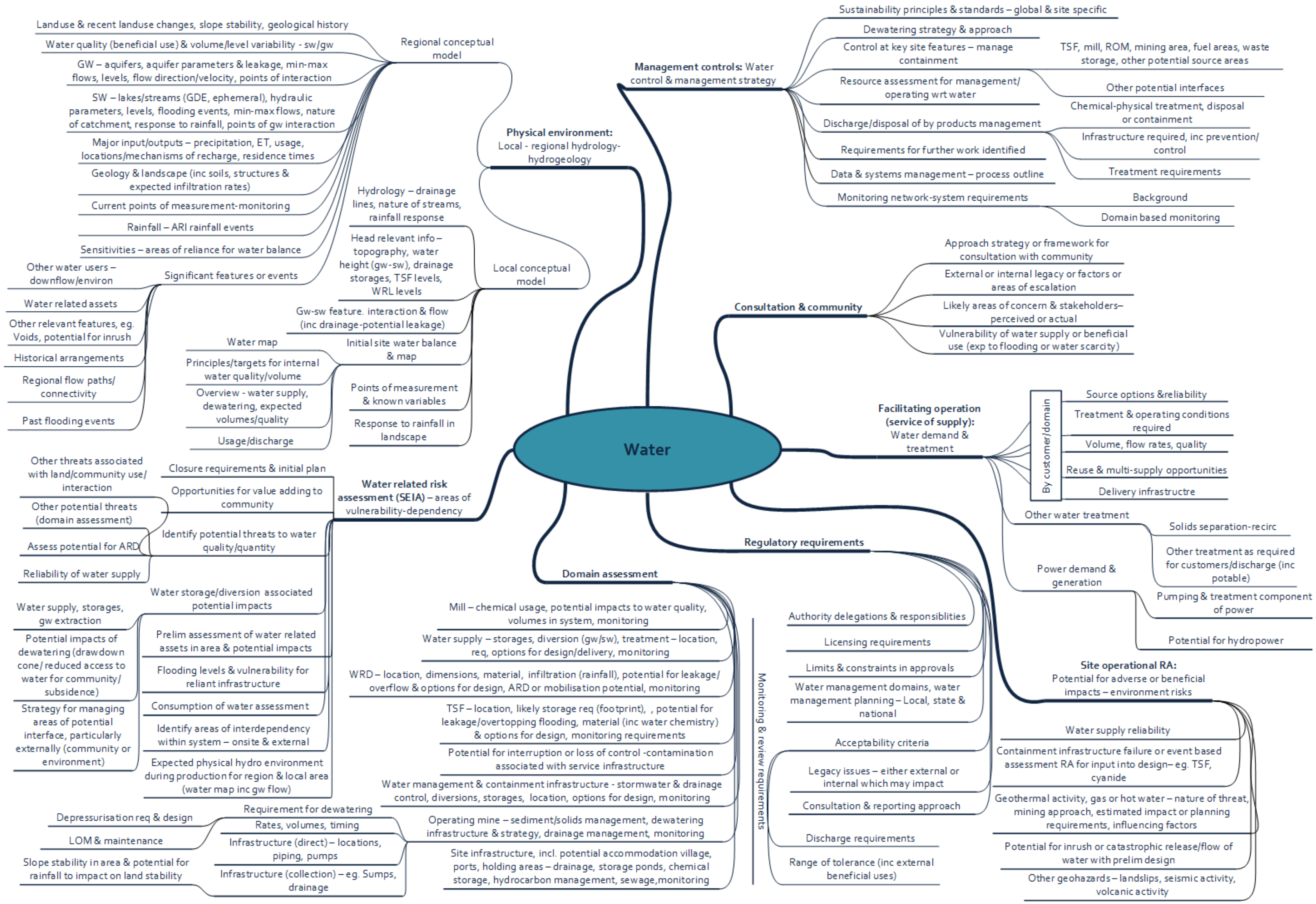


***Figure 2** Schema of water and components across mining activities during feasibility*

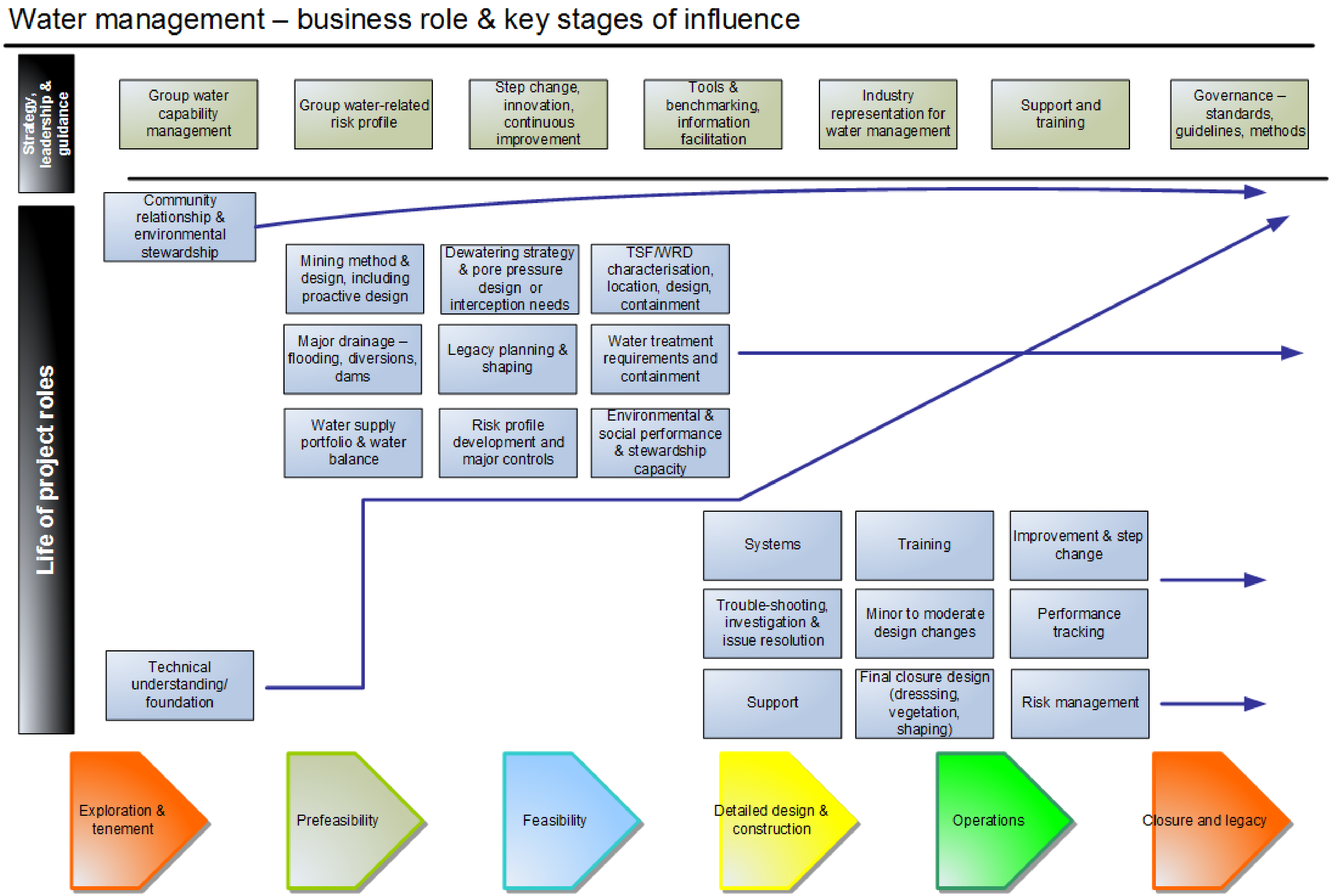


Figure 3 *Map of business role of water and key stages of influence*

Guiding principles of approach

Principles of approach provide strategic guidance of 'how to' mine water management, applicable to feasibility programs, operations and any style of change for water. Developed as a tool for review of options and decision making, the developed key list of principles is as follows:

1. Manage as a system: water, landforms & changes;
2. Design with natural landscape & climate framework;
3. Design with foresight: deploying adaptable or scoped solutions where possible to future needs;
4. Water control: dewatering & mine water for reliability, water movement & handling, safety;
5. Water containment: tailings, impacted water (sediment, metals), discharge program;
6. Water supply resilience: portfolio of sources, including reuse;
7. Stewardship & legacy: landscape design-landform stability, social & environmental outcomes.

Mine water management frameworks

Milestone guidelines by project stage

As a key part of rolling out water management, a series of project guidelines for water were generated for each project stage across the life. Figure 4 shows a guideline template for water at pre-feasibility stage, separating each performance area across the water landscape & listing key information required.

Pre-feasibility is presented as out of analysis of each of the strategy development stages emerges a powerful insight: the most influential, strategic stage underpinning water performance across a mine life is the original design phases, or concept to pre-feasibility. At these stages, economic assumptions and expectations are flagged to Executive and Board level & largely set, major infrastructure such as tailings and pre-feasibility location and design are decided, and mining shapes are determined. Closure fates are also largely governed by major infrastructure decisions. Key work completed at concept to pre-feasibility is fundamental to the success of water performance of the operation.

Mine water management strategy framework

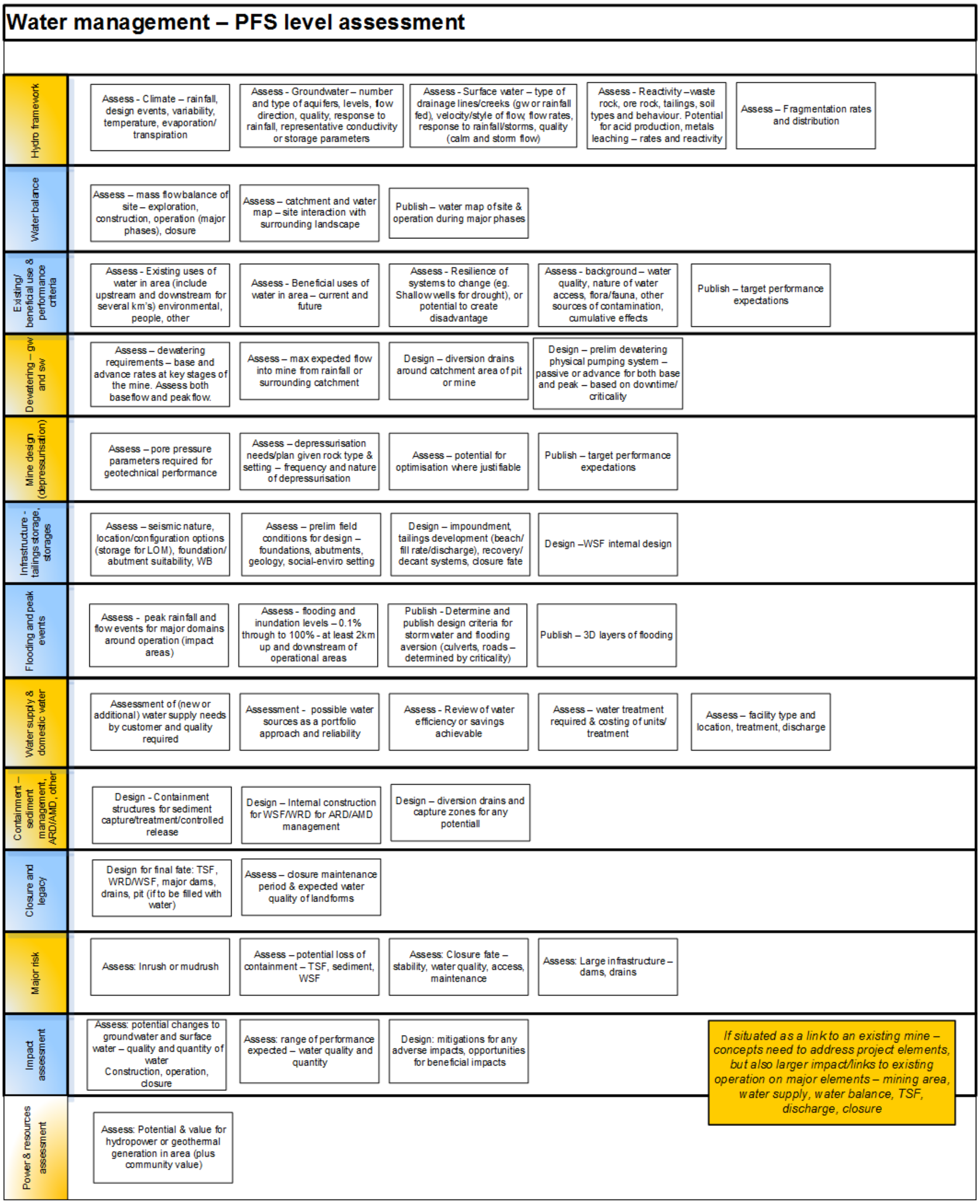
Pulling together mine water management as a cohesive system for operational management is based on forming the strategy & structure of how water functions within a business, how water planning & design is brought together, & what key tools, knowledge/skills & systems are required to deliver strength & adaptability to water performance. As the crux stage, a benchmark framework for holistic mine water management was formed and built as a new way of implementing water for mining and is presented in Figure 5. As a practical and inclusive framework, it works by linking the many together across a shared map of what is required, networking information & planning, and incorporating the diversity of water activity and performance in a common format.

The framework operates under an umbrella of considering acceptable risk, design approaches & potential for change over time. A catchall for overall water performance is reliability, social and environmental outcomes and legacy. As the mechanisms and pragmatics of how, the framework operates across three styles of working:

1. Governance: standards, criteria and metrics - permits & limits, sustainability, risk matrix
2. Core tools and knowledge - mapping technical information needed, plans, core approaches;
3. Capacity to detect and respond - monitoring, training and action response.

Conclusions

In response to an emerging need for improved water management and performance, an innovative and reformed approach for mine water management to deliver water performance across a site or business is presented as discussion & review for the international mine water community. Built by design to bolt into any mine site or business, the philosophy and application is developed and demonstrated through a series of maps, guidelines, and practice frameworks. Implementation with an international mining group has achieved substantial success, realising step change in water performance & long term change and it is shared as a useful resource for the industry moving forward.

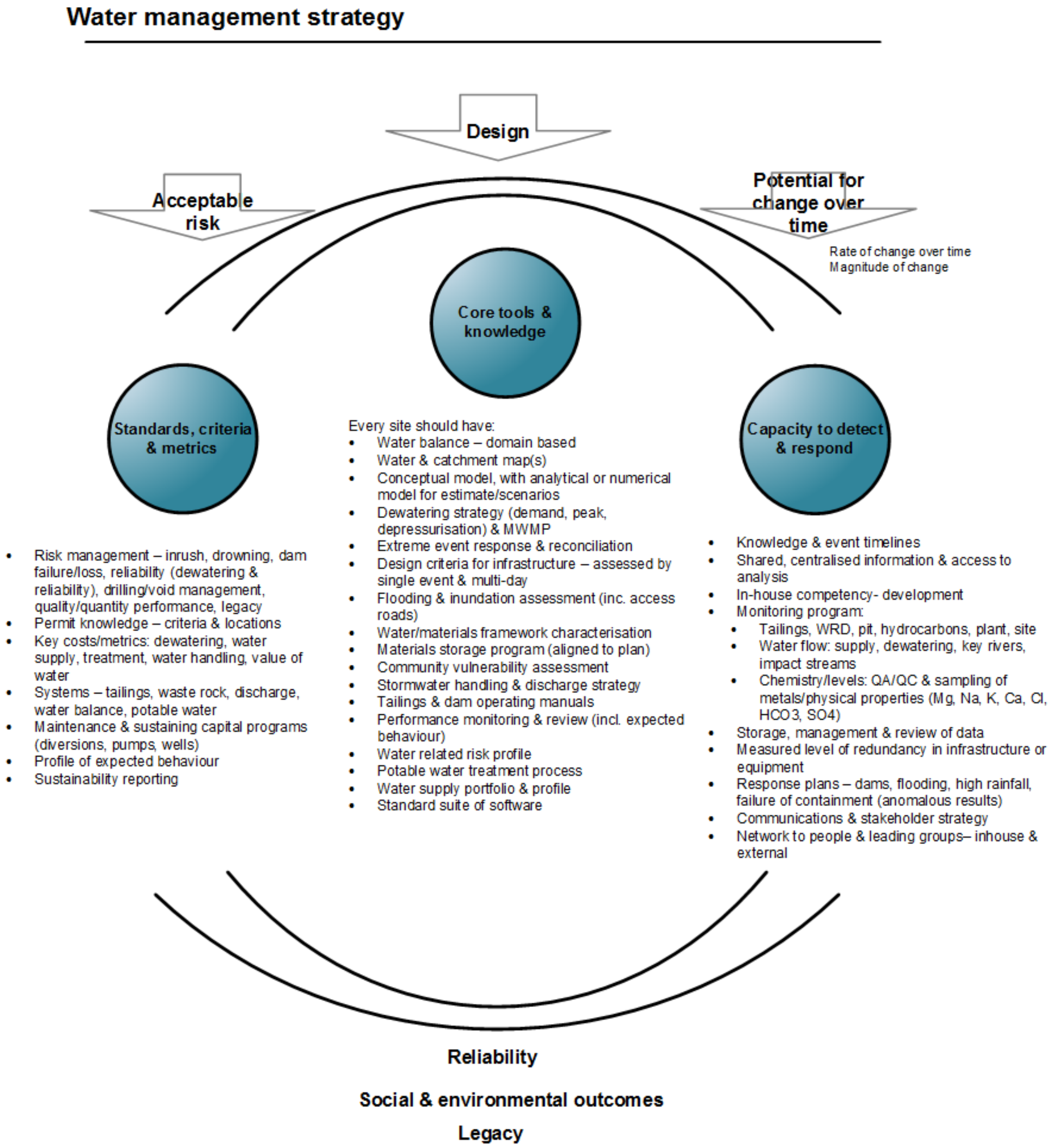


Water management – PFS level assessment

Hydro framework	Assess - Climate – rainfall, design events, variability, temperature, evaporation/ transpiration	Assess - Groundwater – number and type of aquifers, levels, flow direction, quality, response to rainfall, representative conductivity or storage parameters	Assess - Surface water – type of drainage lines/creeks (gw or rainfall fed), velocity/style of flow, flow rates, response to rainfall/storms, quality (calm and storm flow)	Assess - Reactivity –waste rock, ore rock, tailings, soil types and behaviour. Potential for acid production, metals leaching – rates and reactivity	Assess – Fragmentation rates and distribution
Water balance	Assess – mass flowbalance of site – exploration, construction, operation (major phases), closure	Assess – catchment and water map – site interaction with surrounding landscape	Publish – water map of site & operation during major phases		
Existing/ beneficial use & performance criteria	Assess - Existing uses of water in area (include upstream and downstream for several km's) environmental, people, other	Assess - Beneficial uses of water in area – current and future	Assess - Resilience of systems to change (eg. Shallow wells for drought), or potential to create disadvantage	Assess - background – water quality, nature of water access, flora/fauna, other sources of contamination, cumulative effects	Publish – target performance expectations
Dewatering – gw and sw	Assess – dewatering requirements – base and advance rates at key stages of the mine. Assess both baseflow and peak flow.	Assess – max expected flow into mine from rainfall or surrounding catchment	Design – diversion drains around catchment area of pit or mine	Design – prelim dewatering physical pumping system – passive or advance for both base and peak – based on downtime/ criticality	
Mine design (depressurisation)	Assess – pore pressure parameters required for geotechnical performance	Assess – depressurisation needs/plan given rock type & setting – frequency and nature of depressurisation	Assess – potential for optimisation where justifiable	Publish – target performance expectations	
Infrastructure - tailings storage, storages	Assess – seismic nature, location/configuration options (storage for LOM), foundation/ abutment suitability, WB	Assess – prelim field conditions for design – foundations, abutments, geology, social-enviro setting	Design – impoundment, tailings development (beach/ fill rate/discharge), recovery/ decant systems, closure fate	Design –WSF internal design	
Flooding and peak events	Assess - peak rainfall and flow events for major domains around operation (impact areas)	Assess - flooding and inundation levels – 0.1% through to 100% - at least 2km up and downstream of operational areas	Publish - Determine and publish design criteria for stormwater and flooding aversion (culverts, roads – determined by criticality)	Publish – 3D layers of flooding	
Water supply & domestic water	Assessment of (new or additional) water supply needs by customer and quality required	Assessment - possible water sources as a portfolio approach and reliability	Assess - Review of water efficiency or savings achievable	Assess – water treatment required & costing of units/ treatment	Assess – facility type and location, treatment, discharge
Containment – sediment management, ARD/AMD, other	Design - Containment structures for sediment capture/treatment/controlled release	Design – Internal construction for WSF/WRD for ARD/AMD management	Design – diversion drains and capture zones for any potentiall		
Closure and legacy	Design for final fate: TSF, WRD/WSF, major dams, drains, pit (if to be filled with water)	Assess – closure maintenance period & expected water quality of landforms			
Major risk	Assess: Inrush or mudrush	Assess – potential loss of containment – TSF, sediment, WSF	Assess: Closure fate – stability, water quality, access, maintenance	Assess: Large infrastructure – dams, drains	
Impact assessment	Assess: potential changes to groundwater and surface water – quality and quantity of water Construction, operation, closure	Assess: range of performance expected – water quality and quantity	Design: mitigations for any adverse impacts, opportunities for beneficial impacts		
Power & resources assessment	Assess: Potential & value for hydropower or geothermal generation in area (plus community value)				

If situated as a link to an existing mine – concepts need to address project elements, but also larger impact/links to existing operation on major elements – mining area, water supply, water balance, TSF, discharge, closure

Figure 4 *Pre-feasibility water management milestone guideline*



- Risk management – inrush, drowning, dam failure/loss, reliability (dewatering & reliability), drilling/void management, quality/quantity performance, legacy
- Permit knowledge – criteria & locations
- Key costs/metrics: dewatering, water supply, treatment, water handling, value of water
- Systems – tailings, waste rock, discharge, water balance, potable water
- Maintenance & sustaining capital programs (diversions, pumps, wells)
- Profile of expected behaviour
- Sustainability reporting

Every site should have:

- Water balance – domain based
- Water & catchment map(s)
- Conceptual model, with analytical or numerical model for estimate/scenarios
- Dewatering strategy (demand, peak, depressurisation) & MWMP
- Extreme event response & reconciliation
- Design criteria for infrastructure – assessed by single event & multi-day
- Flooding & inundation assessment (inc. access roads)
- Water/materials framework characterisation
- Materials storage program (aligned to plan)
- Community vulnerability assessment
- Stormwater handling & discharge strategy
- Tailings & dam operating manuals
- Performance monitoring & review (incl. expected behaviour)
- Water related risk profile
- Potable water treatment process
- Water supply portfolio & profile
- Standard suite of software

- Knowledge & event timelines
- Shared, centralised information & access to analysis
- In-house competency- development
- Monitoring program:
    - Tailings, WRD, pit, hydrocarbons, plant, site
    - Water flow: supply, dewatering, key rivers, impact streams
    - Chemistry/levels: QA/QC & sampling of metals/physical properties (Mg, Na, K, Ca, Cl, HCO3, SO4)
- Storage, management & review of data
- Measured level of redundancy in infrastructure or equipment
- Response plans – dams, flooding, high rainfall, failure of containment (anomalous results)
- Communications & stakeholder strategy
- Network to people & leading groups– inhouse & external

Figure 5 *Mine water management strategy framework*

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Climate Change and Mine Closure – A Practical Framework for Addressing Risk

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Abstract

The two largest disturbances mining presents which requiring addressing are disturbances to the water balance and energy balance; both of which will be influenced by climate change.

This paper presents a framework to incorporate climate change into mine closure planning from a risk perspective, as risk management will be a key component in decision making for mine closure designs. The newest Representative Concentration Pathway (RCP) emission scenarios allow for ranking climate change outcomes from "very likely" to "less likely" to occur. By combining the likelihood of occurrence for various climate outcomes with the magnitude of the potential failures, a risk based design criteria can be developed for each closure component. This paper will focus on cover systems as closure technology to illustrate application of the framework presented in this paper.

The creation of realistic and attainable design criteria begins on a conceptual framework, allowing non-technical persons to better understand complexities of detailed design. The framework presented utilizes the Köppen-Geiger climate classification system to differentiate climates, largely because of its ability to reflect seasonal differences. Boundaries are determined by a global dataset of long-term monthly precipitation and temperature records, which can been adapted to future climate change predictions. Understanding how climate is expected to change at a seasonal level is more valuable from a planning perspective than from an annual basis. Köppen-Geiger's strong ties to landscape signals such as vegetation and water availability make it ideal for closure planning.

Implications for understanding the required equilibrium between the closure landscape and the existing landscape provide an indication of timescales involved. For example, it is not realistic to believe engineered structures will provide the expected performance following a glaciation event. Closure timeframes are typically 100 years, if not longer, therefore an appropriate framework to address the challenge of designing structures with defensible controls on identified risk is required.

Key words: Climate Change, conceptual design, cover systems.

Introduction

As with all engineering, in particular mine waste management, elements of a closure design are subject to failure and consequently have associated lifespans. To maximize longevity of designs, engineered systems have to be incorporated into landscapes to reach a long- term equilibrium. The two largest disturbances mining presents which require addressing are disturbances to water and energy balances. A mine typically features multiple mine closure domains, each with water and energy balances for creating design criteria. Climate change will act to change components of the water and energy balances and only through novel and innovative designs can one manipulate remaining water balance components to achieve the design criteria. Of fundamental importance, and the subject of this paper, is the overarching influence of site-specific climate conditions, more specifically a methodology for incorporating climate change on site-specific climate conditions for mine closure planning. To effectively plan for the next century and beyond, mine closure planning must incorporate climate change throughout its development.

Climate acts as stressor to designs when water balance components deviate beyond initial conditions towards a new equilibrium; one not anticipated and/or accounted for in the design. Generally, the more closely a design, such as cover system design, is able to maintain equilibrium within the environment and climate, the greater the longevity. Suitably robust designs are therefore required to minimize imbalances through time, such as those imposed by climate change. Designs can be implemented to exploit or enhance attributes of the environment to make cover system designs more robust and resilient. For the purposes of this paper, a robust design refers to a system which can continue functioning in the presence of internal and external stressors without fundamental changes to the original system. In contrast, a resilient design is a system that can adapt to internal and external challenges by changing its method of operations while continuing to function. While components of the original system are present through time, there is a fundamental shift in mechanisms reflecting an adaptation to the new environment.

Therefore, to increase resilience and robustness in design, identification of dominant mechanisms of the cover system is required; then, climate change applied. In the context of climate change and the evolution of cover systems, designs will require a recognition that processes and mechanisms intrinsic to cover system function will evolve. Failure modes will be the result water balance components manifesting themselves in a way not supported by the cover systems design (i.e. runoff, evaporation, interflow, etc.).

Early recognition of risks climate change poses to designs will improve confidence in designs and allow refinement. Therefore, by introducing conceptual analysis of climate on conceptual designs, more front end loading is possible (Thomke and Fujimoto 2000). Here, the view is that design is an iterative process, driven by trial-and-error experiments that are guided by knowledge of underlying relationships between cause and effect. The more refined the starting scope of knowledge is, the more efficient a solution can be determined. To complete this task for mining landscapes, a framework must be used which communicates design risk under the influence of current and future climate.

Methods

The framework for incorporating climate change into mine closure planning as risk management tool will be a key component in decision making for closure designs. To evaluate risk, a formula such as Equation 1 must be considered.

$$Risk = Likelihood\ of\ Occurrence \times Consequence\ , \qquad (1)$$

Likelihood:

Given that this tool will be used as a preliminary identification of risk, at a conceptual level, likelihood of occurrence can be qualitative measures based on the Representative Concentration Pathways (RCP) outlined by the IPCC (IPCC 2013). The IPCC attach no probability or likelihood of occurrence to the four different RCPs. The four scenarios are named after the radiative target forcing level for 2100, based on the forcing of greenhouse gases and other agents (Van Vuuren et al. 2011). These values are relative to pre-industrial levels with the lowest scenario, RCP2.6, requiring stringent global climate policies to limit emissions (Van Vuuren et al. 2011). Both RCP 4.5 and RCP6 represent forcing equating to several climate policies and most non climate policy respectively. The final scenario, RCP8.5, continues the current trend of increasing annual GHG emissions, representing the high range of non-action climate policy scenarios.

The RCPs can be qualified according to each designers/ stakeholders risk profile, however for the examples outlined in this paper, Figure 1 defines these likelihood qualifiers from “very likely” to “very unlikely” (Figure 1).

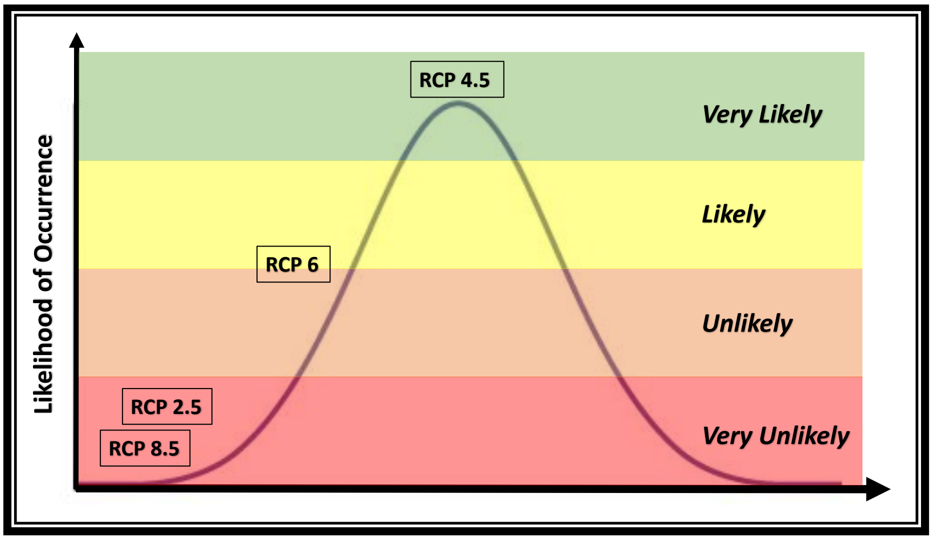


Figure 1 *Proposed qualitative probabilities for using IPCC Representative Concentration Pathways (RCP) to evaluate risk at a conceptual evaluation stage.*

Consequence:

Consequence of a specific failure is required to evaluate the risk of potential cover system designs. In terms of a consequence, it is defined as the qualitative performance metric assigned to the cover system. Typically for cover system design, control of net percolation (NP), oxygen ingress (O_2), and/or stability/erosion will be a design criteria. A continuum of performance for NP, O_2 and erosion rates for a cover system exists for different climate regimes. Within a single climatic regime, the same continuum may be a result of the influence of differing abilities of a cover system to evaporate water and to promote runoff from the landform. These mechanisms combined with attributes of the engineered design (i.e. landform and cover system) yield a performance metric based on climate.

Climate change stressors act on components of the water balance, which will differ for each mine location, between landforms and even across landforms. Conceptually understanding how changes in water balance components will influence design criteria is important because it will be these components that will be manipulated by designers to ensure design criteria for present and future climate are satisfied.

The continuum of cover system performance is presented conceptually in terms of "very low," "low," "moderate" and "high" NP, O_2 and erosion rates. The qualitative descriptors are common across sites and climates, although their nominal performance values will differ. For example, 'very low' NP for a cover system in a tropical climate will still exceed those for a cover providing very low rates in an arid environment.

By defining performance expectations in this qualitative way, designers will begin conceptually understanding early on, what realistic performance expectations are for a design based on climate. Once a conceptual basis for performance is understood, the consequences of not meeting the design criteria can then be assessed.

Therefore, a tool is required to assess the effects of climate on cover system hydrology at scales relevant to landform and cover system design. The Köppen-Geiger climate classification system (Köppen system) is such tool; capable of resolving differences in seasonal climate (Peel et al. 2007). It has been shown that utility of average annual conditions is limiting to cover system design, therefore incorporating seasonality provides a perspective landform hydrology (INAP 2016). Additionally, the Köppen system came into broad use largely through its strong connection to landscape vegetation signals, an important component for many cover system designs. Most sites have access to historical monthly precipitation and temperature data, or through a nearby meteorological organization.

Since the Köppen system system is defined by precipitation and temperature thresholds, it can be easily applied to global climate model output data to re-classify a site for future conditions. Climate change alters hydrology by changing the dominance or expression of certain mechanisms (i.e. runoff, evaporation, etc.). Since the Köppen system can aid designers in understanding conceptually, dominant hydrological mechanisms required by the cover system, that same conceptualization can be applied to future conditions to investigate any differences required for cover system function. This early conceptualization refines design alternatives much earlier in the design process without the need for complex computer simulation. For example, if currently a cover system design is in the 'very low' range for NP performance, an increase to a 'low' or 'moderate' NP increases the consequence of that potential failure. With the likelihood and consequence determined, a conceptual form of risk can qualified for a particular design into the future.

Risk:

By combining the likelihood of occurrence for various climate outcomes (RCPs) with the magnitude of the potential failures (i.e. 'very low, 'moderate'), a risk based design criteria can be developed for closure components (Figure 3).

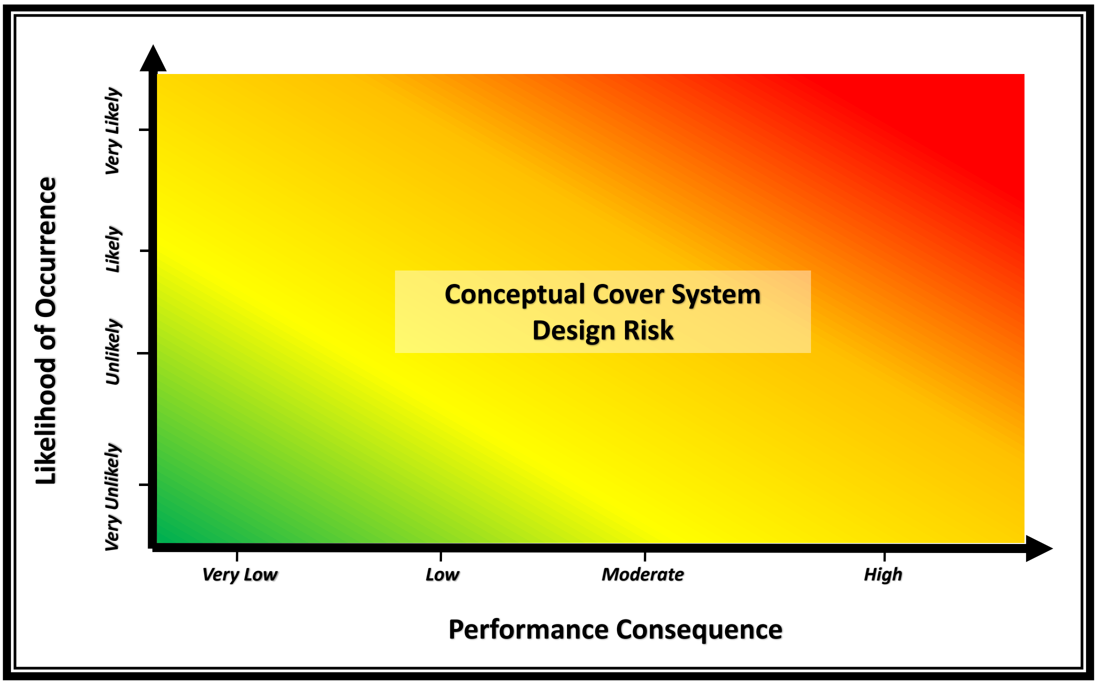


Figure 3 *Qualitative risk assessment based on conceptual climate change understanding.*

Although this approach can be applied to other mine closure activities, this paper focuses on cover systems. Once design risks have been identified, they may be deemed satisfactory by stakeholders, mitigated by additional design elements, or reduced through increased understanding. Activities such as field characterization programs may seek to reduce uncertainty in design elements, reducing risk. In this way, early conceptualization using a risk based approach helps focus future studies on only what is necessary.

This framework is able to incorporate climate change into mine closure planning from a risk perspective, as risk management will be a key component in decision making for mine closure designs.

Case Study- Temperate/Tropical Shift:

To demonstrate the framework's utility for incorporating climate change in mine closure planning from a risk perspective, examples of its application, interpretation and result are presented. An example was selected based on prevalence throughout the mining industry in regards to climate, closure objectives and configuration. Generally, cover system design criteria focus on NP, O_2 and/or landform stability (erosion) and will be the focus the examples below.

Mining in South- Central Africa has long been a productive economy for resources such as copper, cobalt, gold zinc, lead, nickel , and iron to name a few. Countries such as Zimbabwe, Malawi and Zambia belong to geographies rich in these resources as well as mine waste. Zambia for example, contains ~77 million tonnes (388 ha) of waste rock and ~791 million tonnes of tailings (9125ha) (Environmental Council of Zambia 2004).

Likelihood ('Very Likely'):

These countries are located currently in what is classified as a humid subtropical climate (Cwa Köppen classification). Temperatures are considered intermediate with hottest months exceeding 10℃ and the coldest months between 18℃ and freezing. Summers are hot and coincide with the driest months which receive 10 % or less precipitation compared to wettest winter months. Figure 4 presents the range of climate scenarios possible for the region by 2075-2100. All future scenarios identify a shift to a tropical savannah climate. Therefore, a tropical savannah can be considered **'very likely'** to be expected if again we consider the RCP4.5 scenario.

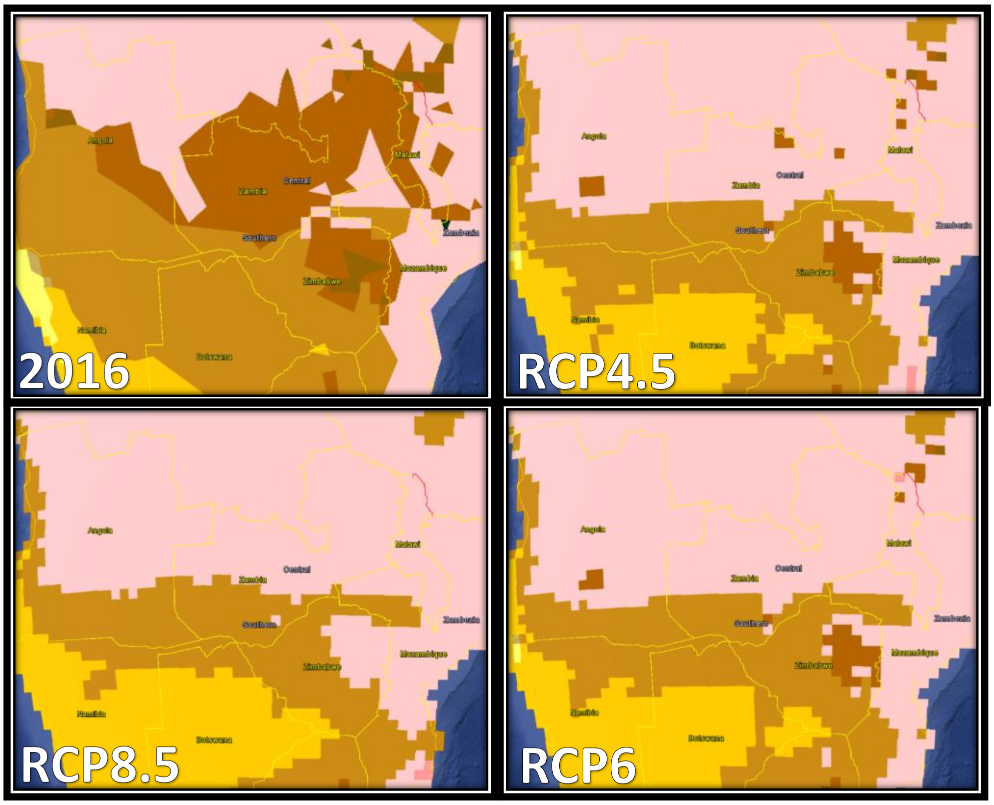
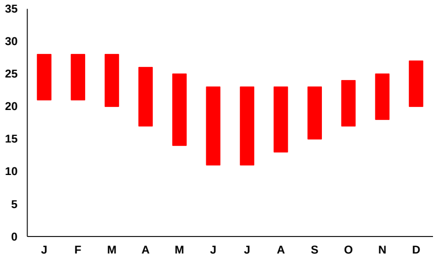
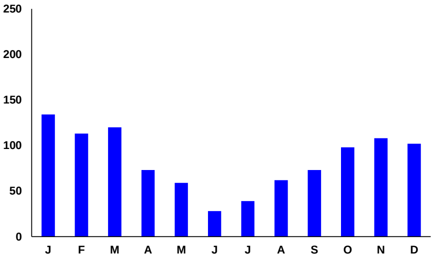
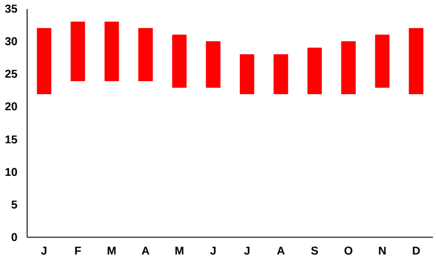
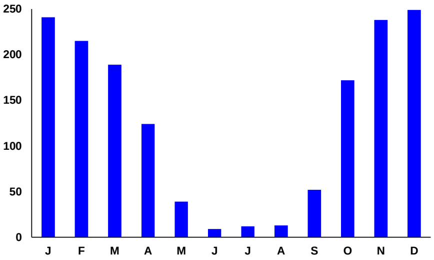


Figure 4 *Köppen-Geiger climate classification for present and future climate change scenarios in Central Africa.*

Consequence ('High'):

This early conceptualization for potential cover systems identifies that for parts of the year (winter), oxygen will be difficult to control due to the absence of water in the soil. Therefore, control of NP will be more appropriate as a design criteria of this cover system. Seasonal conceptualization is not possible when using annual averages, thus re-confirming the utility of the climate classification framework to be used in risk management. To further explore the predicted shifts in seasonal precipitation (PPT) and temperature regimes, Table 1 identifies key attributes of the climate expected to change most.

Table 1 *Comparison of present and future climate for Zamia, Africa region.*

Scenario	Köppen	Temperature	PPT Distribution
Current	Cwa		
RCP4.5	Aw		

A tropical savanna (Aw) climate has monthly mean temperatures above 18°C for every month with a pronounced dry season. In the tropical savanna climate there is a distinct dry winter season, and a wet summer season. In the future with an Aw climate, warmer temperatures prevail throughout the year, with loosely defined seasons. Consequently, potential evaporation can be expected to increase generally; not coinciding with a specific season. The most profound change in climate comes with large increases in precipitation (Table 1). Even though annual total PPT in this region is expected to increase by 50%, more applicable to mine closure planning is its distribution of the PPT throughout the year. An amplification of the bimodal distribution of monthly PPT signifies delivery of more water over shorter time periods to cover systems in the future.

To understand the consequence of this shift on future cover systems, a conceptualization of water balance components present and future is required. At present, a large range of cover system design alternatives exist to manage NP to a 'very low' or 'low' range for a temperate climate. Precipitation is relatively low compared to PE, thus store-and-release type cover systems are most practical to manage NP. However, without revision to the cover system design that accounts for future climate, the water balance components change. With PE increasing slightly over time in response to warming, precipitation increases though, un-proportionally. This discrepancy in PE and PPT has large implications for water the management involving cover systems.

With a surplus of water on the landform, it is diverted to runoff and/or transmitted as NP into underlying waste material. Conceptually, erosion and NP consequences have been identified. If only NP is considered, the difference in PPT and PE translates to a proportional increase in NP.

The original cover system design criteria under current climate may stipulate achieving very low to low NP was necessary. However, it is clear that by conceptually applying climate change to the same cover system, achieving a NP control in that range will no longer be possible without revisions to the design. More likely is that NP consequence will be 'moderate' to **'high'**

Risk:

When risk is re assessed for the climate change scenario by taking the 'very likely' from the likelihood and agreement across all RCP scenarios and combining this with consequence of 'high' we end up in a zone of Very High Risk for this design in the future even though the design in the present climate represents a low risk (Figure 5).

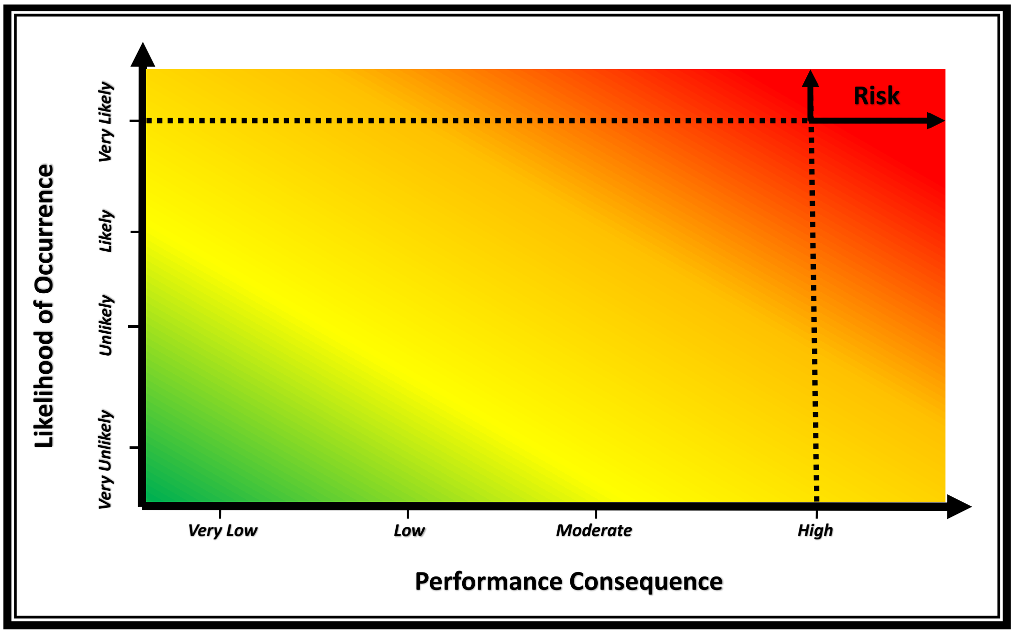


Figure 5 *Qualitative risk assessment for case study example.*

Given the risk ranking has materially increased in the climate change scenario, mechanisms of "failure modes" can be explored to determine what this increase in risk means for design, as well as assessment of design alternatives. By investigating this risk through potential failure modes, we are thus able to identify the mechanisms of the cover system contributing to a large amount of the risk. Those two mechanisms identified in this case are runoff and NP and the consequences for closure risk management are erosion and increased seepage. The realization of these risks will therefore depend on elements of landform design and thus landform design alternatives can then assessed based on the identified mechanisms that require management of risk:

- The exploitation of vegetation to help mitigate both erosion and NP can be explored given the potentially favorable climate that is considered as part of the climate change scenario. Vegetation changes over time need to be balanced with looking at performance over the short to medium term (or even current conditions) to determine if reliance on vegetation is appropriate as a risk management toll over both medium and long time scale as vegetation evolves and begins to take hold.
- The use of an engineered barrier technology can be considered to reduce NP can be explored, in this case the increased drying and wetting cycles inferred in the climate change scenario would reduce the likely performance of compacted clay layer technology and the associated effectiveness into the future. Geomembranes may be more appropriate than compacted clay technology, however, the use of this technology would then necessitate the use of surface and sub surface engineered drainage to transmit the higher precipitation event storms laterally off the landform that would otherwise cause erosion.
- Consideration of a variation on the existing design can also be explored, in this case thicker enhanced store and release cover systems with the aim to maximize the evaporative potential by keeping water accessible by increasing field capacity, and therefore reducing NP. This thickening would offer a larger potential for vegetation support which will be a necessary component to manage runoff induced erosion with the future precipitation regime.

As is evident, by combining conceptual components of future climate change effects and cover system performance, the framework presented allows for more detailed work such as modelling, to begin from a more informed perspective, yielding a more robust design informed by risk.

Conclusions

The creation of realistic and attainable design criteria first begins on a conceptual framework, allowing non-technical persons involved in closure planning to better understand complexities of detailed design. The framework presented within this paper utilizes the Köppen-Geiger climate classification system to differentiate climates, largely because of its ability to reflect seasonal differences. The framework is determined by a global dataset of long-term monthly precipitation and temperature records, which have incorporated the potential effects of future climate change predictions. Understanding how climate is expected to change at a seasonal level is more valuable from a planning perspective than from a strictly annual basis.

Implications for understanding the required equilibrium between the closure landscape and the existing landscape provide an indication of timescales involved. For example, it is not realistic to believe engineered structures will provide the expected performance following a glaciation event. However, given that closure timeframes are typically 100 years, if not longer, an appropriate framework to address the challenge of designing structures with defensible controls on identified risk is required.

Climate change is taken into account in a variety of mining projects. Approaches to incorporate climate change into closure design differ from site to site and are often limited in temporal length. There are currently no clear guidelines as to how to take into account climate change for the long term prediction of closure systems performance. What is presented in this paper is a conceptual tool that provides a greater awareness of climate change and its effects as it pertains to the management of water resources in the context of mine closure design and cover system technologies.

As is evident, by combining conceptual components of future climate change effects and cover system performance, the framework presented allows for more detailed work such as modelling, to begin from a more informed perspective, yielding a more robust design informed by risk. This mechanism allows a return full circle to ensure resilient design

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Cumulative Groundwater Impact of Mining in the Kalahari Manganese Field and the Need for a Strategic Environmental Assessment Approach

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Extended Abstract

During the last few years the mining sector in the Kalahari Manganese Field in the Northern Cape Province of South Africa has increased significantly. Groundwater in the semi-arid Kalahari is a scarce commodity. Therefore water supply for mines, impacts due to mine dewatering and river diversion plans have increased pressure on limited water resources. Groundwater quality and quantity impacts of existing and developing mining projects are investigated individually. This paper presents predictions and results from individual hydrogeological investigations and elaborates how a strategic regional environmental assessment approach can summarise the cumulative impacts to fundamentally understand the regional footprint of mining in the area.

The Kalahari Manganese Field (KMF) is estimated to contain approximately 1,000 Mt of potentially exploitable manganese resources, while its geological simplicity makes the KMF one of the most important manganese resources in the world. The manganese deposits represent structurally preserved erosional relics of the Paleoproterozoic Hotazel Formation of the Voelwater Subgroup (Transvaal Supergroup). It consists of a Superior type iron-formation interbedded with manganese ore in three sedimentary cycles of which the lowermost unit is the most economically viable. Several abandoned mines and a number of active mining operations are located in an area of approximately 550 km^2. Besides, a number of emerging manganese prospects are in the process of obtaining mining licenses.

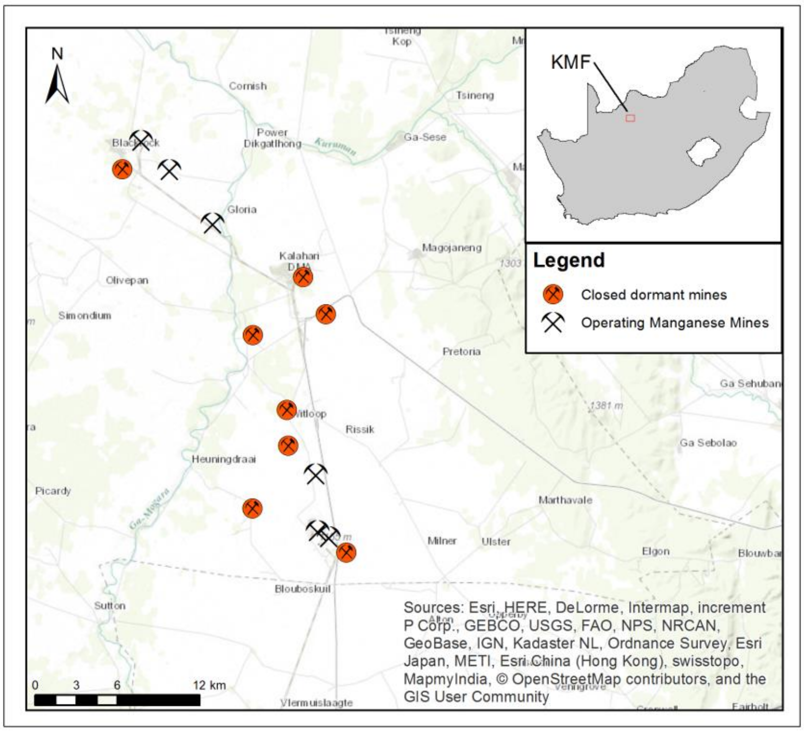

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***Figure 1**: Overview of Mining Activities in the Kalahari Manganese Field (KMF)*

Hydrogeological investigations including numerical groundwater models have been implemented to predict the impacts of the proposed individual mining sites on groundwater quantity and quality in the closer proximity of the development. The groundwater models were developed to predict mine dewatering, contamination plumes, river diversions but also mine water supply. All of them are focused on the closer mining area or relevant concession areas only. Neither regional flow patterns in porous media and fractured aquifers nor cumulative groundwater impacts have been investigated so far. Hydrochemical and water level monitoring results as well as results from groundwater flow models have been taken as basis for risk assessments. Taking these results into consideration it has becomes clear that a broader look at cumulative impacts from numerous smaller mine concessions is needed.

Two different aquifer systems dominate the hydrogeology of the KMF. First the unconsolidated Kalahari sediments as primary, porous aquifer and the secondly the underlying fractured bedrock (secondary aquifer). Ephemeral rivers, mainly the Gamogara River and its tributaries, contribute to the groundwater resources and act as important indirect groundwater recharge sources. However, mine dewatering or more important the artificial diversion of smaller river sections might have significant impacts on the aquifer systems or downstream water users and mine sites. Additional impacts may result from different operational life of mines. With the existing monitoring tools and model predictions at small scales, a reasonable and reliable assessment is impossible.

Environmental Impact Assessments and model predictions will become more significant and reliable when cumulative effects on a regional scale are considered. In order to achieve the above goals the following objectives are proposed:

- Development of a decision support system,
- Collaboration between mining industries, government agencies, experts and specialists to improve data sharing and knowledge etc.,
- Development of a strategic environmental (and socio-economic) management plan to guide mining and third party interests and ensure long-term monitoring,
- Implementation of a regional ground- and surface water monitoring network.

Like other water management plans for mining areas in Namibia and Canada have shown (see [1] and [2]), monitoring networks and regional numerical modelling can be reliable tools for both estimating cumulative impacts and mitigating requirements for mining concessions, avoiding duplication of work and conflict of interests

Key words: Mine Water, Numerical Modeling, Strategic Assessment, Kalahari Manganese Field

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1000 Years of Mining: What Means Geogenic Background of Metals in the Rivers of the Harz Mountains?

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Abstract

Scope of the present study was a holistic approach to investigate the geochemically striking characteristics of the Harz Mountains in order to obtain reliable information about the respective metal concentrations in the overall Harz area. After World War II, the Iron Curtain split the Harz Mountains and since that time neither a common mine water management for the whole Harz Mountains nor a common assessment of the hydrological and hydrochemical data of the surface water monitoring systems of the neighbouring Federal States Saxony-Anhalt and Lower Saxony anymore existed. The present study is the first common assessment of the geogenic background since the Iron Curtain was established. The applied methodology makes use of defined percentiles of a statistically reliable database. The data base comprises a total of approximately 210 sampling locations with recent data after the year 1999, out of which remained after preselection 177 sampling locations. The key geochemically striking elements due to naturally increased metal concentrations in the metallogenic riverine landscape are Al, As, Be, Cd, Co, Fe, Mn, Ni, Pb and Zn in the East Harz as well as Ag, Hg and Pb in the West Harz. Due to the results, the Harz Mountains will be subject to WFD exemptions.

Key words: Natural background level of mining or metallogenic landscapes, Harz Mountains

1. Introduction

With the implementation of the EC Water Framework Directive 2000/60/EC (WFD) [1] and its key objective of a holistic water management at the level of river basins also mining areas are in the focus due to certain geochemically striking characteristics. The objective of the WFD to reach a high level of protection of the aquatic environment, reflected by a good chemical and ecological status by 2015, may not be reached in riverine landscapes with metallogenic origin. However, the WFD provides a number of exemptions that allow for less stringent objectives, including the extension of the implementation deadline maximum by 2027. Such criteria are

1. the technical feasibility is not given within the timeline
2. disproportional increase of costs when completing the measures within the timescale
3. natural conditions do not allow to achieve an improvement of the water body status timely.

Regarding to the last point, natural conditions may include elevated geogenic metal concentrations caused by natural specific local conditions leading to concentrations in surface water, which are not in conformity with the Environmental Quality Standards (EQS) of Directive 2008/105/EC [2]. To determine less stringent objectives for the implementation of the WFD due to naturally elevated geogenic metal concentration, an assessment about the geogenic background concentration in surface waters is necessary. Geogenic background concentrations are defined as concentrations, which naturally occur in surface water without any anthropogenic influences.

The objective of the present study was a holistic approach to investigate the geochemically striking characteristics of the Harz Mountains in order to obtain reliable information about the respective metal concentrations in the surface water of the overall Harz area. The data will be used as a justified and reliable basis for the application of exemptions according to WFD article 4 and the respective EQS according to Directive 2008/105/EC.

2. Geological Setting and Mining Activities in the Harz Area

2.1 Geology of the Harz Mountains

The Harz Mountains were formed during the Variscan orogeny 300 Mio. years ago by folding, uplifting and erosion. The Harz Mountains consist of Paleozoic rocks, mainly Devonian and Carboniferous rock formations. A smaller stripe of the western and southern Harz Mountains consists of Rotliegend and Zechstein as well as Silurian in the Lower Harz. Especially in the Central Harz, around the Brocken area, but also spread over the whole Harz Mountains, there is volcanic rock. Due to a strong diagenetic hardening at metamorphose conditions the rocks are solid without a mentionable permeability.

Geologically and morphologically the Harz Mountains can be separated in three areas (the Upper Harz, Central Harz and Lower Harz), which differ in their geological settings and the magmatic, tectonic, sedimentary and erosional genesis. The Upper Harz is geologically dominated by the Clausthal Culm Fold Belt, the Upper Harz Devonian Saddle and the Acker Bruchberg Zone. The Upper Harz comprises the Oker Granite, the Ecker Gneiss Complex, the Harzburg Gabbronorit Massive, as well as Diabas in the western part of the Brocken Granite. The north western part of the Central Harz is formed by the Blankenburg Fold Belt, including the Elbingeröde Complex, the Tanner Greywacke and the Sieber Depression. The Central Harz consists of Carboniferous intrusions, Devonian schists, Diabas, greywacke and granite (eastern part of the Brocken, Ramberg). The Lower Harz includes the Harzgerode Fold Belt with the Selke und South Harz Depression as well as the Wippra. It is formed by Ordovician and Devonian greywacke formations and molasses basins of the lower Permian ([3], [4], [5]).

All three geological units of the Harz Mountains show the occurrence of vein deposits with different mineralogical characteristics (see figure 2). The ore veins have been formed during the younger tectonic expansion. As a result of multiphase fault tectonic events there exists a system, which typically have an arch shaped course, leads to a crosslinking of all important veins [6]. In the Upper Harz (mining areas amongst others Clausthal-Zellerfeld, Grund-Silbernaal, Lautenthal) Middle and Upper Devonian layer bound lead-zinc-barytes and iron ore deposits have a great significance as well as Mesozoic lead-zinc-mineralisations. In the Central Harz silver-antimony-sulphosalts are of importance. In the south and southwest there are quartz-magnetite-chalcopyrite veins, quartz-hematite veins baryte-hematite veins and baryte-veins. In the Lower Harz there are imports deposits of pyrite, siderite and flourite. Lead-zinc-ores are not as significant as in the Upper Harz [5].

2.2 Mining Activities

The origins of mining in the Harz Mountains date back nearly 1000 years. In the middle age the mining in the Harz Mountains reached a prospering period. Main products of the mining activities were silver, copper, lead and iron and since the 19th century also zinc. From the 16th to the 19th century about 40 to 50 % of the silver produced in Germany had been mined in the Harz Mountains. In the 20th century the mining activities in the Harz Mountains decreased. In 2007 the last mine closed in Bad Lauterberg.

From the middle age until the early 20th century the miners created a huge network of facilities for the production of waterpower and the water management, the so-called "Oberharzer Wasserregal". It consists of at least 143 water-retention basins, more than 500 km ditches and 30 km underground watercourses. The facilities are spread over 200 km² in the western part of the Harz Mountains. Also in the Lower Harz exists a system of ponds and ditches for the water management in the mining areas. However, it does not have the extensions as the system in the western Harz.

2.3 Hydrology

The Harz Mountains form a watershed between the Elbe catchment area in the east and the Weser catchment area in the west. The rivers which drain in the west are the Oker, Oder, Sieber, Söse, Innerste and Weser itself. The rivers which drain in the east are the Wipper, Selke, Helme and Bode with

Rappbode. The subordinated catchments areas and their numbers of water bodies are listed in table 1. Figure 1 shows the spatial location of the catchment areas.

Table 1 *Catchment areas and number of water bodies (in brackets: number of investigated water bodies when different from total number)*

Elbe Basin		Weser Basin			
River	waterbodies	River	waterbodies	River	waterbodies
Wipper	4 (2)	Oker	11	Söse	7
Selke	4 (3)	Oder	9	Innerste	12
Helme	4 (2)	Sieber	7	Weser	2
Bode + Rappbode	16 (14)				

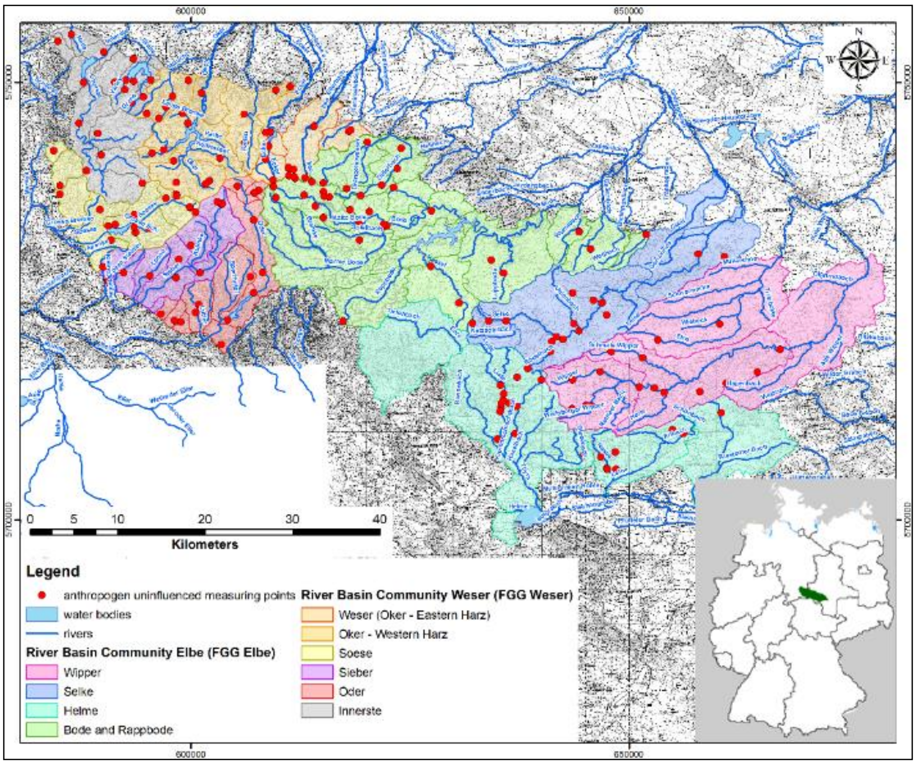

Figure 1: *Overview map of the river basin communities (FGG), the catchment areas in the Harz Mountains and the anthropgenic uninfluenced measuring locations.*

After the classification according to Briem [7] the riverine landscapes of the Harz Mountains are dominated by the metallogenic typ. Smaller parts especially around the Brocken are described as siliceous. Carbonatic-dolomitic landscapes are of minor importance.

3. Methods and Materials

In the EU there is not yet a generally accepted and standardized methodology to assess the geogenic background concentration in surface water. The total concentration of heavy metals in a river is the sum of a complex combination of natural and anthropogenic factors. The applied approach was developed by Schneider et. al. (2003 [8], 2014 [9], and 2016 [10]), the authors adapted and upgraded a general methodology for natural background concentration in groundwater developed by Schleyer & Kerndorff (1992) [11]. The methodology makes use of defined percentiles of a statistically reliable database, which includes metal concentrations of the total phase and the dissolved phase. The data were obtained from the monitoring network of the competent authorities of Saxony-Anhalt (State Authority for Flood Protection and Water Management Saxony-Anhalt) and Lower Saxony (Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency) complemented by additional measurements to close gaps in the existing data base. The procedure was validated through the data of Birke et. al. (2006) [12] and comprises following steps:

- Elimination of all sampling locations from the database which have anthropogenic influence due to point sources (preselection of sampling locations). This applies to sampling locations, in whose catchment areas mining activities, like mines, mining piles, smelters or the Oberharzer Wasserregal are identified (based on date of fig. 2) and also contaminated sites, settlements and industry.
- GIS-based allocation of the sampling points with respect to the catchments areas, being the evaluation units,
- Elimination of the diffuse anthropogenic inputs which were defined as the concentrations larger than the calculated 90% percentile (P(90)).
- Assessment of the geogenic background by statistical calculation of the 90% percentile (P(90)) of the preselected data to find out the anthropogenic uninfluenced concentrations per surface water body.

For the measured data for the eastern Harz the first step was omitted, since already preselected data without anthropogenic influences were provided by the State authority for flood protection and water management Saxony-Anhalt (LHW).

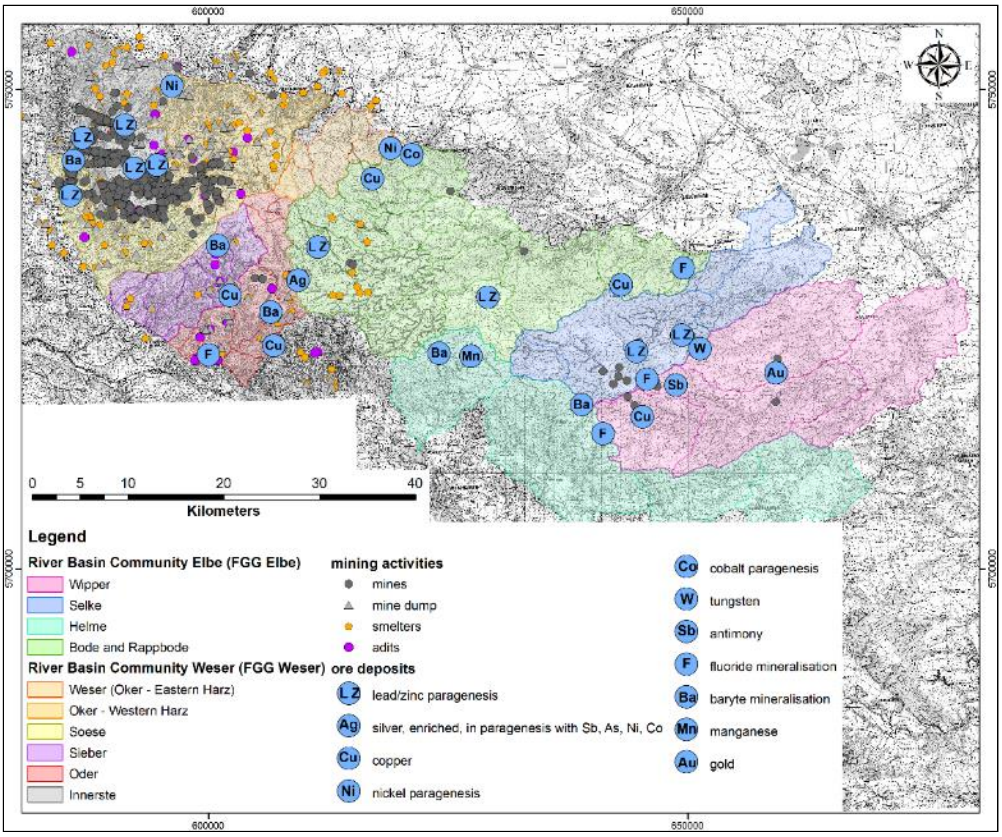

Figure 2: *Overview map with ore metal ore deposits and mining activities in the Harz Mountains.*

4. Results

Figure 1 shows the remaining sampling locations in the Harz Mountains after the method from chapter 3 was applied. Based on these sampling locations and their data, the results were calculated in the following tables.

The calculated geogenic background concentrations for the total phase are presented in table 2 and for the dissolved phase in table 3. For the total phase, only for three elements an EQS is defined. For silver, in all catchments areas of the western Harz the background concentrations exceeds the EQS, but for no catchment area in the eastern Harz. This is accordance with the western Harz as a significant mining area for silver. The other two elements, for which an EQS for the total phase is defined are selenium and thallium, however both are of minor importance in the Harz region, and there is no exceeding of the EQS for both.

Table 2: *Selected geogenic background concentrations of the total phase in the catchment areas of the Harz Mountains, calculated as the arithmetic mean of the 90%-percentile of the single water bodies, and EQS-values (**bold**: concentrations > EQS).*

	Unit	EQS	Oker	Oder	Sieber	Söse	Innerste	Wipper	Selke	Helme	Bode	Weser
			P90	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**
Ag$_{tot}$	µg/l	0,02	**0,92**	**0,25**	**0,24**	**0,27**	**0,32**	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Al$_{tot}$	µg/l		782	693	323	607	651	n.a.	n.a.	< 10	445	290
As$_{tot}$	µg/l		1,16	0,75	0,25	0,63	0,25	4,54	1,69	2,10	4,96	0,67
B$_{tot}$	µg/l		< 30	30	30	48	< 30	< 30	< 30	60	100	36
Ba$_{tot}$	µg/l		41	81	122	89	55	12	51	62	110	13
Cd$_{tot}$	µg/l		0,45	0,14	0,12	0,12	0,38	1,00	<0,10	<0,10	0,22	0,59
Co$_{tot}$	µg/l		0,36	0,23	< 0,2	0,25	0,31	0,50	3,60	0,5	0,5	0,48
Cr$_{tot}$	µg/l		1,2	< 1,0	< 1,0	1,5	1,5	1,5	1,0	1,0	1,0	1,0
Cu$_{tot}$	µg/l		7,2	4,2	4,7	7,2	7,0	3,6	5,6	1,9	2,0	1,1
Fe$_{tot}$	µg/l		603	451	611	474	429	352	800	118	310	170
Hg$_{tot}$	µg/l		< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	0,25	0,03	0,03	0,05	0,05
Mn$_{tot}$	µg/l		28	32	10	22	30	226	642	63	95	62
Mo$_{tot}$	µg/l		< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	0,5	0,5	6,5	1,8	0,5
Ni$_{tot}$	µg/l		4,0	2,0	2,3	2,8	2,9	5,2	11	2,0	2,3	1,2
Pb$_{tot}$	µg/l		13,3	3,2	1,2	6,2	29,7	5,0	1,0	1,1	2,0	3,7
Sb$_{tot}$	µg/l		4,5	1,6	2,5	2,9	6,8	6,2	0,8	2,1	1,0	0,4
Se$_{tot}$	µg/l	3	< 0,80	< 0,80	< 0,80	0,98	0,98	< 0,80	< 0,80	2,90	< 0,80	1,00
Si$_{tot}$	µg/l			4.436	4.407	4.903	5.218	n.a.	n.a.	n.a.	n.a.	n.a.
Tl$_{tot}$	µg/l	0,2	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	0,10	0,10	0,10	0,10	< 0,05
U$_{tot}$	µg/l		0,05	0,07	< 0,05	< 0,05	0,74	0,25	1,26	4,69	0,83	0,25
V$_{tot}$	µg/l		< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	0,46	1,00	2,76	5,00	0,50
Zn$_{tot}$	µg/l		53	15	20	29	37	36	18	53	18	33

For the dissolved phase two different kinds of EQS are defined: The AA-EQS (annual average), which is defined as the arithmetic mean of the concentrations measured on different times during the year and on the other hand the MAC-EQS, which is defined as the *m*aximal *a*llowable *c*oncentration. For the dissolved phase EQS are determined for cadmium, nickel, lead and mercury. However, the latter is of minor importance for the Harz region. For cadmium, in all catchment areas the calculated background concentrations exceeds the AA-EQS, in the Weser catchment area even the MAC-EQS. For nickel the background concentrations exceed the MAC-EQS in the Selke catchment area and for lead in the western catchment areas of the Oker, Oder and Sieber.

Table 3: *Selected geogenic background concentrations of the dissolved phase in the catchment areas of the Harz mountains, calculated as the arithmetic mean of the 90%-percentile of the single water bodies, and EQS-values* (*italics*: concentrations > AA; ***bold and italics***: concentrations > AA and MAC).

	Unit	EQS	Oker	Oder	Sieber	Söse	Innerste	Wipper	Selke	Helme	Bode	Weser
			P90	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**
Ag$_{dis}$	µg/l		0,24	0,08	0,10	0,12	0,13	< 0,02	0,07	0,05	0,05	0,06
Al$_{dis}$	µg/l		358	354	308	86	108	31,4	23,8	< 10	110	546
As$_{dis}$	µg/l		0,8	1,1	1,1	< 0,5	< 0,5	3,1	3,7	1,5	0,9	2,1
B$_{dis}$	µg/l		15	29	21	44	15	15	20	83	148	30
Ba$_{dis}$	µg/l		49	67	91	82	45	16	20	51	110	75

	Unit	EQS	Oker	Oder	Sieber	Söse	Innerste	Wipper	Selke	Helme	Bode	Weser
			P90	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**	**P90**
Cd$_{dis}$	µg/l	AA 0,08 MAC 0,45	*0,40*	*0,22*	*0,24*	*0,10*	*0,20*	*0,17*	*0,30*	*0,10*	*0,13*	***0,47***
Co$_{dis}$	µg/l		0,21	< 0,20	< 0,20	< 0,20	< 0,20	< 0,20	0,82	1,04	< 0,20	0,50
Cr$_{dis}$	µg/l		< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	2,0	1,6	1,8	1,0
Cu$_{dis}$	µg/l		2,4	2,0	2,4	3,2	3,5	1,2	2,7	1,3	3,1	6,5
Fe$_{dis}$	µg/l		323	346	701	88	90	30	504	51	200	210
Hg$_{dis}$	µg/l	AA 0,05 MAC 0,07	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Mn$_{dis}$	µg/l		76	35	59	9,0	19	112	346	59	42	37
Mo$_{dis}$	µg/l		< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	7,2	0,5	0,5
Ni$_{dis}$	µg/l	AA 20 MAC 20	3,1	1,2	1,4	2,1	1,9	3,1	***41***	15,4	2,2	3,3
Pb$_{dis}$	µg/l	AA 7,2 MAC 7,2	***7,9***	***8,1***	***12,11***	1,8	3,9	0,3	2,2	0,5	0,7	2,3
Sb$_{dis}$	µg/l		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1,0	1,0
Se$_{dis}$	µg/l		< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8
Si$_{dis}$	µg/l		5.225	4.593	3.304	4.898	4.698	n.a.	n.a.	n.a.	n.a.	n.a.
Tl$_{dis}$	µg/l		0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
U$_{dis}$	µg/l		< 0,05	0,06	< 0,05	< 0,05	< 0,05	0,12	< 0,05	4,00	0,78	0,09
V$_{dis}$	µg/l		0,8	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	0,3	0,5	0,5	0,5
Zn$_{dis}$.	µg/l		36	17	24	26	30	110	16	44	13	12

5. Discussion

The results show, that the rivers in the Harz Mountains are naturally characterized by relatively high metal concentrations. However, the spatial distribution of the metals for the water bodies can strongly differ for the total phase and the dissolved phase (see figures 3 and 4). The most important origin for the metal concentrations in the water bodies are the geogenic conditions in the Harz Mountains. The high concentrations of iron, zinc, copper reflect the mineral resources, which are mined in the Harz Mountains. The figures 3 and 4 show that the western Harz is a hotspot for high silver and lead concentrations; it is also an important region for the mining of both metals. Also metals, which are of lower importance for the mining in the Harz can be found in the surface waters, like, barium, originating from baryte mineralisation, antimony, manganese, often associated with iron, from oxidic manganese-ores or nickel and arsenic from arsenic nickel-cobalt ores or silver-rich ores. For elements like iron, aluminium or silicon, the weathering of rocks is an important source of their occurrence in the surface waters. For the other elements the origin of their occurrence in the rivers are metallogenic mineralizations.

In addition to the geogenic conditions in the Harz Mountains also the atmospheric deposition must be considered as source for the background concentrations in the surface waters. The input by atmospheric deposition is of importance for copper, cadmium and zinc. For lead the atmospheric deposition declined in the last decades strongly.

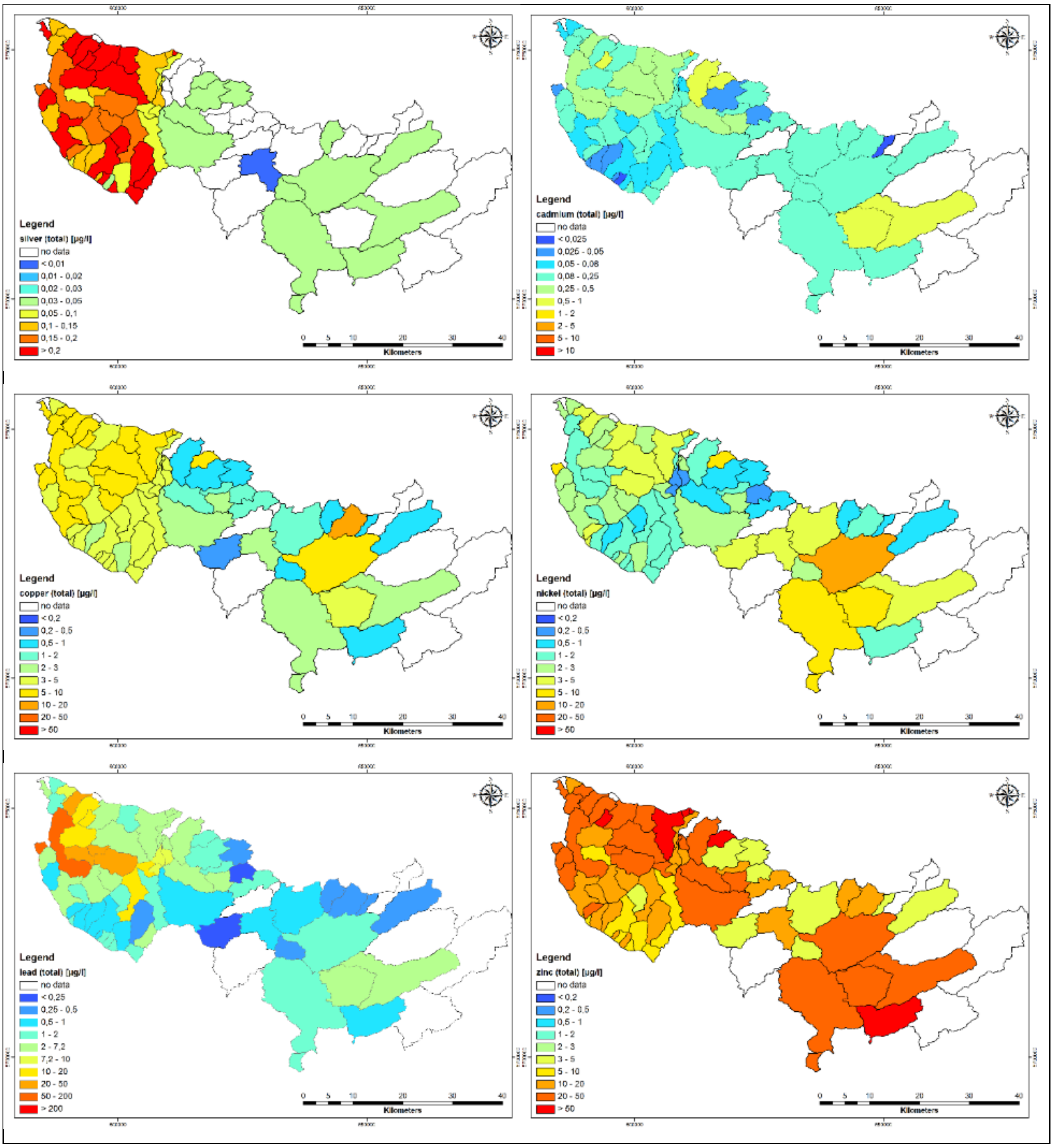

Figure 3: *Geogenic background concentrations of the total phase for cadmium, copper, nickel, lead and zinc in the catchment areas of the Harz Mountains.*

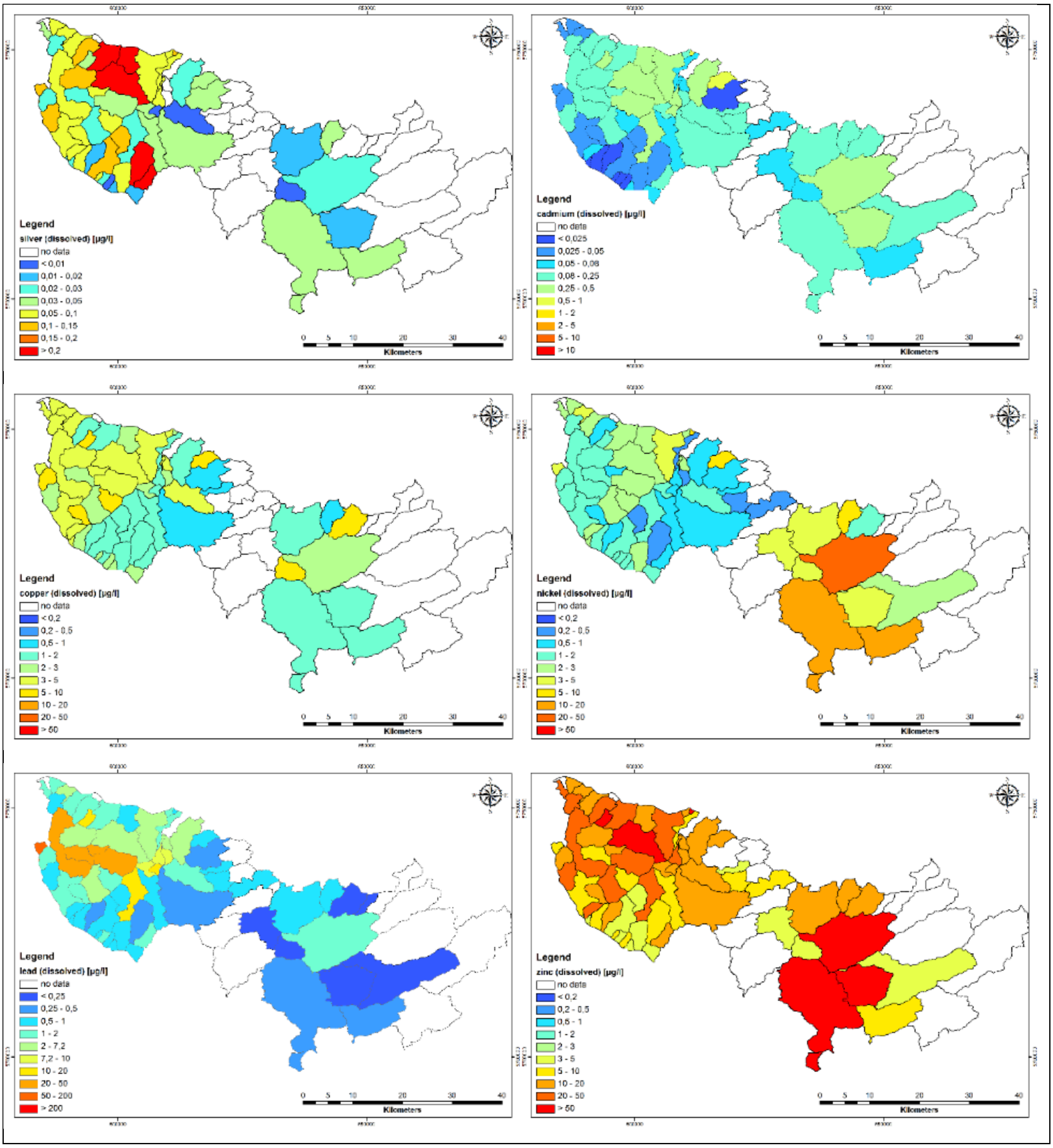

Figure 4: *Geogenic background concentrations of the dissolved phase for cadmium, copper, nickel, lead and zinc in the catchment areas of the Harz Mountains.*

6. Conclusions

The Harz Mountains can be described as a geogenic metallogenic region. Thus, it is expected that because of high geogenic background concentrations in the rivers less stringent objectives for the WFD could be determined. To proof the assumption of high geogenic background concentrations an assessment was made to determine the background concentrations for several metals in the total phase and the dissolved phase in several water bodies of the Harz Mountains. The results show, as for a metallogenic riverine landscapes expected, a high background concentration for several metals. In the total phase, the calculated background concentration of silver exceeds the EQS in all catchment areas of the western Harz. In the dissolved phase the calculated background concentration of cadmium exceeds the AA-EQS in all catchment areas and the MAC-EQS in the Weser catchment area. Moreover the MAC-EQS of the dissolved phase is also exceeded for nickel in the Selke catchment area and for lead in the catchment areas of Oker, Oder and Sieber. Thus the results of the assessment confirm the assumption of high geogenic background concentrations of metals in the water bodies of the Harz Mountains and can serve as a basis for the determination of exemptions for the implementation of the WFD.

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Financial Calculation of Long Term Tasks in Mine Water Management

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1. Introduction

Remediation and aftercare jobs in the mining industry are often characterized by their long-term nature. The economical evaluation, e.g. behavioral alternatives, are therefore based on an inter-temporal valuation approach. As the evaluated objects usually do not create revenue, the valuation criterion will be the expense parameter that is expressed as the cumulative cash value of all costs and the investments still to be decided upon and thus relevant for the payments to be made. This expense parameter will have to be interpreted as a negative revenue item, so that the valuation approach introduced herein is a special case of the approach used to determine the capitalized value of potential earning, which is dominating in the mining industry. This paper introduces typical reasons for a valuation, the valuation model and the conclusions for the model drawn from a sensitivity analysis. Problems arising when the model is applied are highlighted in a case study.

The research work as well as training and further training at the TU Bergakademie Freiberg have focused for years now on problems concerning the commercial evaluation of deposits, of mining technologies, of mining projects and of mining companies, but the same problems have also been the subject of the consulting services and expert opinions provided by the University on behalf of governments, authorities and of the mining companies themselves (Drebenstedt and Slaby, 2007; Drebenstedt, 2006; Slaby and Drebenstedt, 2000a, 2000b, 2003; Slaby and Drebenstedt and Ohlendorf 2002; Steinmetz and Slaby, 1993; Wilke and Slaby 1993).

If the insights are summarized that have been gained on different objects of valuation, during different occasions for such a valuation and by considering the different valuation targets, the following three conclusions and the recommendations derived from them will turn out to be of fundamental importance:

- The fundamental approach to any kind of valuation in the mining industry is to consider the capitalized value of potential earnings. Alternative approaches to the valuation, such as to consider the net asset value as it is favored elsewhere, are either completely unsuitable for the valuation of deposits, inventories and projects or only partly suitable for the valuation of mining companies and plants.
- The evaluation strategy must take into account the valuation of deposits, projects and companies in their entirety.
- Conflicts existing between a mining company's internal economics (the pursuit of profit), between external effects (caused by interfering in the environment and in natural habitats) and with the duty to protect the deposits (caused by high extraction rates) can and will have to be considered in the decision-taking process to a reasonable extent on the basis of opportunity or alternative cost accounting.

Triggered off by the declining rate of the mining output (e.g. in the hard coal and lignite industry) and by the elimination of entire mining sectors (such as the Wismut), we have been increasingly confronted in recent months with the problem of a commercial evaluation of the ecological consequences of these mining activities as well as with the search for measures required to ward off the dangers arising from this situation and to secure a sustainable development. The relevant efforts have been focused on remediation, post-closure and long-term projects in connection with the Wismut and lignite mining activities. In view of the fact that the problem is of fundamental nature and that it concerns or affects all mining sectors, the work results and the experience gained during this work are to be made known in the following paper.

2. Conditions for Mine Remediation

Mining will always affect the environment. Regions where raw materials are produced by surface mining are particularly affected in this respect. The changes in nature caused by mining activities are most varied. They include changes in agriculture and thus to the biosphere, the temporary withdrawal of arable land and living space as well as their devastation, at least for some time, infrastructural changes in the region and the interference in natural and anthropogenic water systems. In order to secure the chances of future generations for a sustainable development, the natural balance affected by mining activities will therefore have to be redressed and the living space once given over to mining will have to be revitalized (Slaby, 1992, 1998; Gerhardt and Slaby, 1994, 2000).

The allocation of the professional, legal and commercial responsibilities will have to be based on the principle of causation. This means that the mining industry, i.e. the mining company causing the post-mining damage, will have to assume responsibility, as it is also stipulated in the German mining law. The general principles of providence and causation will then have to be complemented by the principle of burden-sharing, by the user principle and by the principles of feasibility and reasonableness, depending on the overlapping and distinguishing interests of other parties involved, especially as a result of the ongoing social development processes. One will have to bear in mind that, often enough, the mining companies causing the damage do no longer exist at the time when remediation and post-closure measures will have to be implemented (post-mining reconstruction) and when the contaminated sites will have to be recultivated (long-term obligation).

A major feature of the post-mining consequences caused by the elimination of former mining locations is their long-term character and the special risks as regards the expected and the actual scope of work. This applies particularly to remediation, post-closure and long-term objects in the field of water management, such as to objects for the collection, treatment and disposal of contaminated seepage water from mining slopes, dumpsites and disused industrial facilities, as well as to objects for controlling and limiting the rising ground water levels in old mining locations affected in this respect. Alternative technological and commercial options to solve the problems as well as specific technological and commercial risks are typical of these long-term objects, and they often seem to require an infinite duration to complete them, when one looks at these problems from today's point of view. These specific risks concern the insufficient knowledge of the effectiveness and the reliability of the technological solution applied, the time it will take to reduce the contamination, the required consumption of production factors (such as energy, chemicals etc.) in the course of time, the time involved to treat the relevant quantities of water or the inflow of water and, last but not least, the uncertainties as regards the development of the valuation parameters (such as prices and rates) for the consumption of these production factors during that time. The economical valuation of such objects requires necessarily an appropriate evaluation of the time factor and makes it necessary to take the various risks and trend factors into account. In other words, it is necessary to apply an inter-temporal valuation approach (Slaby and Drebenstedt, 2000a, 2003).

In the current practice of remediation mining, the general problem of the economical valuation of long-term remediation objects is embedded mainly in two fields of the decision-taking process.

First of all, as a pre-requisite for determining the most suitable option of technological and commercial behavioral alternatives. The problem to take a decision in this respect is above all characterized by the fact that the available technological options may oppose each other: one of them may require no or hardly any aftercare, but is cost-intensive, while the other one may require fewer investments, but more aftercare. The problem is here to make an inter-temporal comparison of the expenditure involved (i.e. the investments and the operating costs required), depending on the time when these amounts become due. The problem can only be solved by applying financial and mathematical valuation models.

Secondly, the progress made with the remediation creates the prerequisite for transferring the object into the responsibility of a third party. This transfer often comes along with a change in ownership, i.e. the local authority becomes the new owner, so that the supervision by the mining authority ends, as intended. It might be necessary to pursue the long-term jobs, such as monitoring and water management jobs, also in the future and under the auspices of the new legal owner, in order to contain or ward off post-mining damage affecting the general public.

The readiness of the future owner to accept the commercial responsibility for the project will depend on a reasonable funding. The volume of the funding depends on the services and costs for the relevant object still outstanding at the time of transferring the ownership. The calculation of the amount needed, e.g. a one-off payment to the future owner, will be based on a mathematical valuation model of the financial investments required, i.e. on the calculation of the cumulated capitalized cash value of all outstanding financial obligations.

A suitable approach to a solution of both problems is to mathematically determine the financial investment costs.

3. Financial Valuation Approach

This approach makes it necessary to establish the cumulative cash value of all financially assessed expenses required for the valuation projects over a limited or unlimited time horizon (T) and in accordance with the required safety and remediation standards. These "mathematically calculated financial investment costs", referred to hereinafter as the expense parameter (AW), act as criteria when the commercial advantages of alternative options are compared and when a one-off payment is made to the future owner after the financial responsibility has been transferred. The calculation of the expense parameter AW is determined by the cash-layout costs (operating costs requiring payments) to be established for the period t. As well as by cyclic and non-cyclic investments, that may become necessary. These payments are the input for the calculation. Should payments be received during the period T, such as in the form of revenue or investments, they will have to be offset against the payment made in the same period. Any balances from the liquidation are to be included in the calculation at the end of the project period T.

Calculation of the cumulative cash value of the periodic payments (the mathematically calculated financial investments) related to a base year (0) by taking into account:

- The period required for the relevant measures (T).
- The cash-layout costs at valuation level 0 by taking into account the possibly changing consumption of resources (such as energy, labor etc.) and investments during this period that might become necessary.
- The inflation-adjusted imputed interest (the real rate of interest).
- Trends concerning the changes in the valuation parameters and in the prices for the expense parameter, such as for energy, labor, replacement investments and material.
- A general inflation rate.
- the specific technological and commercial risks concerning the valuation objects.

Investments made and operating costs expended before the base year (0) will be disregarded in the calculation of the cumulated cash value for the payments due, they are irrelevant for the decisions (to be) taken in this respect, they are "sunk costs" by their very nature.

If the expense parameter AW is used as a basis for a one-off payment in the case of transferring the responsibilities, it will be assumed that this capitalized one-off payment made in the base year (0) will be capitalized as an annuity with a safe nominal interest rate over the limited or unlimited time horizon. This periodic annuity is then available with the required amounts to cover the payments, including the calculated trends in the expense and valuation level as well as for specific technological and commercial risks.

$$AW = \sum_{t=1}^{T} \frac{A_{t(0)}}{q^t} \tag{1}$$

where AW = expense parameter; $A_{t(0)}$ = periodic amount for the cash-layout costs and investments in period t at the valuation level in base year (0); q = imputed interest (the real rate of interest).

If AW in equation (1) = constant, the following applies:

$$AW = A_{t(0)} * \frac{q-1}{q(q-1)} = A_{t(0)} * KF \tag{2}$$

where KF = capitalization factor.

The required cyclic and non-cyclic payments, such as for replacement and one-off investments, are included in annuity $A_{t(0)}$ (as an investment annuity) of equation (2). The capitalized expense parameter AW will then be determined by the product of the largest period annuity of all payments and of the capitalization factor. The valuation model shown in figure 1 illustrates the suggested valuation strategy.

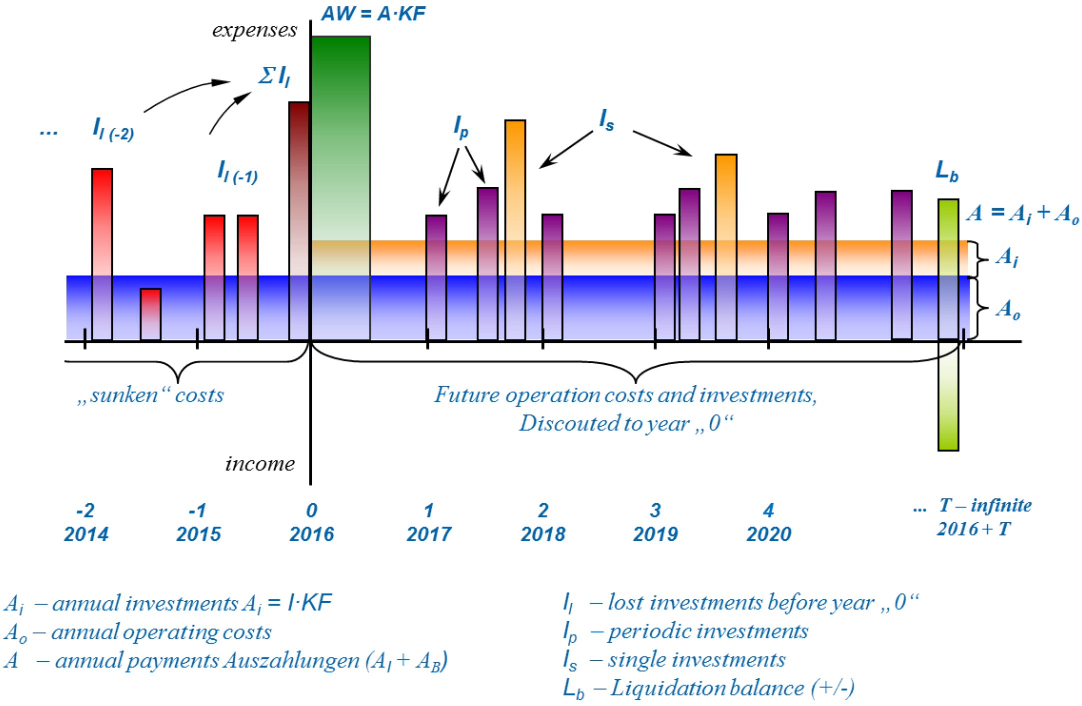

Figure 1 *Valuation strategy*

Prerequisites for calculating the expense parameter AW on the basis of equation (2) are therefore:

- The calculation of the payment/expense annuity $A_{t(0)}$. This includes the preliminary calculation of the cash-layout for the operating costs and other cyclic and non-cyclic payments that may become necessary as well as their calculation as representative expense annuity over the period T.
- The calculation of the capitalization factor KF. This requires decisions to be taken over the period T, decisions as to the rhythm of the cyclic investments (renewal cycle) and the determination of the imputed interest rate q.

If the object to be evaluated is subject to price increases for the consumption of production factors (such as prices and labor rates) to and specific technological and commercial risks, it is recommended to calculate a modified interest rate q, which will then have to be taken into account, and the expected inflation rate as well. Assuming that there is a continuous and steady development over the period T (with the same percentage), the imputed basic interest rate (the real rate of interest) will have to be modified as follows:

$$q = q_R * \frac{q_{Infl.}}{q_V} - \frac{p_R}{100} \tag{3}$$

where q = imputed interest rate now modified; q_R = original imputed real interest rate; $q_{Infl.}$ = inflation factor; q_V = summarized object-related modification factor of the valuation criteria (prices) for the expense factors, such as for labor, energy etc.; p_R = discounted interest rate in % p.a. to take specific technological and commercial risks into account.

The calculation of the expense parameter *AW* on the basis of equation (2) with the given capitalization factor *KF* and an expense annuity $A_{t(0)}$ that remains constant over the period *T* is recommended, when payments for the objects remain unchanged over the period *T* and when the expense parameter *AW* does not change, either. In the case of any deviating conditions, such as changing expense curves and liquidation balances, the calculation regulations will have to be modified further. Should the expense curve fluctuate, the calculation will have to be made on the basis of irregular amounts being paid over the period *T* according to equation (1). In practice, it may be typical that the trend of expenditure is decreasing which can be mathematically described by a digression of the changing amounts. The expense parameter *AW* will have to be interpreted as a negative revenue item.

As a result of the sensitivity analyses carried out and depending on the model input, the following conclusions are generally valid and can be drawn with regard to the sensitivity of the target parameter "capitalized expense parameter" (*AW*) (Drebenstedt, 2006).

- AW responds rather sensitively to changes in the modified interest rate q and shows an exponential growth with a declining interest (rate). *AW*'s sensitivity is therefore felt more strongly in areas with a high interest rate than in areas with a lower interest rate. This, in turn, makes it necessary to define q thoroughly, i.e. the influencing factors must be taken into account in this respect. For the mine closure activities with long term character and risks, a reasonable funding is necessary. The basic of the calculative real interest rate therefore can be only long term and safe investments. Interest rates from such investments are comparable low, in Germany in the rage from 2.5%/a to 3.5%/a.
- The decisions on the structure of these parameters, including the capture of detailed data for individual cost items, will be pushed in the background, while the decisions on the rate of the inflation-adjusted basic interest (*q*) and on the interest rate for risks involved (p_R) will be given much more priority, although the cause/effect relationship between price increases (q_V) and inflation ($q_{Infl.}$) as well as the adjustment between the effects of this relationship on q will have to be given due consideration.
- The influence of *T* on the amounts involved in AW is considerable over a 20 to 30-year period (*T*), but will decline when *T* is in excess of 30 years. This fact points to the necessity that T for the objects with a limited duration must be determined very carefully.
- The safe knowledge of the amounts involved in the expense parameter and of the expense curve in the case of projects with a long (*T* longer than 30 years) and an infinite duration as well as the required knowledge of possible liquidation consequences is less important and fades in the background. The influence of long-term jobs tackling so-called permanent mining damage on AW is almost irrelevant under the aspect of a commercial valuation when $T = 50$ years. The one-off payment in the case of a constant expense annuity over the period $T = \infty$ and a modified interest rate q = 1.05 amounts to only 9.55 percentage points above the amount which would have been due if *T* was 50.
- The expense curve over the period *T* (either constant or declining) is of decisive influence especially on objects with a limited duration. This explains the demand to determine the expense curve for these projects over the period *T* very carefully, apart from the demand to also limit this period T to a reasonable duration.
- Irrespective of the project duration *T*, the statements about the expense volume and the development of the expense curve for a period of up to 20 - 30 years are of the essence.

- In general, AW shows a higher sensitivity in areas with a lower interest rate, also when T, L_T and the expense curve change. Consequently, the claims for funding of these parameters will be higher at a lower interest rate than at a high interest level.
- Should AW be used as a criterion for determining the commercial advantages of (different) options, any variations in the interest level may change the advantageousness of the option hitherto preferred. A higher interest rate favors options and makes them more advantageous, where most of the required expenses become due in the far-away future. In other words: a low interest rate promotes behavioral alternatives requiring a less intensive aftercare, but requiring higher investments.

4. Case study

4.1 The problem

The following typical example often meets in practice: The residual hole of a disused opencast mine is filled with water and used for local recreation. In order to ensure the safety for the general public, it becomes necessary to regulate the water level in the lake and prevent it from rising beyond a specified level. A water level higher than the specified one could cause geo-technological dangers, such as landslides. In order to regulate the water level permanently, two technically feasible solutions are available (Figure 2):

- Option 1: The permanent operation of a pumping station. This option requires comparatively little funding in form of a one-off investment, but incurs comparatively high costs for the cyclic replacement investments and the operating costs.
- Option 2: Construction of a free outflow from the lake. The advantage of this option is that the operating costs and the cyclic replacement investments are fairly low once the free outflow has been constructed, although the initial funding requirements are comparatively high.

4.2 Initial Data and Calculation

In order to compare both options under commercial aspects, all expense-related facts will have to be reviewed.

Option 1

A stationary pump will have to be installed for permanent operations.

- Investments: The investments made in recent years comprise electrical connections, a passage under the road and a building for discharging the water into a near-by creek and have a reinstatement value of some € 21,600. The renewal cycle for these plants has been fixed to be 40 years. Further supplementary investments amounting to approximately € 71,300 are required for the pump station (€ 40,900), the pumping equipment (€ 20,200) and the site mobilization (€ 10,200). As the pump is only used periodically, a reserve pump will not be required. In order to establish the recurring expense items, a distinction must be made between cyclically renewable and one-off investment costs. The one-off investment costs include the site mobilization. The pumping equipment will have to be replaced every 12 years, while a useful life of 40 years is assumed for all other investments.
- Operating costs: The operating costs of € 18,600 can be broken down as follows: energy (€ 0.03/m^3 of water), labor costs for the supervising personnel (10 hours/week at € 23/hour), service and maintenance (2% p.a. of the investment sum over a useful life of 40 years and 8% p.a. of the investment sum over a service life of 12 years) as well as charges and fees (insurance, rental of the land etc.).
- Risk: In order to dimension the pump, a 50-day pump test has been carried out. This period is not considered to be sufficient for making a reliable forecast as to the water quantities to be pumped. This uncertainty will be taken into account by a risk discount of 0.5% on the interest rate.

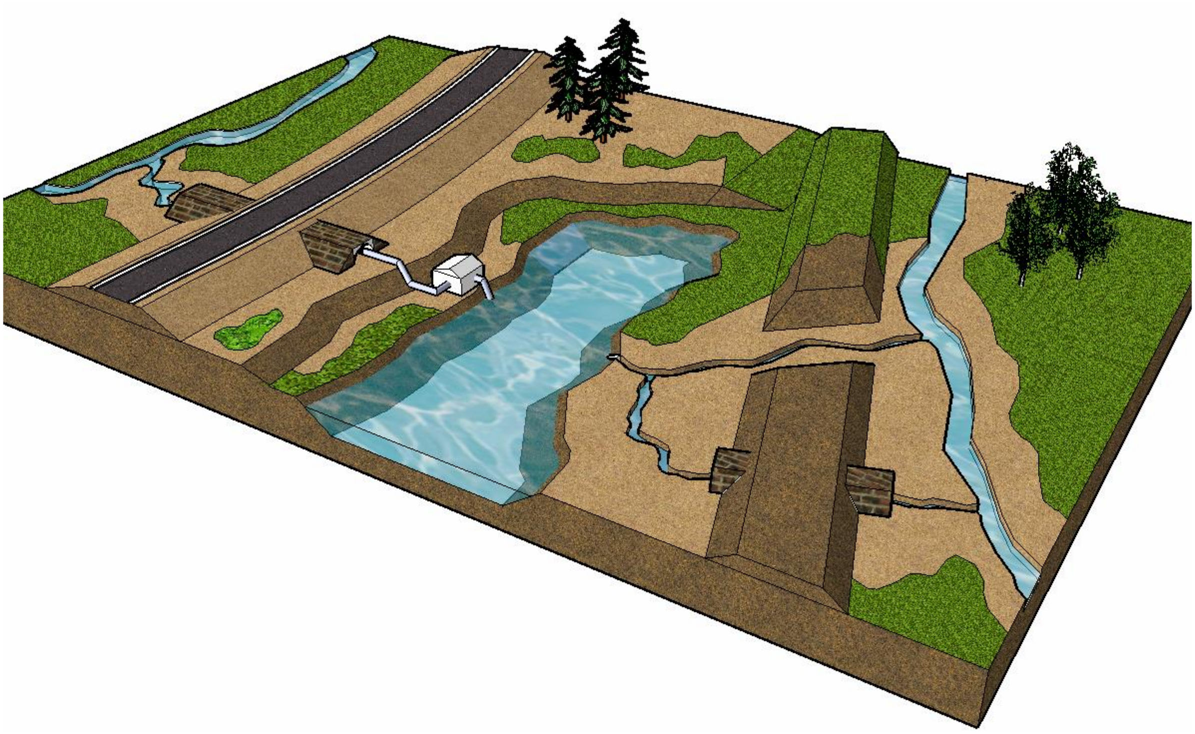

Figure 2 *Scheme of case study options: pump station (left) or free outflow (right), 1- mining lake, 2 – dam, 3a – open ditch, 3b – pipe installation, 4 – river, 5 – pump station, 6 – pipe installation, 7 - road*

Option 2

The water will be discharged partly into an open trench and partly into a pipeline. The different piping sections lead to the sub-options "open trench" and "piping" (Table 1).

- Investments: The earthwork, the vegetation work, the surveying and engineering services as well as the permitting costs will be taken into account as one-off investment costs (€ 524,500 or € 537,300, respectively). The pipelines and the trench construction will have to be renewed cyclically (every 40 years) at a cost of € 19,400 and € 264,800, respectively.
- Operating costs: Checks are necessary in the interest of public safety and to maintain the reliable function of the discharge installation (8 hours/week, € 10,000 p.a.).
- Risk: The water outflow to be constructed runs across an old dumpsite. As no hydrological assessment of the water level in the dumpsite has been prepared, no final statements as to the required construction of the water discharge installations can be made. These risks will also be reflected by an interest rate discounted by 0.5%.

The two options will be commercially evaluated based on the expense parameter AW as applied in equation (1). All necessary payments over the entire project duration will be taken into account, the cyclic investments as investment annuities. The project duration of both options is infinite.

The mathematical calculation of the investment costs assumes a real interest rate of 4% as well as a price and inflation adjustment.

The input data and the result of the mathematical/financial calculation of the expense parameter AW based on equation (1) are summarized in the table 1.

Table 1 The project costs broken down in accordance with the options considered

Elements of the project costs	Option with a pump station (10³ €)	Free outflow option Open trench (10³ €)	Pipeline (10³ €)
1. New investments	71.3	524.5	537.3
1.1 of which: one-off investments	10.2	505,1	272.5
1.2 of which: cyclic renewal, every 12 years	20,2	-	-
1.3 of which: cyclic renewal, every 40 years	40.9	19.4	264.8
2. Renewal of existing plants, every 40 years	21.6	-	-
3. Operating costs per year	18.6	10.2	10.2
Expense parameter *AW*	693.8	825.0	947.3

4.3 Results

A comparison of the options based on the above assumptions shows that the construction of the pump station ensures a relative advantage of about 18.9% over the option with a free open trench outflow. The option involving the free outflow with a pipeline is clearly much more unfavorable due to the high proportion of replacement investments. When looking at the effect the real interest rate has on the expenditure, the following statement can be made: Based on a real interest rate of 3% p.a., both options (with the pump station and with the free outflow) are commercially equivalent. If the real interest rate rises, the option with the pump station will become more advantageous. A relative advantage of 36.4% is already achieved with option 1 when the interest rate rises to 5% p.a., as compared with the other option. These statements underline and confirm how urgent it is to determine the interest rate exactly, i.e. to establish the real interest rate, the price modification rate, the inflation rate and the risk-related interest rate (Equation 3).

Conclusions

A major feature of mine closure activities is their long-term character and the special risk. This applies particularly to remediation in the field of water management, such as to objects for to objects for the collection, treatment and disposal of contaminated seepage water from mining slopes, dumpsites and disused industrial facilities, as well as to objects for controlling and limiting the rising ground water levels in old mining locations affected in this respect. Alternative technological and commercial options to solve the problems as well as specific technological and commercial risks are typical of these long-term objects, and they often seem to require an infinite duration to complete them.

In the current practice of mine closure, the general problem of the commercial valuation of long-term remediation objects is embedded mainly in two fields of the decision-taking process: First of all, as a pre-requisite for determining the most suitable option of technological and commercial behavioral alternatives. Secondly, the progress made with the remediation creates the prerequisite for transferring the object into the responsibility of a third party. The problem is to make an inter-temporal comparison of the expenditure involved, depending on the time when these amounts become due. The problem can only be solved by applying financial and mathematical valuation models. The approach is to establish the cumulative cash value of all financially assessed expenses required for the valuation projects over a limited or unlimited time horizon and in accordance with the required safety and remediation standards. These "mathematically calculated financial investment costs", referred as the expense parameter (AW), act as criteria when the commercial advantages of alternative options are compared and when a one-off payment is made to the future owner after the financial responsibility has been transferred.

The paper introduces typical reasons for a valuation, the valuation model and the conclusions for the model drawn from a sensitivity analysis. Problems arising when the model is applied are highlighted in a case study.

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Recogniton and external reporting of mine water treatment costs according to IFRS Standards

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Extended Abstract

The costs of treatment of mine water may have a considerable impact on the economic viability of mining operations. In some cases, after mine closure and during rehabilitation, such cost may still occur for long-time periods or even eternity. In this context, it is of importance to assess and recognize such costs in an appropriate way and report them in the financial reporting documents in the best possible way to reflect the fair value of the mining operations. The presentation intends to give an overview of the rules and practice for (internal) recognition and (external reporting) in accordance with the International Finance Reporting Standards with a specific focus on mining.

Issues to be dealt with:

(i) Under which conditions are costs of mine water treatment „fully lost“ and charged against revenues?

(ii) If such costs, in contrast, increase the value of the mining operation, can they be capitalized?

(iii) Under which conditions can such costs be considered as investments?

(iv) How will depreciation in such conditions take place?

(v) Under which conditions is it possible to create liabilities for mine water treatment?

(vi) Which IFRS standards apply specifically to mining operations?

(vii) How to illustrate these issues in a case example?

(viii) How to apply the standards in practice?

Key words: mine water, costs, IFRS standards

Environmental risk mitigation resulting from implementation of mine water treatment technologies developed within project MANAGER

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Abstract

Contamination of surface water by the mine water discharges is one of several problematic environmental issues related to coal mining. The discharges of mine water have a significant impact on water quality and aquatic ecosystem. Mine water released to the river ecosystem may increase salinity, temperature and concentration of heavy metals. Therefore, water management including implementation of solutions allowing to minimize the environmental impact of mining operations plays an increasingly important role. Assessment of environmental risk mitigation resulting from application of possible treatment solution should be a part of the technology selection process depending on existing environmental problem.

Approach based on the treatment technologies efficiency and water quality standards was applied to estimate the potential environmental risk reduction. The performed analysis showed that implementation of treatment technologies have a positive impact on the aquatic environment by removing a significant loads of pollutants, thereby supporting the prevention of deterioration of aquatic ecosystems exposed to contaminants from mining water. Performed process of technologies assessment in terms of risk mitigation confirmed that due to selectivity for specific type of contaminants, different flexibility to concentration changes and limitations the process of solution selection should be performed individually for selected specific case conditions. During this process besides the technology parameters physico-chemical parameters of discharged mine water and river as well as river flow rate should be taken into account.

Key words: mine water, treatment technologies, environmental risk, aquatic ecosystem

Introduction

Activity of hard coal mining is associated with pumping mine water to the surface and then discharges to nearby watercourses. Impact of the mining on surface water was undertaken within many papers (Absalon and Matysik 2007; Dogaru et al. 2009; Office of Environment and Heritage NSW 2012). Water discharged from both operating and abandoned mines causes degradation of water quality and introduces alteration of aquatic habitat. Mine water from European coalfields is often characterized by high salinity and temperature (Belmer et al. 2014). Substances present in discharged mine water such as heavy metals, radioactive isotopes, sulphate and chloride (Bondaruk et al. 2016; Canedo-Arguelles et al. 2013; Janson et al. 2009; Chałupnik and Wysocka 2009; Younger and Wolkersdorfer 2004) may have an significant impact on water quality and in consequence may damage or alert the structure of biological communities in aquatic ecosystem (Besser et al. 2007). One of the most important document, in the field of water resources management and protection is the Water Framework Directive (WFD). According to the Article 4.1 the general aim is to achieve in all surface bodies good status by 2015 as well as introduce the principle which allow to prevent any further status deterioration (European Communities, 2009).

Therefore, water management including implementation of solution such as treatment technologies allowing to minimize the environmental impact of mining operations plays an increasingly important role. Assessment of environmental risk mitigation resulting from application of possible treatment solution should be a part of the technology selection process depending on existing environmental problem. MANAGER project (full title: Management of mine water discharges to mitigate environmental risks for post-mining period) implemented within Research Fund for Coal and Steel was aimed at development and evaluation of treatment technologies in terms of risk reduction for aquatic ecosystem. Among technologies developed within the project were semi-passive and active solutions focused on treatment of different hazardous substances occurring in mine water discharge.

Within this paper results of the analysis of environmental risk mitigation performed based on treatment efficiency and comparison to EQS (Environmental Quality Standard) set out by Directive 2013/39/EU are presented. The results of laboratory analysis to estimate the pollutant load reduction for zinc, nickel, cadmium, copper, lead, mercury, iron, manganese, magnesium, barium were used. Annual Average Environmental Quality Standards (AA-EQS) values for heavy metals from priority list - nickel, cadmium and lead were applied to calculate the required dilution degree of treated mine water. Analysis was performed to assess how implementation of treatment technology may mitigate the environmental risk posed by discharge of mine water including metals. The implemented approach may become an important part of management practices reducing the environmental impact of mining operations.

Methods

The analysis of environmental risk mitigation was performed for selected technologies developed and tested in MANAGER project which are dedicated to treat mine water from metals such as Zn, Ni, Cd, Cu, Pb, Hg, Fe, Mn, Mg, Ba. Based on the collected information concerning physico-chemical parameters characterizing mine water in Europe coalfields the matrix of artificial mine water was developed within the project MANAGER by DMT GmbH & Co. KG (Table 1). This matrix includes five type of artificial mine water with different characteristics was used in order to create comparable conditions of treatment efficiency analysis in laboratory scale.

Table 1 *Artificial mine water matrix*

Parameters	Type1 Groundwater	Type2 Low salinity	Type3 Intermediate salinity, flooding	Type4 High salinity, sulfate	Type5 High salinity, barium
pH	7,00	7,00	7,00	7,00	7,00
Sodium Na (mg/l)	170	1 380	8 300	30 170	26 850
Potassium K (mg/l)	20	80	180	250	330
Calcium Ca (mg/l)	200	400	1 000	1 000	2 800
Magnesium Mg (mg/l)	85	250	450	1 000	1 000
Iron Fe (mg/l)	4,317	10,793	43,173	129,520	129,520
Manganese Mn	1,882	4,706	18,823	56,470	56,470
Zinc Zn (mg/l)	0,236	0,590	2,361	7,082	7,082
Lead Pb (mg/l)	0,047	0,118	0,473	1,418	1,418
Cadmium Cd (mg/l)	0,004	0,009	0,038	0,113	0,113
Chromium Cr (mg/l)	0,000	0,000	0,000	0,000	0,000
Copper Cu (mg/l)	0,012	0,029	0,117	0,352	0,352
Nickel Ni (mg/l)	0,013	0,031	0,126	0,377	0,377
Mercury Hg (mg/l)	0,000	0,000	0,001	0,002	0,002
Barium Ba (mg/l)	0	0	0	0	400
Strontium Sr (mg/l)	0	0	30	0	333
Sum of cations (mg/l)	475	2110	10020	32420	31713
Hydroxid (OH) (mg/l)	0	0	0	0	0
Chloride Cl (mg/l)	185	2 500	15 000	50 000	50 000
Sulfate SO_4 (mg/l)	400	1 000	1 400	1 800	0
Nitrate NO_3 (mg/l)	5	0	0	5	0
Bromide Br (mg/l)	0	5	20	60	60
HCO_3 (mg/l)	600	650	200	200	110
Sum of anions (mg/l)	1190	4150	16600	52005	50110
Sum of salts (mg/l)	1 665	6 260	26 620	84 425	81 823
Ion balance (mg/l)		3,8	4,3	3,2	1,0

Parameters	Type1 Groundwater	Type2 Low salinity	Type3 Intermediate salinity, flooding	Type4 High salinity, sulfate	Type5 High salinity, barium
Dissolved salt calc. (mg/l)	1 665	6 265	26 640	84 485	81 883
Total hardness calc (mg/l)	285	650	1 450	2 000	3 800
Electr. conductivity calc	2 440	9 110	37 398	106 531	103 777

Assessment of the environmental risk mitigation included in the first step the calculation of percentage of pollutant load reduction and in the second the step comparison to recommended AA-EQS for Ni, Cd, and Pb. Within this paper technologies for metal removal were investigated. The estimation of environmental risk mitigation was performed for the following treatment technologies:

- Active technology based on precipitation process using a sodium sulphide Na_2S as a reagent - tested by DMT GmbH & Co. KG,
- Active technology based on precipitation process using a sodium hydroxide NaOH as a reagent - tested by DMT GmbH & Co. KG,
- Active technology based on precipitation process using a calcium hydroxide $Ca(OH)_2$ as a reagent - tested by DMT GmbH & Co. KG,
- Active treatment by sparging with hydrogen sulphide (H_2S) gas generated using an off-line sulphidogenic bioreactor – tested by Coal Authority,
- Semi-passive synthetic zeolite technology – developed and tested by CERTH,
- Semi-passive algae bio-technology – developed and tested by University of Almeria,
- Passive compost systems – tested by Coal Authority.

To perform the analysis data concerning concentration of specific contaminants present in mine water before and after implementation of treatment technologies was used. The percentage of pollutant load reduction was calculated comparing the concentration at the entrance and at the exit of the technology for each type of artificial mine water (Figure 1, Figure 2, Figure 3, Figure 4, Figure 5). The basis for the initial concentrations before treatment was matrix for five mine water types (Table 1). Due to differences between treatment technologies resulting from their specifics such as removal only of certain type of pollution the common list of metals allowing calculation of percentage of pollutant load reduction was created. Concentration of Zn, Ni, Cd, Cu, Pb, Hg, Fe, Mn, Mg, Ba in mine water samples were used to estimate the environmental risk mitigation resulting from loads reduction.

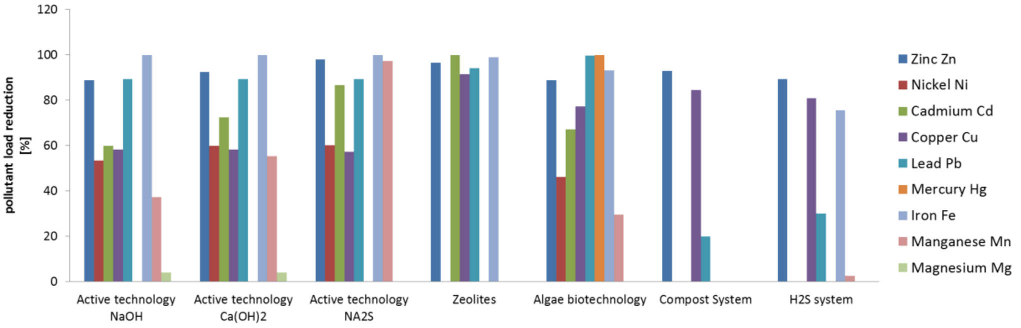

Figure 1 *Percentage of metal load reduction by treatment technologies (artificial mine water type 1)*

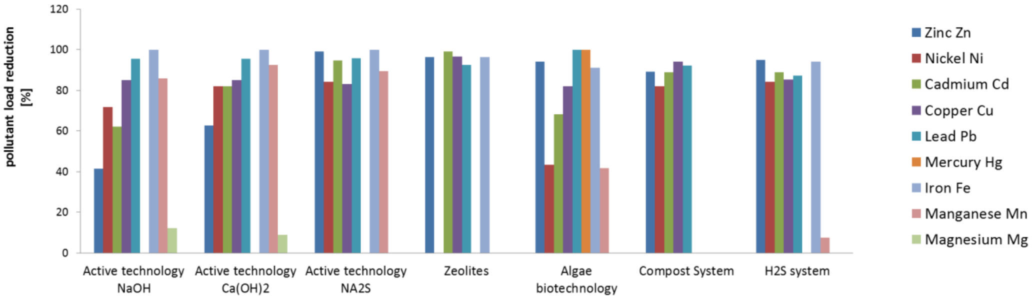

Figure 2 *Percentage of metal load reduction by treatment technologies (artificial mine water type 2)*

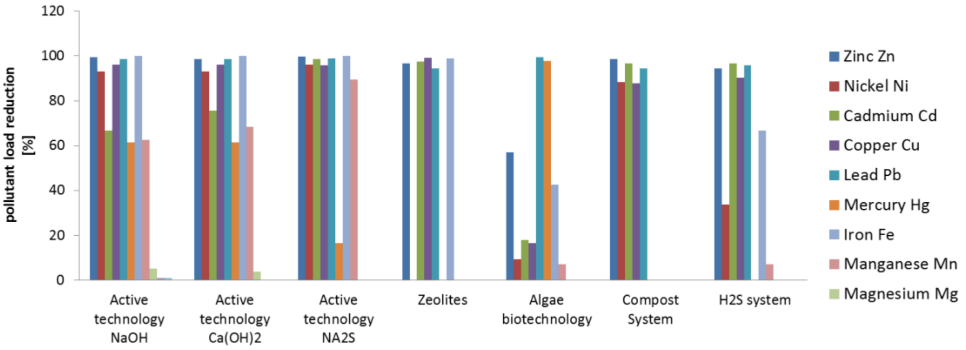

***Figure 3** Percentage of metal load reduction by treatment technologies (artificial mine water type 3)*

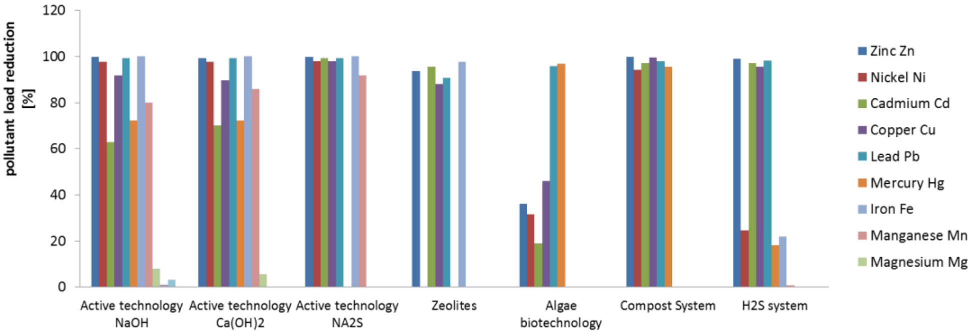

***Figure 4** Percentage of metal load reduction by treatment technologies (artificial mine water type 4)*

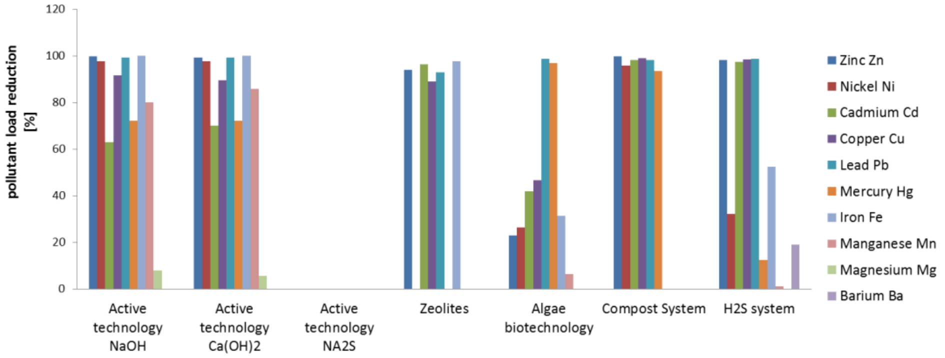

***Figure 5** Percentage of metal load reduction by treatment technologies (artificial mine water type 5)*

The achieved results showed that the range of treated pollutants is different depending on the technology and mine water type. The most wide range of treated pollutants characterizing active technologies (using NaOH, Na_2S, $Ca(OH)_2$ as a reagent) regardless mine water types, however the pollutant load reduction was most effective in case of the 3rd, 4th and 5th mine water type. The active technologies are particularly effective to treat mine water from Fe, Pb, Ni, Zn. The active technology using Na_2S as a reagent to precipitation process is not applicable for 5 mine water type. Zeolites technology is specific only for selected pollutants: Zn, Cd, Cu, Pb, Mn and the pollution load reduction in case of all mine water types was in most cases nearly 100%. Algae biotechnology reduced the metals concentration most effectively in 1st and 2nd mine water type. Algae biotechnology is dedicated to mine water contaminated mainly by Fe and Mn (around 100 % for all mine water type). The compost system can be also implemented to treat mine waters from heavy metals such as Zn, Ni, Cd, Cu, Pb and Hg but the highest effectiveness of treatment was observed in case of high salinity waters (type 4 and 5). The active treatment by sparging with hydrogen sulphide (H_2S) allow effectively for reduction of heavy metals such as Pb, Cu, Zn and Cd. However this technology is not dedicated for chemical parameters characteristic for 1st type of mine water.

Within the second step of environmental risk mitigation analysis the concentration of priority substances present in the outflow from treatment technologies were compared with environmental quality standards of priority substances set out in Directive 2013/39/EU (Table 2).

Table 2 *Environmental quality standards in the field of water policy (Directive 2013/39/EU amending 2000/60/EC and 2008/105/EC) used in the environmental risk assessment*

Parameters	AA-EQS [uq/l]	MAC-EQS [uq/l]
Nickel Ni	4	34
Cadmium Cd	0,08-0,25	0,45 - 1,5
Lead Pb	1,2	14
Mercury Hg		0,07

Subsequently, the annual average concentrations AA-EQS of selected priority substances (Ni, Cd, Pb) were used to estimate required degree of dilution (fold of dilution resulting from level exceedance of AA-EQS). The required degree of dilution of treated mine water by zero concentration river ensuring achievement of water quality standards was calculated. The achieved results are presented from Figure 6 to Figure 10.

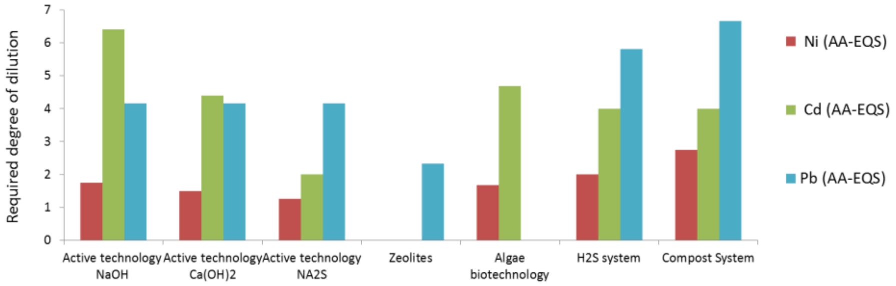

Figure 6 *Required degree of dilution of mine water after treatment in order to achieve the required water quality standards for mine water type 1*

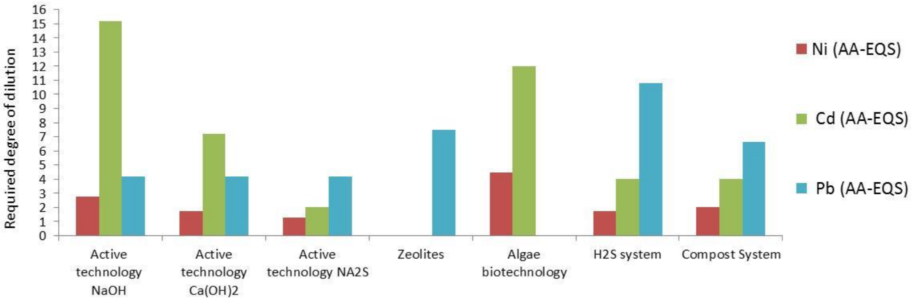

Figure 7 *Required degree of dilution of mine water after treatment in order to achieve the required water quality standards for mine water type 2*

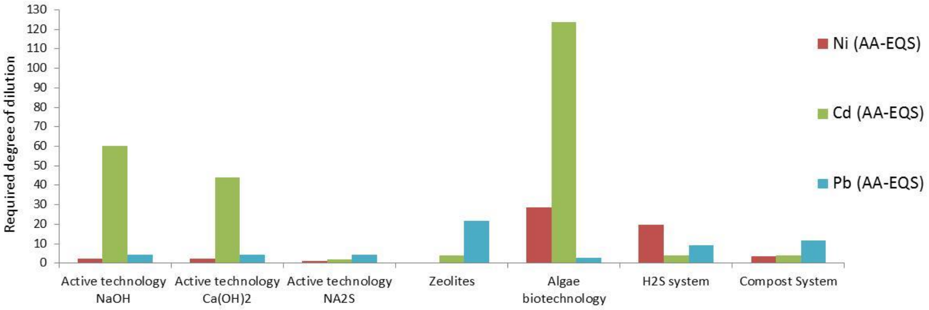

Figure 8 *Required degree of dilution of mine water after treatment in order to achieve the required water quality standards for mine water type 3*

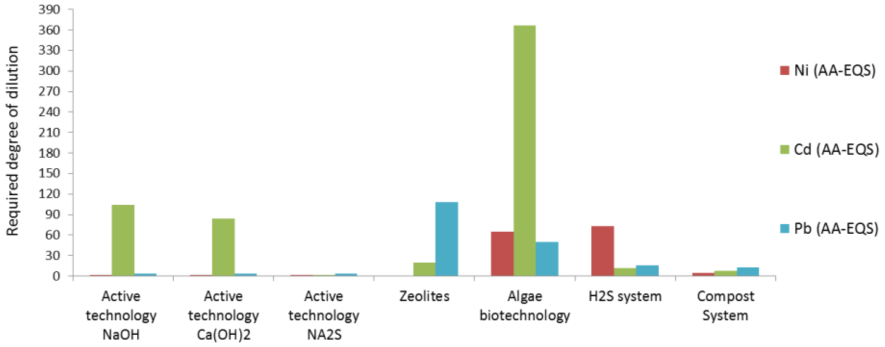

Figure 9 *Required degree of dilution of mine water after treatment in order to achieve the required water quality standards for mine water type 4*

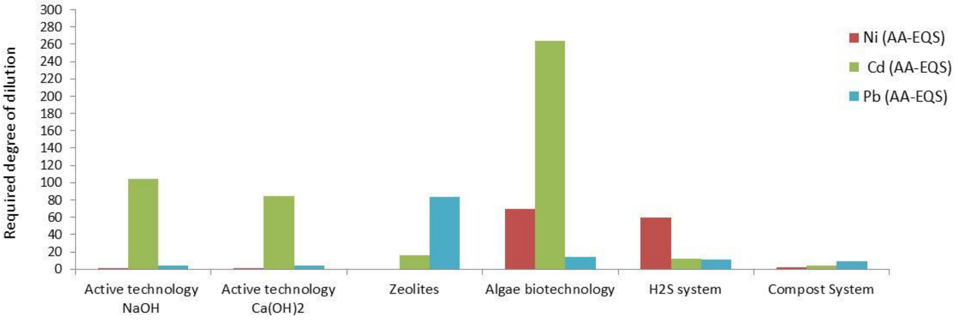

Figure 10 *Required degree of dilution of mine water after treatment in order to achieve the required water quality standards for mine water type 5*

The results showed that despite the high treatment efficiency required environmental quality standards are difficult to achieve and the further reduction of pollutant is required. Due to the dilution effect the river flow as an important factor should be taken into account during the technology selection process. In terms of environmental risk reduction caused by Cd, Ni and Pb, each technology has its limitations and the effectiveness was dependent on chemical composition of water. Comparing technology for different types of water showed that active technologies are more flexible in relation to changes in the concentration of contaminants.

In case of active technologies (using reagents NaOH, $Ca(OH)_2$), the relatively low degree of dilution of Pb and Ni is required for 3rd,4th,5th type of artificial mine water, however the concentration of Cd significantly exceeded the required limits. Environmental risk is effectively reduce by active technology using Na_2S in case of 3rd and 4th mine water type (Figure 8, Figure 9). However, this type of technology is not dedicated to treatment the water with parameters characteristic for 5th type of artificial mine water. The zeolite technology is very effective to reduce the risk caused by Ni and Cd, however to meet the environmental limit for Pb the further dilution is required. Algae-biotechnology allow to gain the required environmental quality standard for Pb in experiment performed for 1st and 2nd type of artificial mine water. The algae biotechnology is more selective regarding the treatment of different types of contaminants. In case of technology using for treatment hydrogen sulphide (H_2S) the risk was effectively mitigated and relatively stable regardless the changing water parameters, however the Ni concentration required higher dilution to meet AA-EQS value. The results concerning passive treatment based on compost system, showed that required dilution degree maintained at the similar level for all types of artificial mine water.

Discussion & Conclusions

The environmental risk is posed by discharged mine water due to the fact that they include elevated concentrations of metals and metalloids (Johnson and Hallberg 2005). Therefore, the implementation of treatment methods mitigating the risk and allowing to meet the set out environmental quality standards plays increasingly important role in mine water management systems. The performed analysis showed that comparison of the technologies between each other in terms of environmental risk mitigation is a complex and multidimensional process. The achieved results confirmed that active treatment technologies are more chemically flexible than passive systems (Taylor et al. 2005) and may effectively remove wide range of pollutants. Moreover appropriately designed active technologies may be less limited by operational parameters but this results in relatively high operating costs (Degens 2009). While active treatment technologies need power and input of (bio)chemicals to operate, the passive technologies require low energy input and smaller maintenance costs (Younger et al. 2002).

However, well-constructed passive technologies, carefully selected for occurring environmental problem and specific conditions, can be an effective ecological treatment systems successfully mitigating the environmental risk. The coal mining community is becoming increasingly interested in passive solutions which constitutes less expensive alternative to more costly active treatment technologies (Watzlaf et al. 2004). Additionally, if it is required the active and passive solutions may be combined to meet the existing environmental standards. As many experts indicated the treatment systems usually consists of multiple steps involving to the treatment process more than one technology (US EPA 2014). Consequently, the achieved results presented within this paper should not be interpreted unambiguously due to differences between technologies specifications. The performed analysis showed that treatment technologies may prevent further water body status deterioration, however during the assessment process each technology should be considered individually depending on site specific local conditions and type of mine water (Younger 2000).

The approach to assess and select suitable solution for environmental risk mitigation should involve estimation of pollutant load reduction as well as a required dilution degree. To perform complex assessment the process should start from collection of data about exceedances occurring in mine water and receiving river. The assessment of the technology risk mitigation should estimate not only improvement of parameters in mine water discharge but also the impact on the water body. Accordingly, the flow rate of the receiving river is an important factor due to dilution effect which can decide on the applicability of the selected technologies. In order to estimate the final concentration of contaminants and assess the risk mitigation resulting from technology implementation, parameters such as water chemical composition of discharge and river as well as technology and river flow rate should be considered.

The environmental risk mitigation is an important factor in decision making process in selection of the treatment technology. For this reason the assessment of environmental risk mitigation resulting from application of possible treatment methods should be a part of the technology selection process depending on existing environmental problem. However, in addition to environmental aspects factors such as available size of land, system longevity, maintenance requirements, flow rate, site accessibility, availability of power sources; economic aspects (capital and operation costs); climate impacts on system efficiency should be also important elements of technology selection (US EPA, 2014). Therefore in the further step the cost benefit analysis including estimation of potential costs and benefits resulting from treatment technologies implementation is required.

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Mine Water Issues addressed in the project train@mine

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Abstract

In the joint project train@mine two German mining companies (RAG and MIBRAG), a water consulting company (Emscher Wassertechnik) and a University (Leipzig University, chair of service management) were making up a consortium to develop professional training courses. The aim of the project was “Internationalising of Professional Training in the Mining Sector to Support Sustainability in Resource Management”. Vietnams coal mining sector was chosen as an example and the state owned holding VINACOMIN acted as a local partner. A thorough assessment phase during the first year of the project revealed a number of issues that were addressed in training courses designed on a pilot scale. Four two-day pilot courses were developed: Mine Management, Project Management in Mining, Water- and Environmental Management and Occupational Safety in Underground Mines. These courses were documenting best practice in the named fields by giving lively examples of relevant proceedings and methods.

The Water- and Environmental Management course contained the four topics “Water management and safety issues”, “Impact of underground mining on the land surface”, “Water treatment” and “Public concerns and management”. One key aspect of the first topic was the dewatering of underground mine areas with stagnant water that can endanger the mine workings by sudden water intrusion. The comparison of the working practice in a Vietnamese mine as observed during the assessment phase with the common practice in a German mine lead to the presented example. The lifespan of the dewatering example was covering several months. It started with the utilization of a 3D underground GIS System to identify the area filled with stagnant water and illustrated the technical aspects of identifying the expected water volume and the efforts made to safely dewater the area. The mining authority was permanently kept informed about the monitoring of the progress of the works. This routine action was documented and explained in the pilot course. Not only for safety reasons it was noticed that old goaf workings in the Vietnamese mine were not closed and separated from the active parts of the mine. This practice leads to a higher air ventilation and consumption in the mine as well as a higher potential for mine water reactions induced by oxidation.

Sharing of professional experiences was viewed as a beneficial way to improve best practice. We had a very positive feed back from our pilot courses, although they could not cover topics in full detail. Future effort is needed to implement full scale training, as this project was partly funded by the German ministry for education and research. Underground coal mining will be ceased in Germany within a few years. It is in general of gaining importance to secure sustainable resource management in all countries that supply resources to countries without domestic resources or resources that cannot be economically mined. Looking ahead it is necessary to make sure our environmental standards will stay valid for all our goods all along the supply chain.

Key words: Mine water, training, best practice

Introduction

The approach of our training project was not to deliver text book courses but to create custom made training courses. The idea was to bring together experts and collect upcoming questions. The advantage of this method is the involvement of the future trainees in the design of the courses. Many educational trainers support the assumption that learning is only possible through self-discovery and self-appropriation (Rodgers 1969). For that purpose a team of around ten German experts visited repeatedly the Vietnamese hard coal production region Quang Ninh and met with Vietnamese experts. The project was partly funded by a German government initiative to propagate vocational education (BEX 2016). A number of open cast mines and underground mines were visited. The Vietnamese experts were interviewed and a broad spectrum of themes were addressed. Vietnamese experts were in turn invited to visit German mines (see fig.1).

Hard coal mining in the Quang Ninh region is conducted in open cast mines and underground mines. About 20 open cast mines and 34 underground mines were producing a mass of 34 million tons in 2011 according to the data presented to the project team. The depth of the open cast mines is continuously increasing and at some places mining is switching from open cast mining to underground mining.

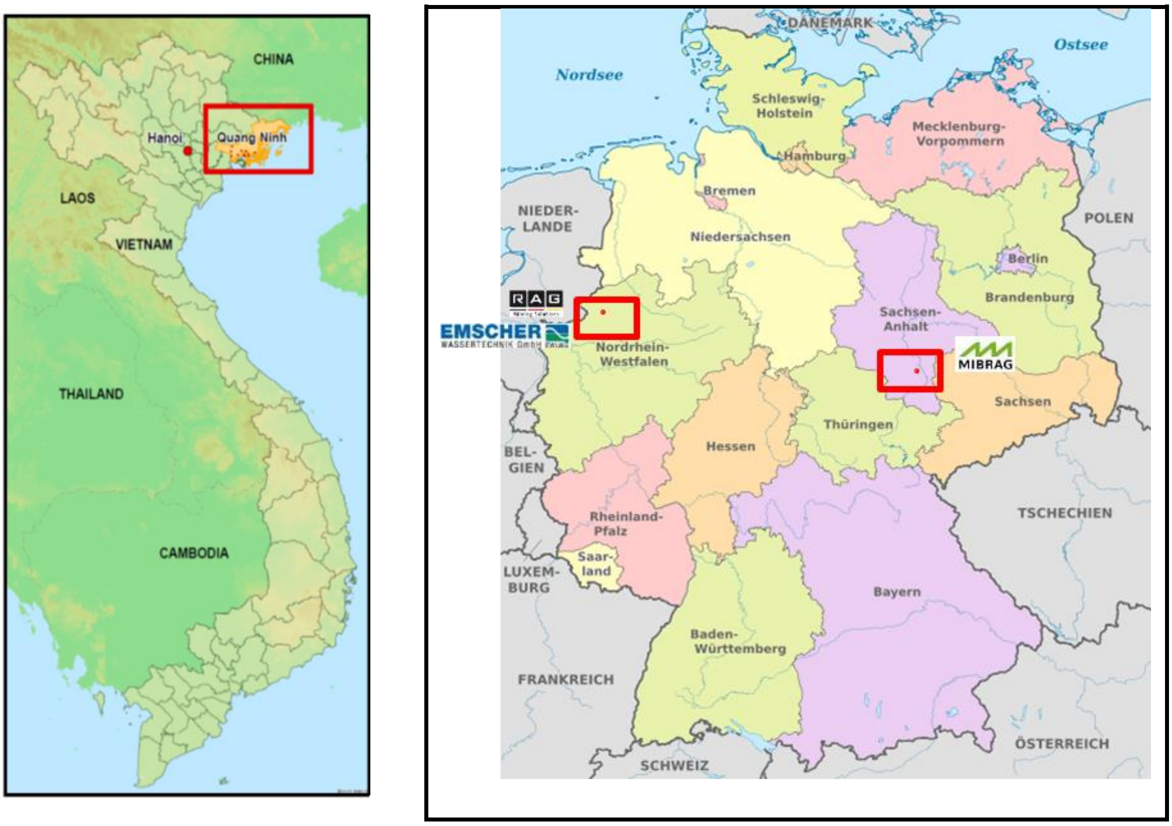

***Figure 1** Mines visited by the joint project team in Vietnam and Germany.*

To our German underground mining expert approaching the Quang Ninh mining region was reminiscent of Germany‘s Ruhr district in the early 1970s, with shades of grey everywhere, turning to black in places. The inspection report reads as follows. At the roadsides, locals would prepare meals over briquettes made from coal dust swept together and moulded in special presses. There was inadequate binding of the dust from underground, and particularly from the opencast mines, so residents could make use of the fuel they found on the surface. On arrival we saw several buildings with recreational rooms, a comparatively large washhouse for staff, a changing room for more senior staff and a small store. Our group received sets of clothing reserved for what seemed to be rare visitors – blue dungarees, a jacket, foot rags and half boots but no gloves, goggles or earmuffs. Off we went to the portal. On the way to the production site it was remarkable to see that disused roads and galleries were not dammed off. Instead, a cross made from wooden slats was put up as a No Entry sign. There was therefore a serious risk of producing fugitive air with dangerous gas concentrations. The condition of the entire roadway was not state of the art, with hardly any of the support segments connecting up to the rock. While this is tolerable at prevailing roof pressures, it would be unpardonable when mining at greater depths with running water in galleries and no pump sumps, making accidents on the travelling ways a serious possibility. The production site, with a seam thickness of about 2 m and a cutting drum in operation, lacked sufficient support resistance in the area of face-to-roadway transition. Except for a wooden prop on the face conveyor gear box, no other support segment was visible. The cutter pick had sprinkling similar to RAG's own Eickhoff cutting drums (fig. 2). Miners would walk across the conveyor and move around in unprotected environments. During the inspection, no miners who could be identified as managers were in sight. Earlier interviews had revealed the shortage of qualified personnel in this mining region, which was clearly borne out by appearances. Not a single member of staff had personal protective gear. Nearby we heard pneumatic hammers being used in manual coaling, which provides most of the output.

Figure 2 *Drum shearer seen in the visited underground mine.*

During the discussions with Vietnamese experts the two subjects in the field of mine water that attracted most interest were dealing with mine water from an operational viewpoint, and eco-friendly regional water management.

As regards mine drainage, draining dead water ("pockets" as they are known in Vietnam) was of main interest. This operation is very different from conditions in Germany where dead water is limited to regions without drainage which have been created in the rock mass by previous mining. These are visualised with a digital mine plan and provisionally drained by selective boring using highly skilled personnel underground, who have to follow very specific procedures and are supervised by the Mining Authority. When draining these regions, water pressures and flows are constantly monitored, with continuous adjustment of expected and actual readings. Safety equipment (pumps) is kept ready on site, and mine rescue squads are on standby to minimise the risk of inundation.

Training Courses

Four major topics for training courses were defined during workshops held at VINACOMIN's headquarters in Hanoi. During the workshops each topic itself was divided into subtopics according to the expressed requirements. The course Water- and Environmental Management contained four main subjects. Water management and safety issues contained the most prominent issues that had been discussed.

The mine water management of stagnant waters encountered in the underground when approaching areas that had been worked in before was extensively discussed with experts from the Auguste Victoria colliery at Marl/Germany in order to derive a model case for presentation at the pilot course in Vietnam. The methods used in Germany were debated and documented in detail to make the model as practical and comprehensible as possible. German mining techniques were illustrated by a variety of maps, sketches and photos provided by the project partners (fig. 3).

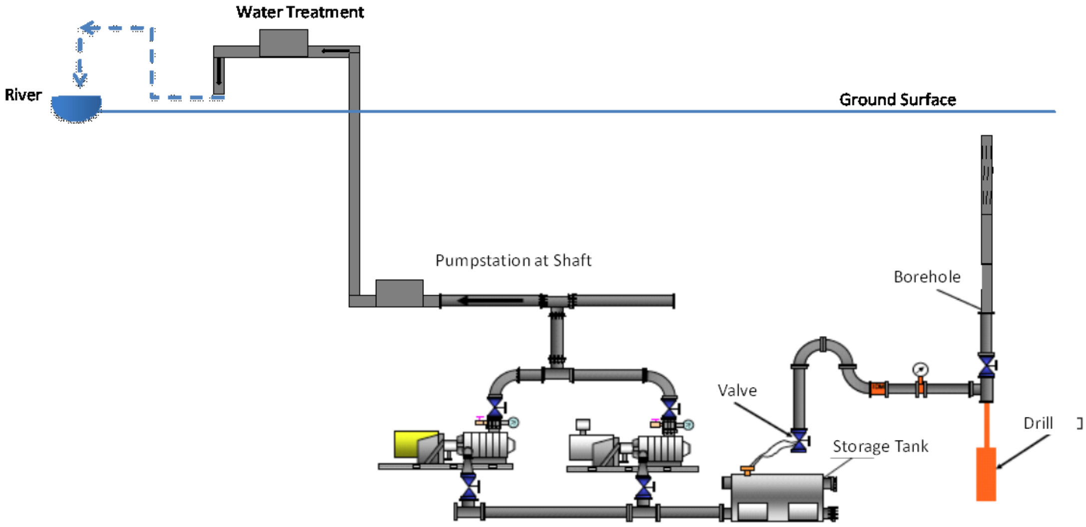

Figure 3 *Dewatering scheme to manage stagnant water in a RAG mine.*

Many of those on the Vietnamese side had been to the above mentioned colliery during an excursion organised for the Vietnamese project group. Work underground is not a prestigious job in Vietnam, and mines find it difficult to recruit suitable trainees. Mines are located in remote areas, and higher wages cannot compensate for what is available in terms of housing and leisure facilities; it remains an unattractive option. Flooding is a major risk when working underground, and water pockets may turn out to be crevasse zones with links to the surface. These are not explored in advance and are not shown in the mine plan, which consists of paper maps. In geohydraulic calculations, empirical formulas are inserted for analytical purposes without any numerical simulation. There is no close monitoring of drainage procedures by the Mining Authority. This subject was addressed in the public concerns and management part.

The pilot courses were designed to show the advantages of mechanisation in mine operations, and the German experts have tried to illustrate their own procedures in a comprehensible and practical manner. The environmental compatibility of water management in mining regions also differs from the situation in Germany. For example, a first mine water treatment plant had been built under Germany's RAME project (Bilek 2011).

At Halong, water-borne coal dust and other substances entering the bay are a major problem. In this connection, tourism can be a compelling reason for reducing the many environmental burdens generated by mining. One of the aims of the pilot course was to illustrate the German approach to mining and the environment, including forecasts of expected negative effects and suitable steps to avert or abate them. We have tried to show how planning to adapt surface starts years before mining subsidence can occur. Examples have been given of how forecasting and planning tools interact at technical level, and of cooperation between mining companies, regulatory agencies and experts at administrative level.

Mine water treatment was also discussed in detail during the pilot course. This included a presentation on general strategies to avoid or minimise the generation of polluted mine water. Details of modern and efficient mine water treatment plants recently built in central Germany were also presented, with planning and implementation described by those who had done the job (fig 4). But also technical simple in-situ-conditioning methods as operated for iron abatement in central Germany and its implementation in the mine operation processes were discussed. The idea was to convey an experience that was highly authentic, and to avoid lecturing. Some trainees knew the plants and equipment involved already from the excursion mentioned. The gathering of data needed to design a treatment plant was illustrated. In the mining context this means the prediction processes expected in the future.

Figure 4 *MIBRAG Mine water treatment plant.*

An example for unwanted effects of mining on the ground surface in Germany is shown in fig 5. In this case the anticipatory regulation of surface waters by hydraulic construction was not appropriate to avoid water logging. The negative effects had to be cured after the event. In the courses it was shown, how predictions of future ground water levels were made and how these facts are communicated with the public and the authorities. The role of certified expert referees in Germany was explained. It was presented how participation of public is organized in the process of mine planning and the planning of the compensation of negative effects.

Figure 5 *Water logging caused by land subsidence in the German Ruhr coal area.*

Conclusions

With our training courses we were able to point out a number of technical aspects that we believed are part of best practice when dealing with mine water management. On the other hand we encountered a number of non-technical reasons for many shortcomings. One reason being the lack of skilled labor. The reason for that often is that people consider the work in mines as unattractive. We met a large number of highly qualified and university/college trained managers and executives in mines, at corporate headquarters and at the Hanoi Mining University who had often studied in Germany or other countries. While modern technology is on the advance in everyday urban life, it has bypassed the workers in mining industry.

A number of parallels were found when problems in different mining regions were discussed; our Vietnamese colleagues found it hard to understand the concept of water management which involves the long-term raising of water, to be conducted in the Ruhr district in perpetuity. This is in strong contrast to the Vietnamese principle of leaving most environmental effects unregulated. The country will hopefully find a middle course here in the future. Germany's experience in the field can be very useful, as has been confirmed by many of the trainees who attended courses in Vietnam. From our point of view, the introduction of German commercial products for education and training could be hampered by competing services granted free of charge as part of German development aid to Vietnam.

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Waters of Deep Ground – Mine Water and Emotions

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Abstract

This paper will present the findings of a participatory observation conducted through interviews with different mine water related stakeholders in South Africa. The aim of the study was to describe the different viewpoints and expectations that key stakeholders in South Africa have with regards to acid mine water. This is the first study of this kind ever conducted in South Africa and it will help decision makers to deal with mine water issues outside the scientific context.

Using an interdisciplinary approach, this project aims to describe a phenomenon that by now mainly has been seen as technical, chemical or in a geological dimension. Therefore, it will also use techniques that differ from the engineering-scientific usage, such as ethnographic methods. One difference is that the project used an open format and therefore allowed an aesthetic, poetic approach in order to describe and explore metaphors of mine water, which will be presented in the paper.

In fact, mine water is as much an aesthetic as a cultural object. The questions that will be asked and answered by the stakeholders are: What is Mine Water? How is Mine Water different from "Natural Water"? What do stakeholders relate with one or the other? How do they speak about them, how do different people call it? What concepts of understanding do they have? How do concepts differ from each other?

Metaphors and beliefs direct the emotions. According to the A-B-C-model of "Rational Emotive Behavior Therapy" (REBT), all humans "construct their views of reality through their language, evaluative beliefs, meanings and philosophies about the world, themselves and others" – 'A' stands for activating event, 'B' for beliefs and 'C' for emotional and behavioural consequence. As much as it is called consequence, it is no use to discuss emotions in order to change them (Ellis 2004). Once a belief/metaphor/interpretation is set, the emotion is almost determined. Originally designed to treat emotional difficulties, this research project explicitly does not aim to change any beliefs, it is an approach to get a deeper understanding of what stakeholders think of mine water and its treatment.

Key words: Mine water, art, South Africa

Subjective Introduction

This paper is about mine water and emotions – and since it is different from a technical paper, it will also include "subjective", *i.e.* "personal" perspectives. This might be an unusual concept for an engineer or a scientist, but new problems need new solutions, and therefore we are trying to tackle the mine water issue in South Africa from a new perspective:

"There was a natural well in a flood plain next to the village, about which my mother kept telling stories. One day we went searching for the well, but we couldn't find any traces anymore. She used to know the landscape as a child before mining started. I became more interested in the topic that made the well disappear. Taking artistic practice as a point of departure, I added spatial planning, ethnography and hydrology to document and explore the post-mining landscape, where I have been living since 2012. My thesis in the progress at Bauhaus Universität Weimar, Germany, deals with the effects of Uranium mining of WISMUT Inc. in Thuringia, Germany. Together with Christian Wolkersdorfer, whom I met during a mine water meeting in Thuringia, we started a collaboration of interdisciplinary research of the post-mining effects in Gauteng, South Africa, where he teaches Mine Water Management at Tshwane University of Technology. He told me that he became devoted to mining and decided to study this subject ever since he first explored an abandoned underground mine in Austria's Tyrol at the age of 14. Finally, substantial similarities between the Witwatersrand and Ronneburg inspired this project. Both mining sites are within striking distance of populated areas and both deposits, besides other substances, contain radioactive Uranium in the mine water, tailings and waste rock piles. With Christian Wolkersdorfer's support and local knowledge, I interviewed seven different people on their knowledge, relation and feelings towards mine water in their area: Two researchers, two local authorities, two environmental activists and one local resident. This paper aims to combine theory and data-collection from the field in order to explore the topic in a holistic way."

At this stage, we did not investigate the cultural differences of South Africa and the perceptions in regards to mine water that might arise from those differences. Instead, a baseline approach was taken to identify various interpretations of mine water in South Africa, mainly in the Witwatersrand area. Yet, it might be interesting, to study whether people with different ethnical backgrounds or even the various languages in the country have different points of views when it comes to mine water and pollution.

Fig 1: Young South African men in eMalahleni near an acid mine water discharge which leaves acidic white crusts of metal sulphates.

Scientific Introduction

Acid mine drainage (AMD) became an eminent problem in South Africa when it first discharged from the Western Pool of the Witwatersrand gold fields in 2002 (Coetzee 2003). Yet, the "problem" did not begin in the year 2002, and first scientific investigations about AMD and potential health issues date back to the 1970s (*e.g.* Smit 1977, Wittman & Förstner 1976). Since then, and to this day, AMD in South Africa is an issue that is regularly covered by the media and NGOs (Liefferink 2010), especially when drinking water supplies are directly affected by mine water pollution (May 2012). As there is currently no uniformly accepted definition of mine water or acid mine drainage, the chemical evolution of mine water is highly complex. A large number of disciplines are dealing with mine water, so confusion for stakeholders that are scientific novices is inevitable – not only in South Africa, but world-wide (*e.g.* Brazil, Germany, Alaska, USA). Not everybody might immediately understand the definitions of mine water presented by Nordstrom (2011), who clearly identifies acid, circum-neutral and alkaline mine drainage. In addition, as soon as the number of chemical equations in a scientific paper or presentation exceeds (1), many people certainly claim that scientists want to hide the issue of acid mine drainage by using "scientific" language. This paper describes first results of an effort to combine scientific and artistic thinking by investigating the perceptions that stakeholders in the South African mine water context have (Fig. 1). Its starting point are identifying the philosophical concepts of "water", the concepts of "risk" and finally the concepts of "mine water" from a stakeholder's point of view.

Water, not solely technical "stuff"

This project starts with examining assembling aspects on the topic of water as a philosophical matter. A book concerning this topic one encounters frequently is ‹L'Eau et les rêves› (Water and dreams) by Gaston Bachelard, chair in history and philosophy of science at the University of Paris (Sorbonne). Written in the middle of the past century, it describes and analyses various qualities of "archetypes" of water. It might be of relevance to know that the author stated the production of scientific knowledge not as "a gradually increasing total body of truth, but as an active dialogue between reason and experiment" (Blackburn 1996).

Water has a long record in the history of philosophy, documented *i.e.* in the pre-Socratic western philosophy in Greece. Around 600 B.C., Thales of Miletus (the inventor of the eponymous theorem) regarded water as a primary matter (*arche*), which is alive and responsible for change and the diversity of things. A few centuries later, Empedokles, around 400 B.C., defined four primary elements consolidating the world: water, earth, fire and air – united or separated by love and hate. He was coeval of Leukipp and Demokrit, who developed the theory of undividable elements (*a-tomos*) – antecessors of modern physics and chemistry (Kunzmann et al. 2002).

Water as cognitive interest was not solely a European phenomenon. Asian philosophy of Dao, in the same era, appreciated water as a very general paradigm of all existence. In Chapter 78 of "Tao te Ching", Laozi says:

"Nothing in the world
is as soft as water.
Yet for dissolving the hard and the inflexible
nothing can surpass it.

The soft overcomes the hard;
the gentle overcomes the rigid.
Everyone knows, this is true,
but few can put this into practise" (McAnally 2007, 5–6)

More metaphorical cognition can be found in the even older divination-system "I-Ching" (The book of changes), assumingly written between 1100–600 B.C., during the Zhou-Dynasty of ancient China. It is based on observations of political, social and natural phenomena. Famous psychologist Carl Gustav Jung used and practised it as a "method of exploring the unconscious" (Richard 1950). "The book of Changes" is compiled from eight hexagrams – where water is used as a source of metaphorical imagination and cosmology – it represents a building block ("trigram") of life. Within a complex system, the elements (wind, water, rock, sky …) interact with each other, create images and divination, which those who inquired adjusted and interpreted with regard to their own lives.

Our cultures are mainly rooted in these and similar stories, metaphors and beliefs of cosmology. This is, in other words, what Gaston Bachelard calls "imagination". His concept of "water" is defined as based on the pre-Socratic ancient Greek philosophy of the four elements (Bachelard 1983, 3). For his examination, he also analyses poetry – works by Samuel Beckett and Edgar Allen Poe. Especially the chapter on "Deep Water" is contextualised with dark, melancholic aspects such as: "to contemplate water is to slip away, dissolve, and die" (Bachelard 1983, 47). In his chapter on "Imagination and Matter", he states, that "Water is truly a transitory element. It is the essential, ontological metamorphosis between fire and earth. He [sic!] dies every minute; something of this substance is constantly falling away. (…) Water always flows, always falls, always ends in horizontal death." (Bachelard 1983, 6). But water can also be maternal and nourishing (Bachelard 1983, 119). Another quality of water is its ability to reflect – more truly than a solid mirror could, as the story of Narcissus tells us. Furthermore, it has the ability to assimilate "all kinds of substances, even contrary matters joining its fluidity" (Bachelard 1983, 93) – it even "moderates the other elements". And most of all, it "radiates purity" (Bachelard 1983, 143).

Ivan Illich's book "H_2O and the waters of forgetfulness", which basically refers to "Water and Dreams", draws various lines even further. Not only, that this "tangible", but "elusive" element would dilute other substances, even more it has a "nearly unlimited ability to carry metaphors". It "always possesses two sides" – in some African languages "water of beginning" was also detonated as twins: "Water is deep and shallow, life-giving and murderous. Twinned, water arises from chaos and waters cannot be, but dual" (Illich 1986, 24–25).

Across cultures, when a person dies and travels from life to death, the "other world" often lies beyond a body of water – a river, an ocean, a bay – sometimes by walking, sometimes with a ferry. "The slow, flowing waters the traveler crosses are everywhere emblematic of the stream of forgetfulness; the water has the power to strip those who cross it of memories that attach to life" (Illich 1986, 30).

Besides his work on further development of the interpretation of the qualities of water, Ivan Illichs merit in the 1980s was to outline the dichotomy of the two concepts about this "stuff": "From the start I shall refuse to assume that all waters may be reduced to H_2O. (…) For not only does the way an epoch treats water and space have a history: the very substances that are shaped by the imagination – and thereby given explicit meanings – are themselves social creations to some degree" (Illich 1986, 4).

From Roman aqueducts to contemporary plumbing systems, he describes the process of an alienation. H_2O to him became just a scarce, technical resource to be managed, without a history, without imagination. In the beginning of the last century, due to fear of newly discovered bacteria, people started "to abstain from drinking water unless it came from an approved faucet or bottle". People (in the US) stopped having contact to untested, untreated natural water. In the second half of the century, this process increased: "entirely new and unthought-of pollutants became known. Many people refused to serve it to their children as drink. The transformation of H_2O into a cleaning fluid was complete. (...) Water throughout history has been perceived as the stuff which radiates purity: H_2O is the new stuff, on whose purification human survival now depends" (Illich 1986, 75).

Perception of risk

As mentioned above, water in general became associated with a "risk". According to Ulrich Beck, whose famous book "Risikogesellschaft" (Risk society) was first published in 1986, "risk [has become] the defining characteristic of our age" (Beck 1992, quoted in Adams 2002, 180). Unlike more traditional human concepts of dangers, risks are expansive, invisible and can only be judged by experts. Ortwin Renn, Chair in Technik- und Umweltsoziologie at the University of Stuttgart, adds his concept of "creeping danger", as most risks we experience today, are imperceptible through our senses and impossible to assess through experience, but are "communicative signals, that cause specific recognition". This can clearly be seen by the results of the study by Munnik et al. (2010) in the Witbank Area of Mpumalanga, where post-mining "conditions worry the residents". Exposure to radiation, toxic chemicals in the air and drinking water – all these are risks perceived through communicative signs. Therefore "it is typical for creeping danger that it takes place outside of our personal, sensory perception. We depend on others to believe – or not –, whether there is a risk". While technical understanding of risk mainly includes the probability and the magnitude of harm (Renn 2014b), the "public" adds much more components involved into their highly individual risk assessment.

Researchers in the field of cultural theory criticized the hegemony of statistics and technical risk assessment. For example, John Adams claims in his book "Risk", that statistics of fatal crashes with their great volume and distinct causes are one of a few subjects of "reliable statistics" (Adams 2002, 11). Usually, "league tables" that show "probabilities of death from different causes – from 'radiation' to 'being a coal miner' – are constructed from data of immensely variable quality". While statistics, created by the number of accidents "per unit of time (…) are interpreted by experts as objective indices of risk and are sometimes compared with the subjective judgements of lay people, usually with the aim of demonstrating the hopeless inaccuracy of the latter" (Adams 2002, 12–14).

Risk assessment is not a one-way-track and it is a dynamic process – "Risk is culturally constructed" (Adams 2002, 9). The perception of risk may for example depend on age, gender, nationality, mental state, personal experiences – interpreting statistics "as objective measures of risk for individuals" would be an "insuperable problem" (Adams 2002, 14). Furthermore, risk assessment is an interactive process, since "both individuals and institutions respond to their perceptions of risk by seeking to manage it, they alter that which is predicted as it is predicted" (Adams 2002, 14).

The psychometric paradigm of risk research originates mainly in the work of the "Oregon Group" of Baruch Fischhoff, Sarah Lichtenstein and Paul Slovic. Some of their risk-related variables, as listed in Rohrmann (1999, 8), are: risk level aspects (such as estimated annual number of fatalities, magnitude of risk, (un)avoidability of accidents/disasters and danger of health) or qualitative features: dreadfulness, associations with fear, (un)familarity, known to exposed, (not) observable, un(controllability), (un)known to science, immediate *vs.* delayed effects, impacts for future generations – plus all personal relations to hazard, such as being (in)voluntarily exposed, personal influence on choice, degree of concern, being worried, personal exposure, being personally affected and the desired distance to hazardous facility. On the other hand, there are benefit aspects such as those provided by risk source for an individual, social benefits, revenge for human needs and acceptability aspects including the social acceptability of a risk or willingness-to-pay (for risk mitigation) (Renn 2000, 21).

Ortwin Renn specifically outlines the freedom of choice to be exposed to the risk as a main factor in risk assessment, as well as whether a source of risk is perceived as "artificial or natural" (Renn 2014a, 257). Risks from "natural" sources are judged less critical compared to "artificial" ones. Also, the state of knowledge, both personal and scientific, influences the perception of risk and contributes to individual risk perception. Associated with this knowledge factor is the public trust in quality of information and "performance" distributed with the source of risk by experts, as outlined in the introduction. Components which build "credibility" are impartiality, openness, transparency and honesty. The component which is judged as "performance" is compiled by competence, fairness and the commitment a person perceives.

Interviews

We collected data in seven qualitative interviews with stakeholders being involved in post mining and mine water issues in the South African Gauteng Province, mainly in the Witwatersrand, as this has not been done before within this context. All seven interviews were conducted in a semi-structured manner, six were arranged, while only one was captured spontaneously in the field. As mentioned above, they are not categorized by name, gender, nationality, ethnical background nor along the level of education or the like. Build categories of relation towards mine water are: expert, representative of local authorities, environmental activist and local lay person. This section is a first trial to interpret these interviews.

The opening questions were always asking for a definition of what the interviewee regards as mine water; secondly, whether he or she considers it as a natural or artificial phenomenon; and thirdly which was his/her relation towards it.

Concerning definitions of mine water, the answers overlapped each other. Most trained experts, either scientists employed by institutes or officials from local authorities stated definitions similar to the following: "Mine water is any water which is involved in or affected by mining processes. So it is water flowing into mines, flowing out of mines, water used on mines". Especially the environmental activists endeavoured for a comprehensive definition including suggesting a row of examples while stressing that mine water does not necessarily need to be acidic. One found that "different definitions are confusing", while he claimed that there are "very active NGOs in the area – and they love confusion, they love vagueness". He thinks that they benefit from this inaccuracy, which is why he created his own definitions. Only one person within the interviews, a local layperson, admitted: "I don't want to lie to you. I don't have no clue what I define as mine water". However, she is confronted daily with the observation and contact: "the water was running from that side. Normally they [*i.e.* the experts, G.R.] said, there was something that they said, 'How did this water grow on that side?', because they said, its coming from a certain somewhere and pulling through and that's why it's just accumulating and stuff like that. Really I want to say to you: I really don't have any clue, but when you go nearer to the water, you can see: it's not clear water! There is different kind of chemicals or different designs that is also flowing in that water. I think, the water is also more poisoning". As can be seen, her relation to mine water seems different from the others, possibly because she is much more personally affected and does not have reliable, easily understandable information on this subject. Furthermore, she is involuntarily exposed to the source of risk. With emphasis she said: "My feeling towards this water on the right hand site is to say: they have to remove it! We are really not happy with it. We don't want it, it doesn't belong to us and there is no other area that people can move us to". Another substantial statement within this first question on definition was that one of the researchers addressed it first of all as a "serious, environmental problem world wide", that is costly to the public. Fitting this statement, an authority interviewee found a "negative connotation" to the term "mine water".

Answers to the "natural/artificial" questions varied much more. The only person who found it clearly "artificial", claiming that it was against the "normal geological formation", was a representative of local authorities. The other representative found it "natural, but partly modified". One of the activists evaded the question saying it was "disturbed and changed", the other regarded it as "natural". One expert called it "both", as acid rock drainage was a natural phenomenon, while acid mine drainage arose through human activities and therefore is artificial. Another one called it "allogenic", he suggested to use the term "anthropogenic" instead of "artificial", although, this term to him "doesn't mean much, when it comes to water resources".

Conclusions

As has been shown in this baseline investigation, the judgement on mine water substantially depends on the information on the subject and voluntary nature or freedom of choice to its exposure. A local person personally affected, possessing almost no resources to escape or unwilling to move (*e.g.* because of social local networks), may perceive the threat more intensively than someone less engaged and with more spatial and social distance. Risk – as has been seen – is not objective, but subjective. It is important to acknowledge this fact and respect it when communicating with the public or communities. As Renn says, trust is nothing that can be built, but only facilitated through credibility and fairness (Renn 2014a).

Concerning the "naturality" of the source of risk, it remains an open question why the interviewees varied so much in their assessments. One interpretation could be that they separate mining activities and mine water from each other.

Drawing together all findings, it emanates that the dual nature of water reveals itself once more in mine water – especially, when it is perceived at least as partly natural. It takes up substances from an unknown realm – dark, deep and disturbed through human activities. This fact may also contribute to the qualitative feature of hazard: namely fear association.

If we extend the argument further concerning imagination, the question is whether there could be an archetype of mine water and if so, what would it look like? If we agree with Illich/Bachelard, there is a lack of metaphorical embedding – a rather general approach is missing, not only a technical approach or treatment, stressing aspects of controlling, but also cultural and philosophic concept of this matter. It may be similar to what James Griffith (Department of Forestry Engineering, University of Vicosa, Brazil) suggests as "narration incorporated into ecological restauration", specifically speaking about post mining sites in Brazil (Griffith 2014). His argument is that "narration" would support a more subjective approach towards a landscape. As water is a part of a landscape, mine water is too. This is the case even if it is an unplanned and an unwanted entity or process. Suppression and ignorance from the cultural perspective may not lead to a sustainable and reliable practise with this entity.

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Environmental risk caused by high salinity mine water discharges from active and closed mines located in the Upper Silesian Coal Basin (Poland)

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Abstract

Mine waters, due to the wide spectrum of pollutants, represent a serious problem from an environmental point of view. Therefore, the main goal of the research was to assess the environmental risk posed by highly saline discharges of mine water. In this study the impact of mine water discharged from active and abandoned Polish coal mines located in Upper Silesian Coal Basin region (USCB) on Przemsza river ecosystems has been assessed. The impact of increasing river salinity on inhabiting them aquatic organisms was performed according to Environmental Risk Assessment (ERA) methodology specified by European Commission in Technical Guidance Document on Risk Assessment (TGD 2003). Based on the ERA results for all section of analyzed Przemsza river basin a map of hazards resulting from exceeding the acceptable environmental salinity levels was performed. The studies confirm that discharge of mine water cause the increase in the concentration of pollutants in river waters which in turn may lead to an imbalance in the ecosystem of Przemsza river basin and its tributaries and caused irreversible environmental damage. The study results confirm also that the assessment of surface water quality based on both, ecotoxicological and physicochemical indicators is more favorable than the mandatory classification of pollution.

Key words: mine water discharges, environmental risk, salinity, USCB

Introduction

Water Framework Directive (WFD) is one of the most important document in the field of water protection and water resources management. The main purpose of this document was to establish a framework for the protection of inland surface water and groundwater (Directive 2000/60/EC). The WFD consists of different steps and monitoring procedures which ensure that “good chemical” and “good ecological” status of all European water bodies will be met in 2027. The water quality issue is especially important in Poland, which compared with other European countries has comparatively poor water resources (Mankiewicz-Boczek et. al 2008). The high level of industrialization and urbanization directly affects the quantity and quality of pollutants discharged into the environment (Absalon et al. 2007). Due to the large load of pollutants in discharged mine waters (heavy metals, high salinity, presence of radioactive nuclides, etc.) serious threat to ecosystems is increasing. Taking into consideration the nature of water from Polish coal mines the particular attention in this study was paid to high salinity. The problem of increasing salinity in the surface waters and its impact on ecosystems was already described in the literature. For example, Cañedo-Argűelles described the negative effects of repeated salt pulses resulting from cyclical discharge of mine waters on river and stream ecosystem (Cañedo-Argűelles et al. 2014). Wright et. al described the effect caused by salinity on shellfish populations (Wright et al. 2011), and Bellmer in his work showed a negative effect of salinity and heavy metals on diversity and abundance of organisms inhabiting ecosystem affected by mine water discharges (Belmer et al. 2014). Literature data clearly shows, that excessive exposure caused by increasing salinity load, can lead to death of organisms living in contaminated ecosystems, which in turn, may contribute to the total biological degradation of water reservoir (Kroll et al. 2002). If water monitoring is based mainly on physicochemical analysis it is difficult to predict the full response of living structures on increasing pollution level. Therefore, it is necessary to use a procedures and methods which allow to

assess the potential environmental risks caused by anthropogenic pollution. The need for conducted this type of analysis was documented by Swart and Jarvis. (Jarvis et al. 2000; Swart et al. 1998).
One of the methods for environmental risk assessment (ERA) is the procedure recommended by European Commission, described in Technical Guidance Document on Risk Assessment (TGD 2003). In this study ERA procedure was used to assess the environmental risk posed by discharges of mine waters into the rivers located in Przemsza river basin. Obtained results allowed to develop a map of hazards posed by rising salinity loads in the rivers. Due to the fact, that ERA procedure includes the species sensitivity to pollution, applied methodology allowed to estimate a scale of exposure and predict potential of the environmental damage. Results of the analyses are particularly important, because real scale of environmental problems posed by mine water discharges in the USCB region has not been thoroughly investigated.

Methods

Study Area – Przemsza river basin

The Przemsza river basin belongs to the upper Vistula river catchment. The area of the Przemsza river basin covers about 2121 km^2, and the length of the river is 87.6 km. The basin is situated in the area of the Upper Silesian Coal Basin (USCB). Przemsza river basin consists of 41 bodies of surface water, of which 10 were classified as artificial and 13 were defined as heavily modified. More than 30% of all river channels situated in study area is regulated. Regarding to water management Przemsza river basin can be divided into 2 different subregions: the lower and the upper part of the river. The lower part of Przemsza basin is significantly exposed to the impact of mining activities, including land deformations and surface water pollution related to the discharge of mine water. Due to the location in highly industrialized part of the Silesian Region, this area is exposed to numerous anthropogenic impacts. Cities located within the basin are: Katowice, Bytom, Sosnowiec, Bedzin, Jaworzno, and Mysłowice. This area covers just 27% of the total Przemsza basin but it is a place of living more than 85% of its population. The area is comprised by the Brynica sub-basin situated below the Kozłowa Góra reservoir, the Biała Przemsza sub-basin situated below the confluence with Kozi Bród, lower part of the Czarna Przemsza sub-basin situated below the Przeczyce reservoir and the whole basin below the cofluence of rivers Biała Przemsza and Czarna Przemsza. Almost all from among 20 surface water bodies in this region do not meet the objectives of WFD. Unlike to lower part, the upper part of Przemsza basin is not seriously impacted by mine water. In the area of Biała Przemsza sub-basin there occur a large depression sink which arose in result of mine water pumping. The indirect adverse effect of mining activities to surface water resources is being partially compensated by freshwater discharge from mine draining into rivers. Water quality as well as ecological status of water bodies in upper part of Przemsza basin are in better quality and quantity than in the lower one.

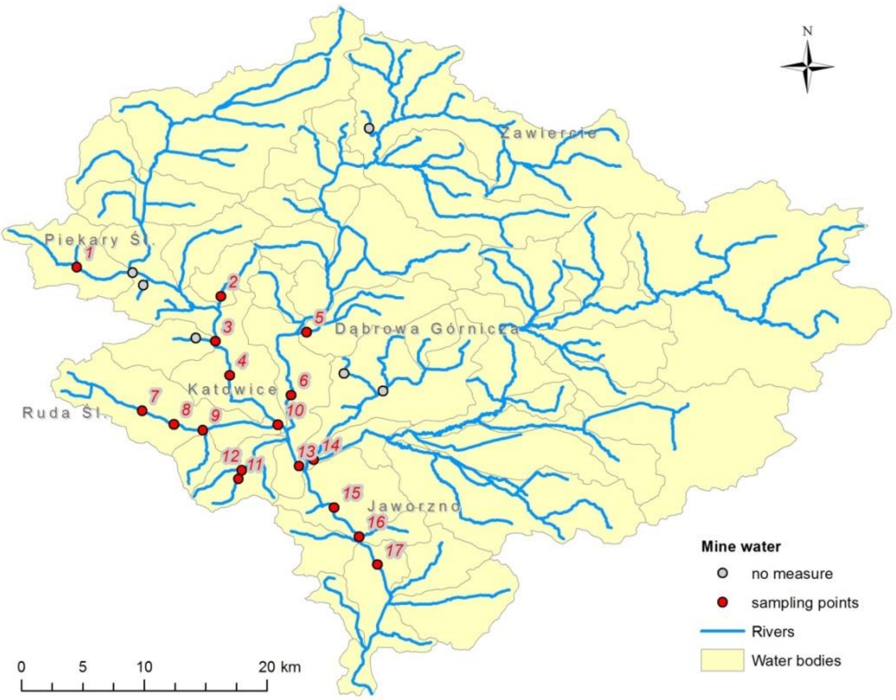

Figure 1 *Przemsza river basin – location of sampling points.*

(1-Szarlejka river above the discharge from CZOK from the Powstańców Śląskich region; 2-Wielonka river above the discharge from CZOK from the Grodziec region; 3-Brynica river above the estuary of Rów Michałkowicki; 4-Brynica river above the discharge from CZOK from the region Saturn; 5-Pogoria river above the discharge from CZOK from the Paryż region; 6-Przemsza river above the discharge from CZOK from the Sosnowiec region; 7-Rawa river above the discharge from CZOK from the Kleofas region; 8-Rawa river above the mine water discharge from KWK Ruch Wujek; 9-Rawa river above the discharge from CZOK from the Katowice region; 10-Rawa river above the discharge from KWK Mysłowice-Wesoła; 11-Bolina Południowa river above the discharge from KWK Wieczorek; 12-Bolina Południowa river above the discharge from KWK Murcki Staszic; 13-Biała Przemsza river above the Bobrek river estuary; 14-Przemsza river above the discharge from CZOK from the Jan Kanty region; 15-Przemsza river above the discharge from ZG Sobieski; 16-Przemsza river water gauge "Jeleń")

Samples collection

In order to estimate the actual salinity level of Przemsza river basin, nineteen sampling points located directly on the Przemsza river and its tributaries were selected. Sampling points were selected in order to capture the main sources of highly saline water inflows from active and abandoned coal mines. Locations of sampling points in comparison with other discharge of mine water is shown in Figure 1.Water samples were collected from March to October 2015. For all river samples a comprehensive analysis of physicochemical properties were performed. Due to the fact that the aim of research was to assess the environmental risk caused by highly saline mine water, only selected water quality indicators were used (chlorides, sulphates, and hardness) (Table 1). During the analyses data from a national monitoring of quality of the surface waters, conducted by the Regional Inspectorate of Environmental Protection in Katowice were also used (Table 2).

Ecological Risk Assessment (ERA) procedure

The Environmental Risk Assessment (ERA) was performed according to methodology described in Technical Guidance Document on Risk Assessment (TGD 2003). Simplified ERA procedure is based on determining two values: PEC (*Predicted Environmental Concentration*) and PNEC (*Predicted No-Effect Environmental Concentration*), which are finally compared in order to estimate the RL ratio (*Risk Level*). The PEC is defined as an expected concentration of a substances in the environment. PEC value reflect the level of pollution (scale of exposure) on which the organisms inhabiting an ecosystem are exposed to. The levels of threat to aquatic species caused by high salinity for all sampling points were expressed as a PEC values. During the ERA analysis as a PEC values both, results of physicochemical analyses (Table 1) and the monitoring data of surface water quality conducted by Regional Inspectorate for Environmental Protection were used (Table 2). In a next step, the PNEC values was estimated. PNEC values is defined as concentration below which exposure to a substance is not expected to cause adverse effects to species in the environment. Therefore, the PNEC is the threshold value of the negative effects caused by exposure to the contaminant are observed. Accordance with the ERA methodology described in the TGD guidelines there are at least two approaches for the determination of the PNEC (deterministic and probabilistic approach). Within the study the probabilistic approach was applied. Probabilistic approach is based on the assumption, that well-characterized population is represent by inherent heterogeneity and biodiversity. The approach assumes that PNEC value is expressed as a HC_5 ratio (*Hazardous Concentration)* estimated within the SSD analyses (*Species Sensitivity Distributions*). HC_5 value is defined as a concentration of substance, dangerous for 5% of all exposed species, while the SSD determined a cumulative probability distributions of toxicity values for multiple species. All available ecotoxicological data gathered in database were used to determine PNEC threshold values (PNEC-chlorides; PNEC-sulphates). During the database formation the following data sources were used: ECOTOX database (U.S.EPA), EU Risk Assessment Reports, research centre publications, recommendation of the EU member states, etc. The finally PNEC values (expressed as HC_5) were determined using the ETX2.0 software made available on the websites of the Dutch Environmental Protection Agency. Estimated PNEC values amounted respectively: PNEC chloride:139,06 [mg/l]; PNEC sulphate: 299,90 [mg/l]. The estimated PNEC values represent safe concentration for 95% of species living in affected ecosystem, beyond which the negative effects caused by exposure will be observed. Additionally the PNEC value for chlorides was determined by the use of existing algorithm. Added value of the algorithm is that the estimated PNEC depend on local and background conditions (*Chronic criteria value [mg/l] = 177,87(Hardness [mg/l])*^{0,205797}*(Sulfate [mg/l])*$^{-0,07452}$*)*. Environmental risk posed by high concentrations of chlorides and sulphates according to aquatic ecosystems was expressed by the RL (Risk Level). RL was determined as the ratio of PEC to PNEC (HC_5). The general rule for interpretation of the obtained results assumed that if the RL is less than 1 it means that there is no risk of negative impact from the stressors in relation to the aquatic ecosystem and there is no need to take action to reduce the environmental risk. Contrary, if RL value is higher than 1, it means there is a high risk of negative impact from the stressors to the aquatic ecosystem. In such situations, action to reduce the present environmental risk is needed.

Results and Discussion

The results of physicochemical analyses confirm that Przemsza river basin is highly affected by mining activities. Discharges of mine water into Przemsza river and its tributaries caused an increase of chlorides and sulphates concentrations in surface waters (Table 1). Results of the analyses showed that water salinity expressed as individual concentrations of chloride and sulphate ions, remains respectively in the range: from 40,32 [mg/l] (№ 2, 11) to 729,91 [mg/l] (№12) for chlorides and from 98,97 [mg/l] (№ 11) to 680,77 [mg/l] (№12) for sulphates (Table 1). Data provided by Regional Inspectorate for Environmental Protection in Katowice indicated that the average concentration of chloride ions in the water of Przemsza river basin maintained in the range from 9,79 [mg/l] (Centuria river) to 7.809,21 [mg/l] (Bolina river). Similarly, the concentration of sulfate ions was maintained in the range from 41,98 [mg/l] (Strumień Błedowski river) to 812,79 [mg/l] (Rów Michałkowicki river). The highest salinity was recorded in the rivers most affected by the impact of mine water discharges, which include: Szarlejka river (chlorides concentration 1.042,25 [mg/l]; sulphates concentration 302,90 [mg/l]); Rów Michałkowicki river (chlorides concentration 1.042,25 [mg/l]; sulphates concentration 812,72 [mg/l]), Rawa river (chlorides concentration 1.747,35 [mg/l]; sulphates concentration 476,0 [mg/l]), and Bolina river (chlorides concentration 7.809,0 [mg/l]; sulphates concentration 461,84 [mg/l]). The results shown that location along the river successive emission sources, closely related with increasing pollution load discharge into the river, directly affect the growth of water samples salinity. The estimated contaminant concentrations are similar to the values obtained by other researchers, whose study concern the source and the scale of water pollution in the area of USCB (Absalon et al. 2007; Lewin et al. 2006; Olkowska et al. 2014).

Table 1 *ERA - based on PEC expressed as physicochemical analysis results of surface waters of Przemsza river basin.*

River	№	Physicochemical parameters			ERA RL		
		Cl	SO_4	hardness	Probabilistic approach		Cl algorithm
		[mg/l]	[mg/l]	[mgCaCO$_3$/l]	Cl	SO_4	
Szarlejka	1	109,83	170,94	214,75	0,79	0,57	0,30
Wielonka	2	40,32	110,96	184,67	0,29	0,37	0,11
Brynica *(form Kozłowa Góra river to estuary)*	3	510,24	3208,93	512,22	3,67	10,7	1,45
	4	469,92	380,87	250,50	3,38	1,27	1,32
Pogoria	5	76,47	128,96	239,38	0,55	0,43	0,20
Przemsza (*from Przerzyce reservoir to Biała Przemsza estuary)*	6	48,66	98,97	196,21	0,35	0,33	0,13
	13	539,44	308,90	243,92	3,88	1,03	1,50
Rawa	7	100,10	185,94	120,27	0,72	0,62	0,31
	8	169,62	269,91	144,57	1,22	0,90	0,52
	9	519,97	770,74	220,71	3,74	2,57	1,58
	10	250,25	338,89	164,36	1,80	1,13	0,76
Bolina Południowa	11	40,32	62,98	66,80	0,29	0,21	0,13
	12	729,91	680,77	425,31	5,25	2,27	1,92
Biała Przemsza (*from Kozi Bród river to estuary)*	14	65,34	200,93	218,32	0,47	0,67	0,18
Przemsza (*form Biała Przemsza river to estuary)*	15	350,36	230,92	213,32	2,52	0,77	0,98
	16	329,50	230,92	215,20	2,37	0,77	0,92
	17	379,55	239,92	217,95	2,73	0,80	1,06

***Table 2** ERA based on the monitoring data of surface water quality conducted by Regional Inspectorate for Environmental Protection.*

River	ERA – RL ratio			River water quality - National Monitoring data		Mine water impact
	Probabilistic approach		Cl algorithm	Physico-chemical status	Ecological status/ potential	
	Cl	SO_4				
Przemsza (*from river spring to Przerzyce reservoir)*	0,22	0,21	0,07	good	moderate	-
Brynica (*from river spring to Kozłowa Góra reservoir)*	0,14	0,21	0,05	good	good	-
Szarlejka	7,45	1,01	2,44	bad	poor	D
Jaworznik	0,23	0,32	0,08	bad	moderate	-
Wielonka	0,25	0,36	0,09	bad	moderate	D
Rów Michałkowicki	7,45	2,71	2,44	bad	good	D
Potok Leśny	1,06	0,48	0,37	good	poor	D
Rawa	12,49	1,59	3,79	bad	moderate	D
Brynica *(from Kozłowa Góra river estuary)*	4,91	1,29	1,58	bad	moderate	D/I
Bolina	55,82	1,54	14,64	bad	bad	D/I
Przemsza (*from Przeczyce reservoir to Biała Przemsza river estuary)*	4,28	0,74	1,4	bad	moderate	D/I
Centuria	0,07	0,15	0,03	high	bad	-
Strumień Błędowski	0,15	0,14	0,05	good	poor	-
Biała	0,10	0,91	0,04	bad	bad	D
Biała Przemsza (*from Biała to Kozi Bród river estuary)*	0,21	0,65	0,07	bad	moderate	I
Kozi Bród	0,61	0,78	0,22	bad	good	-
Rakówka	2,68	0,49	0,88	bad	moderate	-
Bobrek	3,73	0,97	1,23	bad	moderate	D/I
Biała Przemsza (*from Kozi Bród estuary to the confluence with Czarna Przemsza river)*	0,08	0,69	0,09	bad	moderate	D
Wąwolnica	2,11	1,08	0,7	bad	poor	D
Byczyna	0,58	0,26	0,20	good	bad	D

Matylda	0,18	0,19	0,07	bad	poor	-
Przemsza *(from Biała Przemsza to Przemsza river estuary)*	2,81	0,76	0,93	bad	poor	D/I

D- direct impact of mine water discharges; I – indirect impact of mine water discharges

Research results clearly indicate that discharge of waters from coal mines located in study area is associated with pollution-related changes to the water quality properties, particularly with respect to its physicochemical parameters. Mine waters discharges into the Przemsza river basin caused a significant modification to water chemistry. The study results confirm the poor chemical and ecological status of Przemsza river basin. Most of analyzed samples do not meet the requirements for the surface water set by Regulation of the Minister of the Environment, on the classification status of surface waters and environmental quality standards for priority substances (Dz.U.2014.1482). For majority of sampling points the existing environmental standards set by the national regulation were exceeded. Determined within ERA analyses acceptable environmental levels of chlorides and sulphates, amounts respectively: 139,06 [mg/l] (PNEC-Cl) and 299,9 [mg/l] (PNEC – SO_4). Obtained values are similar to the environmental standards applicable in other countries. For example, according to Canadian Water Quality Guidelines (CWQG) acceptable chlorides concentration in surface waters is 120 [mg/l], while according to the EPA acceptable chlorides level for surface water is 230 [mg/l]. In relation to the suphates, the obtained value can be only compared with existing standards for drinking water which reach respectively: 500 [mg/l] (CWQG) and 250 [mg/l] (Drinking Water Directive 98/83/EC). Obtained PNEC values were compared with actual concentrations of chlorides and sulfates in the rivers. Based on the results the areas of Przemsza river basin for which the acceptable environmental level has been exceeded (RL> 1) were identified. Exceeding the acceptable risk levels in appointed areas may lead to the occurrence of adverse environmental effects. Summary results of ERA analyses are shown in tables above. The results in form of maps illustrating the environmental hazard posed by high concentration of chlorides and sulphates are shown respectively at Figure 1 and Figure 2. The attached figure illustrating the areas of Przemsza river basin for which the acceptable environmental limits were exceeded (RL >1). Exceeding the acceptable level for chlorides was recorded for 21 of 40 analysed samples. Adequately acceptable level for sulphates was exceed in 12 of 40 analyzed samples. Comparison of the ERA results shown that with algorithm approaches, which requires input a data concerning background condition, environmental risks are identified less frequently than in the case of probabilistic approaches based only on ecotoxicological data (RL>1 for chlorides were reported for 13 from 40 analyzed samples).

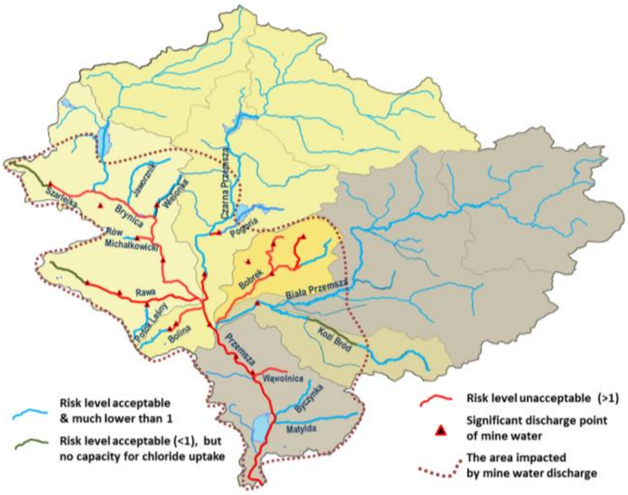

Figure 1 *Risk of chloride impact on aquatic ecosystems of Przemsza river basin – probabilistic approach*

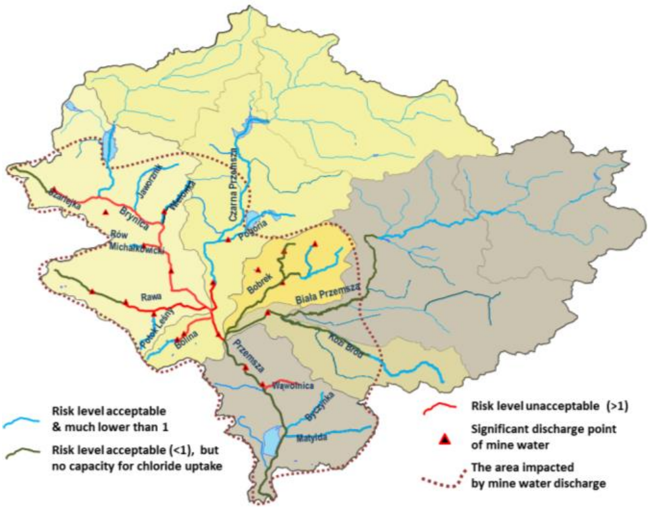

Figure 2 *Risk of sulphate impact on aquatic ecosystems of Przemsza river basin- probabilistic approach*

Data presented in tables and figures above revealed that high salinity in Szarlejka, Rawa and Rów Michałkowicki rivers as well as in middle and lower part of Brynica river is not accepted with respect to risk levels determined under ERA assessment. Moreover, high concentrations of chlorides and sulphates in river waters prevents the achievement of good or moderate ecological status/potential. Additionally in the middle and lower part of Brynica sub-basin the acceptable environmental risk level for chlorides (PNEC) has been exceeded several times. The possibility to reduce the potential environmental damages caused by high salinity is to limit the amount of discharged mine water to Brynica river basin, or to dislocate of mine water discharge points outside the Brynica river basin. However, it should be noted that biological degradation and bad chemical status of Brynica river is not only caused by impact of mine water but it is rather a cumulative effect of all anthropogenic activities carried out in the region (e.g. industrial emission, discharge from WWT, etc.). Therefore, the positive effects of the reduction of inflow of a highly saline water from mining areas will be seen only with simultaneous application of sewage management ensuring fulfilment of environmental requirements. Chemical degradation of water as well as poor/bad ecological status/potential in middle part of Przemsza river and its tributaries is the result of discharge of mine waters and pressure exerted by other users of the basin. The acceptable risk level for chlorides in the main part of Przemsza river was exceeded mainly due to a large load of salt introduced into the Przemsza river by its tributaries: Brynica and Bolina. The negative impact of sulphates ions introduced into the Przemsza river by its tributaries: Bobrek, Biała and Biała Przemsza rivers is relatively low according to ERA criteria, however, simultaneously, sulphates concentration is higher than the threshold value determined by Polish law. In general, the needs and the challenges concerning chlorides and sulphates risk reduction are similar to described for Brynica sub-basin. In the lower section of Przemsza river the acceptable risk level for chlorides was also exceeded. However, exceeded of risk levels were not as significant as in the case of Brynica river and in the middle part of Przemsza river. Most likely is that self-cleaning processes of river affected the reduction of nutrients concentrations. It seems that it is possible to reduce the impact of mine waters on the lower part of Przemsza river basin, however to achieve this a complete control over a mine water discharges is necessary (control of the quality and quantity of salt water discharges).

Conclusions

The main objectives of the management of Przemsza river basin in a field of mine water discharges should be set taking into account the environmental risk analysis including integrated data concerning: river flow, biological parameters/indicators of river ecosystems and physicochemical conditions (background conditions). The fact is, that even if the impact of mine water discharge on aquatic ecosystem will be skipped, or solved still a lot of streams and rivers of Przemsza catchment will not achieve a good status/ecological potential in the near future. The study confirmed that the assessment of water quality based on the ecotoxicological data illustrating the potential impact of pollutants on aquatic ecosystem (ERA) is more favorable than the mandatory classification of pollution. Due to the fact, that

ERA includes sensitivity of aquatic species to the pollution and/or background conditions, this methods allows to assess the real scale of exposure and predicted potential environmental effects. The regulations concerning the discharge of mine water into rivers currently fails to impose any discharge salinity limits on mine waters or on any other significant type of pollution (e.g. major cation or anion) (Wright et al. 2011). The area of legal regulation in respect to any discharge of mine water requires further examination. In view of the study results, as well as bearing in mind the guidelines of the WFD in particular the achievement of good water status of Przemsza river, there is still need for further research to provide evidence for authorities on direct and cumulative impacts of water chemistry changes on aquatic ecosystems.

Acknowledgements

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Kenyan-German Centre of Excellence for Mining, Environmental Engineering and Resource Management (CEMEREM)

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Abstract

Sustainable resource management is a formidable challenge to most economies, calling for an interdisciplinary and practice-oriented training of resource experts and managers. Informed by this fact, the establishment of academic centres of excellence has become a strategic feature of the German-African partnership in key areas of regional development priorities. A call for Expression of Interest for the establishment of a Kenyan-German Centre of Excellence for Applied Resource Management under the DAAD's Centres of African Excellence Programme was subsequently advertised in June 2015. A consortium of collaborating universities comprising Taita Taveta University College (TTUC), HTW-Dresden and TU-Freiberg in collaboration with personnel from the Hochschule Zittau/Goerlitz developed and submitted an Expression of Interest to compete with other Kenyan universities to have TTUC be the host of the Centre of excellence. In December 2015, the consortium succeeded in having TTUC as the hosting African institution of the Centre for Mining, Environmental Engineering and Resource Management (CEMEREM). It is the eight (8th) German-African centres of academic excellence and *the first one with a niche in engineering for sustainable resource management*. The formation of the centre was motivated by the need to implement training in Bachelors, Masters and PhD through curriculum review and development in mining and Environmental engineering, and applied resource management for the extractive sector to assure sustainability of future staff needs in the region. This central focus will be supplemented with development of the requisite training infrastructure, staff development, staff and student exchange with German partner universities and intense partnership with industry in research and training. The centre's core values shall be relevance, sustainability and efficiency and research activities in mining, environmental engineering and resource management. This paper details the process of forming CEMEREM, its strategic focus, and the lessons arising from the process forming it that can inform future similar engagements.

Key words: CEMEREM, DAAD, HTW-Dresden, KENGER, mining, Taita Taveta University College, TU Bergakademie Freiberg

Introduction

Sustainable resource management is gaining in importance in a world where technology is rapidly transforming the manner and cost of doing business. Quality education remains a key pillar of the world's most competitive economies. Such education must provide opportunities for practice-oriented training in well-networked centres of excellence that promote strong research collaborations with government and industry. The ensuing robust nexus produces a critical mass of innovative practising experts and researchers, as evidenced in the countries that topped the list of the global competitiveness index (2014-2015), namely Switzerland, Singapore, the USA, Finland, Germany, and Japan.

The extractive sector is gaining importance in Kenya and Greater East Africa; following the discovery of substantial deposits of oil, coal, iron ore, rare earth minerals, and other minerals, the development of mineral resources is among the six priority sectors under the Economic Pillar of Kenya Vision 2030 Strategic Development Blueprint GOK(2007 and 2013). The contribution of Kenya's mining sector is expected to increase from 1% to 6.5% of the GDP in the medium term, with Base Titanium Ltd's Mineral Sands Project alone contributing to 1% of the GDP. However, an underdeveloped human resource base undermines the potential of this sector.

The German Academic Exchange Service (DAAD) advertised a call for Expression of Interest for the establishment of a Kenyan-German Centre of Excellence (KENGER) for Applied Resource Management under the DAAD's Centres of African Excellence Programme in June 2015 contained in DAAD(2015). The Government of Kenya supported the process through the National Commission for Science, Technology and Innovation (NACOSTI).

A consortium of collaborating universities comprising Taita Taveta University College (TTUC), HTW-Dresden and TU-Freiberg in collaboration with personnel from the Hochschule Zittau/Goerlitz developed and submitted an Expression of Interest to compete with other Kenyan universities to have TTUC be the host of the Centre of excellence. In December 2015, the consortium succeeded having TTUC as the hosting African institution of the Centre for Mining, Environmental Engineering and Resource Management (CEMEREM). The Centre promises to empower the Government of Kenya and local industry to prepare, nurture and sustain technical and managerial skills to support the development of the emerging mineral, oil and gas sector. For the last 50 years, Kenya has not trained enough human capacity to run the sector. This led to an acute shortage of local practice-oriented experts who can lead the relevant teaching, research and development. It was only 2007 that Taita Taveta University College, then a campus of Jomo Kenyatta University of Agriculture and Technology, was set up to formally offer training in Mining and Mineral Processing Engineering.

The idea of the Centre draws motivation from the gaps evident in the training of resource and environmental engineers and managers in Kenya, especially in the highly specialised mining and extractive sector. The discovery of significant mineral resources in Eastern Africa further enhances the visibility of this gap, given the huge deficit of specialists with the technical and managerial skills necessary to sustainably reap the benefits of this resource boon. A new pedagogical paradigm is therefore required to empower governments in producing a new generation of hands-on engineers and managers who can help Kenya and the Greater Eastern African region make good use of its rich natural resource base, for the current and future generations.

TTUC is located in Kenya's coastal mining belt, astride the vast and renowned Tsavo conservation and tourism zone, and has charted a path towards becoming the University of Mining in the region. TTUC will address the huge regional deficit in research and practice-oriented specialists with the research, technical and managerial skills required to reap and transmit the benefits of the region's rich mineral resources in a sustainable manner. The Centre of Excellence for Mining, Environmental Engineering and Resource Management (CEMEREM) brings together a consortium involving Taita Taveta University College (TTUC), the University of Applied Sciences Dresden (HTWD), Technische Universitaet Bergakademie Freiberg (TU Bergakademie Freiberg) and personnel from the Hochschule Zittau/Goerlitz (HSZG) to implement training and research activities in mining, environmental engineering and resource management.

Strategic Focus of CEMEREM

The vision of the centre is "to be an international centre of excellence for mining and resource education for sustainable development in Africa" while her motto is "Networking for excellence in mineral resource education for sustainable development".

The formation of the centre was motivated by the need to implement training in Bachelors, Masters and PhD through curriculum review and development in mining engineering, Environmental engineering, and applied resource management for the extractive sector to assure sustainability of future teaching staff needs in the region. This central focus will be supplemented with development of the requisite training infrastructure, staff development, staff and student exchange with German partner universities and intense partnership with industry in research and training. The centre's core values shall be relevance, sustainability and efficiency and research activities in mining, environmental engineering and resource management.

Figure 1*Panoramic view of Taita Taveta University College in Voi - Kenya.*

Figure 2 *Architectural Impression of the building under construction at TTUC that will house CEMEREM*

CEMEREM will be hosted at TTUC shown in Figure 1 and housed in the building whose architectural impression is shown in Figure 2. This centre is the eight (8th) German-African centres of academic excellence and the first one with a niche in engineering for sustainable resource management.

Scope of CEMEREM

The goal is to develop the first-ever Kenyan-German **Centre for Mining, Environmental Engineering and Resource Management (CEMEREM)** at Taita Taveta University College, in collaboration with HTW Dresden, TU Bergakademie Freiberg, and HS Zittau/Goerlitz, the DAAD, the Kenya Government, and industry partners. A budget of **800,000** Euros per year is envisaged to cover the first two years, with a possible extension to the seventh year. CEMEREM's goal will be pursued through the following specific objectives:

a) To develop and/or improve curricula for new and existing academic programmes (Bachelors, Masters and PhD) in order to ensure practice-oriented education and training of local engineers and managers to meet the increasing needs of Eastern Africa's industrial labour market.

b) To train a new generation of mining, process and environmental engineers and resource managers for industry and government through the new and improved programmes.

c) To build the human capacity at TTUC to offer training in Mining and Environmental Engineering and Resource Management.

d) To network with industry and governments in the region in quality assurance for the proposed training programmes as well as research and training of engineers and resource managers.

e) To integrate sustainability concepts (societal, environmental, spatial and economic) into the pedagogical and implementation framework of the training, research and project activities undertaken by CEMEREM and partners.

Strategic Framework

To accelerate the achievement of the goal through the given specific objectives, CEMEREM will ensure the following enabling strategic framework:

a) Equipping teaching staff at TTUC with the necessary advanced pedagogical, research and soft skills for effective curriculum delivery, leadership, and project management. Third-party funding for postgraduate training and continuing professional development will be pursued consistently to grow a strong network for sustained training and capacity development. Productive staff and student exchange programmes between TTUC, the German university partners and Kenyan industry will be undertaken.

b) Growing and developing the training infrastructure at TTUC using local resources and support drawn widely from long-term partnerships with the key industry and government stakeholders.

c) Building a strong peer-review and feedback network for monitoring and updating the quality of CEMEREM's training programmes at TTUC to match the changing needs of the region, including global innovations and sustainable development obligations. To capture the big picture in a systems approach, this network will draw membership from the academia, government, industry experts, and the public including alumni of CEMEREM. The staff who will have benefitted from CEMEREM will find active roles to play within this network, as part of the incentives framework.

Work Packages and Activities

The project has eight (8) Work Packages (WP) with a range of activities that will ultimately lead to full implementation of CEMEREM: Students will be educated and research in the fields of mining and mining-related issues including environment will be carried out within this programme, complete with exchange programmes and summer schools.

PhD and MSc training will be increased through the scholarships competitively offered from a variety of sources, structured programmes, and continued staff training support by TTUC with sound incentives for staff retention. Granting paid study leave to staff who are away for training, assuring them of commensurate deployment or promotion after return with a reasonable bonding agreement, and expanding their mentor network as alumni form part of the key incentives. This will ensure that the human resources required to run the centre will be available and guarantee the success of a second phase with the focus shifted to active international exchange and research.

Table 1 *Summary of Work Packages.*

WP	Description	Deliverables
WP 1	Preparatory work and needs assessment	Needs and priorities list
WP 2	Curricula review and development	New and revised curricula
WP 3	Human resources development and capacity building	Trained personnel
WP 4	Implementation of BSc and MSc courses at TTUC	Trained students/graduates
WP 5	Infrastructure development at TTUC	Training infrastructure
WP 6	Networking and capacity building with industry and government	Sustainable troika of networks
WP 7	International exchange and research	Research publications and patents
WP 8	Management and quality assurance	Key Performance Indicators

The WPs include the revision of already running curricula as well as the development of new curricula for MSc and BSc programmes in mining and environmental engineering. In order to ensure implementation and to address the current staff problems, special attention is paid to human resource development and capacity building. One WP will ensure the infrastructure for the education of students is in place and that staff will be trained to run the facilities, such as laboratories. Another WP focuses on networking with the industry and the provision of support in training for practitioners in the region. Another WP has its emphasis on the establishment of a vibrant international exchange – in particular with the German partners – and the commencement of research activities. In Table 1 is an overview of the eight (8) Work Packages.

Lessons on the Process of Establishing African Centres of Excellence

TTUC has acquired important experience and derived lessons from her year-long engagement in the competitive process of setting up the first African Centre of Excellence for Mining, Environmental Engineering and Resource Management (CEMEREM). The experience and lessons can be discussed under internal success factors and external success factors.

Internal Success Factors

Internal success factors are mainly the comparative advantages the host can inject into the proposed centre of excellence. The process requires sound preparation on the part of the hosting African institution, both in terms of intellectual resources and enabling infrastructure. Records of adequate staff capacity, sex-differentiated student enrolment, student internships, alumni tracer surveys and key milestones need to be well-managed and centralized using ICT for real-time updates and sharing. The hosting institution must identify the advantages of geographical location and existing activities and networks, which together constitute the unique endowment of comparative advantages the host promises. TTUC, for instance, could capitalize on her favorable location in Kenya's rich coastal mineral and mining belt, proximity to the region's main transport corridors, and the vast Tsavo conservation zone. Practice-oriented training requires these internal factors to provide ready case studies in a cost-effective manner.

External Success Factors

External success factors are mainly the competitive advantages and opportunities arising from the host's rich network with existing institutions. TTUC stands out in Kenya for her extensive network with the central government agencies, county governments, policy think tanks, and industries dealing with mining and resource management – all of which she has signed Memoranda of Understanding (MoUs). Partnership with German universities with a record of excellence in the proposed niche area of training is therefore indispensable. TTUC receives international professors and students on a well-established exchange programme every year, a feat that is unmatched in the region. For CEMEREM, the inclusion of HTW-Dresden introduced a key advantage in practice-oriented training for resource management on the one hand. On the other hand, TU-Bergakademie Freiberg brought in a strong component of mining and environmental engineering training.

Conclusions

The process of competing to host the eighth Centre of African Academic Excellence was completed in 2015, with TTUC emerging the winner in a consortium bringing together HTW-Dresden and TU-Bergakademie Freiberg as the key implementing partners. The process revealed key lessons informed by a matrix of internal and external success factors, of which the comparative advantages of the hosting African institution and competitive advantages arising from demonstrated records of excellence and networking strategies are critical. The vision of this new Centre of Excellence, which is also the first Kenyan-German Centre of Excellence, is to be an international centre of excellence for mining and resource education for sustainable development in Africa – hence the name Centre for Mining, Environmental Engineering and Resource Management (CEMEREM). The first two years will see the establishment of robust training programmes and infrastructure, complemented with frequent quality reviews. The subsequent years will entrench the Centre of Excellence and contribute substantially to bridging the gap in practice-oriented pool of resources engineers and managers for the extractive sector. The main outlook from this experience of establishing CEMEREM for the future of Africa's education and training is instructive in terms of the following key success ingredients: inter-university partnerships built upon partner strengths in definite niche areas and staff capacity; practice-oriented location advantages; practice-oriented curricula; private sector support; and strong bilateral or multilateral funding support.

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The waves of change in water resource management & the rising challenge for water professionals: calling time for a Water Resource Classification & Reporting Code (WRCRC)

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Extended Abstract

The role & setting of water professionals is changing in water resource management. Multiple factors are driving the change – changing stakeholders, regulatory environments, markets, cost pressures, climate & water uses, technology, society & so on. Demand for water resources has grown, bringing greater competition for water, expanding water markets & potential for challenges, disputes & impact [1]. Carried on the tide of these changes, water professionals are now assessing more complex systems, with higher consequences & wider audiences than in the past, as guidance in legal proceedings, policy development, impact assessments & investments. Given the gravity of the outcomes, there is an increased expectation of leading practice, consistency, disclosure, transparency & integrity on & between the work of water professionals with effective communication of findings & confidence as qualification of risk via uncertainty. The intensifying environment is a wave of change, & it is essential that water professionals recognise & adapt to the changing conditions to deliver both reputation & service value – for now & for the future.

In searching strategy options for response, a review of approaches of other industries who have faced similar challenges previously for professional outputs revealed a shared style of action: development & implementation an industry-level tool or code which enables & guides classification & reporting in the public space. Both the mining & petroleum industry have reporting codes: in Australia, the JORC Code [2] was introduced in the 1980's as a Code for Reporting of Exploration results, Mineral resources & Ore reserves following a series of events breaching market & consumer confidence, now with versions in place internationally; & similarly, the petroleum industry began introducing standards in the 1930's, with an international Petroleum Resources Management System achieved in 1997 [3]. More broadly, the International Standards Organisation (ISO) develops & publishes an array of international standards, such as ISO14000: Environmental Management [4]. Compliance to these standards or codes are strictly required for public communication & establish benchmark methods of industry communications, development strategies & measurement.

As an innovative, adapted approach, a Water Resources Classification & Reporting Code [5] (WRCRC) was developed as could be applied to water professionals as an example. The draft Code outlines guiding principles of transparency, accountability, discernibility, competency, adaptability & accessibility for reporting & a two-component classification system, allocating a separation in technical definition & knowledge of 'water sources' from the applied use & management of 'water resources' or water management units (shown in Figure 1). Conversion from a water source into a resource requires consideration of modifying factors, such as environment, social or economic factors, or measures of resilience. Multiple levels of classification allow description of varying levels of confidence, certainty (uncertainty) or management capacity, increasing down the matrix with advancement, with limitations of what can be converted to/from sources or resources to align technical knowledge & management capacity. A number of classification examples are developed, along with a WRCRC style report as demonstration & discussion.

As water management decisions become more complex, critical & wide reaching, it is fundamental the industry recognise new tools are required to maintain integrity & public trust for the present & future. History of comparable industries shows classification & reporting codes as powerful instruments able to deliver accountability, technical & risk veracity in the public arena, & the development & implementation of a code for the water industry is a major opportunity for reform & leadership to take the industry forward.

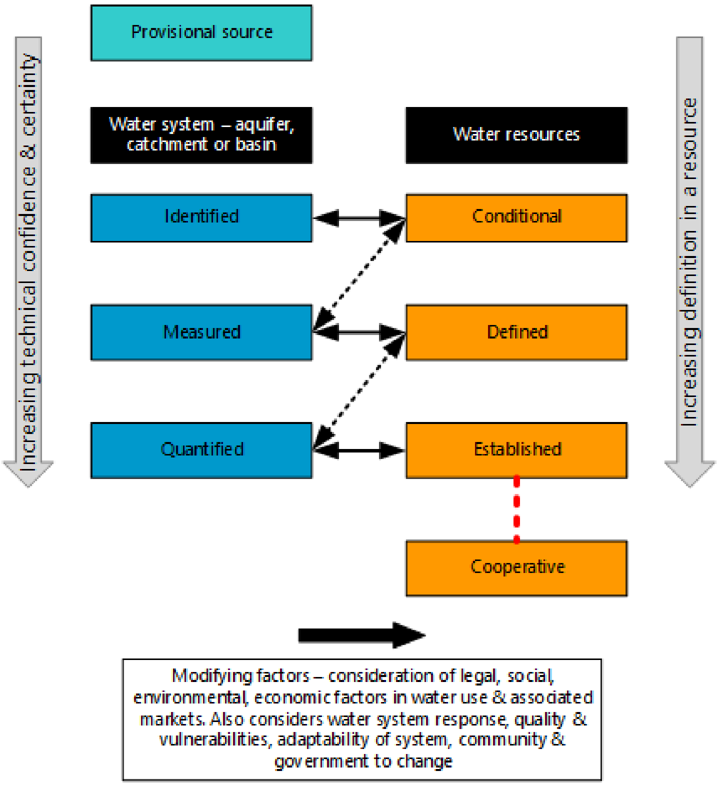

Figure 1*: A starting framework for a WRCRC (adapted from Kennedy, 2008)*[5]

Key words: Water resources, water professions, industry, reporting, classification, futures, foresight

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CHAPTER 2

Mine Water Hydrogeology

Earthquakes and Groundwater and Surface Water Management at Mines Sites

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Abstract

The design of water management infrastructure in mines and the assessment of the impact of proposed mining operations on groundwater and surface water typically draws on baseline studies of surface water levels and flows and hydrological investigations encompassing groundwater occurrence, piezometric levels, and the hydraulic conductivity of the identified hydrostratigraphic units. As part of the design and or impact assessment process account is taken of the current and future demands of the mine infrastructure, capturing inflows and outflows to and from the system as part of a water balance, often including the potential for increases or decreases in future water flows resulting from, for example, climate change.

Although the impact of earthquakes is taken into account in the design of structures and an assessment of the impact of major hazards from, for example, tailings dams, the impact of earthquakes on the groundwater and surface water regimes is rarely considered. The impact of earthquakes on groundwater has long been recognised (e.g. Cooper *et al* 1965), and following significant earthquakes significant changes to groundwater and surface water hydrology (e.g. [2]) can occur, including increased surface water flows and changes in groundwater levels. There changes can be of sufficient magnitude to have not inconsequential implications for mine water management.

This paper sets out the impact of earthquakes on groundwater and surface water hydrology and the potential implications for groundwater and surface water management in mines.

Key words: mine water, groundwater, surface water, earthquake, seismicity, mine

Introduction

The design of mine infrastructure, including for example tailings management facilities (TMF), pit slopes and processing plants, typically takes into account the potential risks from earthquakes and is based on long established local and international design codes. These are often codified within local legislation. The design of water management infrastructure typically draws on baseline studies of surface water levels and flows and hydrological investigations encompassing groundwater occurrence, piezometric levels and the hydraulic conductivity of the identified hydrostratigraphic units. This information also supports the assessment of the impact of proposed mining operations on groundwater and surface water. During the design process (be they feasibility type studies or detailed design) and or the completion of an environmental and social impact assessment (ESIA) account is taken of the current and future demands of the mine infrastructure typically through the development of a water balance. The water balance will capture the inflows and outflows to and from the mine site, often including the potential for increases or decreases in future water flows resulting from, for example, climate change.

However, although the impact of earthquakes is taken into account in the design of structures and an assessment of the impact of major hazards from, for example, tailings dams, the impact of earthquakes on the groundwater and surface water regimes is rarely considered, even though the impact of earthquakes on groundwater and surface water regimes has long been recognised (e.g. [1]) and significant coseismic changes to groundwater and surface water hydrology (e.g. [2]) can occur. Such changes can include increased surface water flows and changes in groundwater levels. These changes can be of sufficient scale to have not inconsequential implications for mine water management. This paper examines some of the causative mechanisms and risk factors with regards to considering the impact of earthquake seismicity on mine water management.

Groundwater Response to Earthquakes

Earthquakes generate seismic waves which have an effect on groundwater in two principal ways. Firstly they can cause oscillations in groundwater levels and secondly they may cause permanent changes in groundwater levels, where groundwater is in continuity with surface water there may be consequential impacts such as changes in surface water flow. The response of groundwater, and hence surface water, to earthquakes is complex and occurs on varying timescales and through a number of different mechanisms. The processes involved as summarised in Figure 1 below.

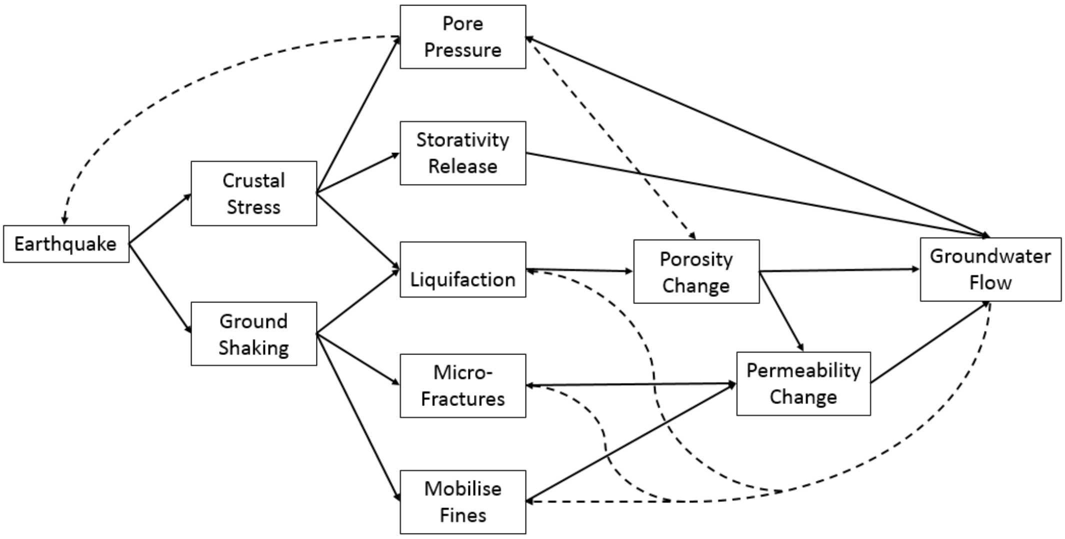

***Figure 1** Relationships between earthquakes and groundwater processes (adapted from: http://seismo.berkeley.edu/~manga/eps200-2006.html).*

The impact of an earthquake on the groundwater and surface water regime may be considered in three parts: before, during and after an earthquake.

In the area proximal to a fault zone before an earthquake there may be an increase in pore pressure (in a compressional regime) or decrease in pore pressure (in an extensional regime) as the result of poroelastic deformation resulting from changes in stress. In an unconfined aquifer, or a high permeability confined aquifer, the increase/decrease in pore pressure will be quickly dissipated and no significant effects, in terms of changes in groundwater or surface water flow, will be observed.

During an earthquake the dynamic motion (ground deformation) resulting from the passage of seismic waves will cause changes of pore pressure within an aquifer. These changes will typically occur at a frequency which does not allow for the excess pore pressure to dissipate through the flow of groundwater. Manga and Wang (2007) indicate that the cyclic dynamic stress changes associated with a magnitude 8 earthquake are on the order of 3 MPa at 100 km from the focal point decreasing to 0.06 MPa at 1000 km from the focal point. This is clearly very dependant on the geomechanical properties of the rock/soil, for example in high stiffness granites relatively small strain will give rise to large changes in stress. Understanding of changes in pore pressure associated with dynamic strain is crucial to understanding the stability impacts of an earthquake in proximity to a mine site. There are a number of geotechnical/geomechanical modelling tools that may be used to understand these changes under a given set of conditions (for example, assuming the fracture regime is isotropic, QUAKE/W or in anisotropic scenarios: ELFEN, FLAC and FracMan).

Oscillation of pore water pressures (groundwater levels) has been recorded in aquifers at very large distances (>5000 km) from the earthquake focus as a result of resonance within the well with the passage of the Rayleigh waves. While this response, which may amplify the change in pore pressure, may be of academic interest in terms of understanding the cause of oscillation or water levels in wells or understanding the magnitude of seismic response at distance from an earthquake zone in the absence of seismometers it is not significant in terms of understanding responses of structures at the site, or flows to the mine pit, as a result of earthquakes. Large amplitude fluctuations in response to distant large earthquakes could potentially damage in-situ monitoring equipment in the wells. The oscillation can be calculated using the method of Cooper *et al* (1965) as a function of dynamic strain caused by the Rayleigh wave and is dependent on the dimensions of the well, the transmisivity, storage coefficient, and porosity of the aquifer as well as the type, period, and amplitude of the seismic wave. If accurate site specific data is available regarding aquifer permeability and well construction it may be possible to assess the possible order of magnitude of groundwater level fluctuations that may occur at a mine site for a given magnitude earthquake focused at a given distance from the site. It is suggested that if groundwater level fluctuations are recorded that cannot be ascribed to other causes then it may be of value, in areas of known high seismic hazard, to asses this mechanism at such a time.

Static strain changes as a result of crustal movements occur during an earthquake, but are typically orders of magnitude smaller than dynamic strains. The effect of static strain changes are discussed further below.

Following an earthquake the static stress changes associated with crustal movements can cause poroelastic strain resulting in an increase in pore pressure in a compressional regime and a decrease in pressure in a dilatational regime. It should be noted that in strike slip fault regimes there would be both zones of dilatation and zones compression. Manga and Wang (2007) indicate that static stress changes associated with a magnitude 8 earthquake are on the order of 0.01 MPa at 100 km from the focal point decreasing to 0.0001 MPa at 1000 km of the focal point. The change in pore pressure (p) is related to the mean stress change (σ) by the equation:

$$p = \frac{B}{3}\sigma$$

Where B is Skempton's coefficient and is a variable related to the porosity and compressibility of the pore fluid, solid grains and saturated rock and has a value between 0 and 1, with 'hard rocks' having a value between 0.5 and 0.9 and unconsolidated materials having a value close to 1 (Manga and Wang 2007).

Whilst increase in pore fluid pressure as a result of coseismic strain in a compressional regime is reported to cause flow following large earthquakes, significant effects are limited to areas close to the fault zone and the equilibration period will typically be short in an unconfined aquifer. It is unlikely, for example, that the occurrence of a Magnitude 4 (M4) or M5 earthquake several hundred kilometres from a location would result in a significant increase in groundwater flow as a result of coseismic strain. Even in the case of a large earthquake in closer proximity to the mine, work by numerous authors (for example see Manga and Wang 2007) has demonstrated that coseismic strain does not contribute a significant groundwater flow and that much larger groundwater flows are typically associated with other processes.

In dilatational regimes, coseismic strain can result in large increases in permeability in the area within hundreds of kilometres of the fault zone following an earthquake causing a significant increase in groundwater discharges and fall in groundwater levels. For example Tokunaga (1999) reported a 100% increase in discharge rates declining to 50% above baseline over the first 4 months following the 1995 Kobe quake and calculate this as equivalent to a five fold increase in hydraulic conductivity. A 70 m drop in water level was observed in groundwater wells in the affected zone.

In addition to coseismic strain, there are a number of other processes which may act to cause increased groundwater flows, which may act at greater distances from the fault zone and also may act to cause groundwater response opposite to those predicted based on coseismic strain (Wang *et al* 2001). Long term step changes in groundwater level, both up and down, can occur as a result of major earthquakes close to the rupture zone, or at significant distances from it.

Dynamic stress (i.e. ground shaking) during an earthquake can cause the permanent deformation of rocks and sediments resulting in changes in groundwater flow associated with both increases and decreases in groundwater level. In the case of unconsolidated soils this may result in rapid consolidation and ultimately liquefaction. If consolidation occurs, the pore pressures in the sediments will increase, resulting in an increased groundwater discharge. In competent rocks and consolidated sediments, cyclical ground shaking may result in microscopic and or macroscopic fracturing, resulting in an increase in permeability and therefore the potential for an increase in groundwater flow. Wang *et al* (2001) reported both of these processes occurring in response to the M7.5 Chi-Chi earthquake in Taiwan.

Unconsolidated alluvial sediments may be vulnerable to liquefaction in response to earthquake movement. In various geological regimes correlations have been made between the distance from the epicentre at which liquefaction occurs and earthquake magnitude (e.g. Wang *et al* 2006). However, such empirical studies cannot be transferred directly to different locations and geological regimes. Liquefaction (as well as having severe consequences for the stability and survival of any overlying structures) will result in consolidation and increases in pore pressure. Long term changes in water level have been observed at boreholes some distance from the zone of liquefaction as a result of diffusion of the pressure front following the event.

Although it is not common, long term (6 to 12 month) changes in water level have been observed in response to earthquakes at great distance from the monitoring locations (e.g. Brodsky *et al* 2003). The mechanism for these changes are not fully understood but may result from aquifer compaction and changes in permeability changes.

Surface water response to earthquakes

Large earthquakes are often associated with changes in surface hydrology (e.g. Kargel *et al* 2016). These alterations to surface hydrology may result from physical changes in topography, damming of water courses by landslides or rockfalls and increased input of snow from earthquake induced avalanches. All of these were observed at various locations in Nepal following the 2015 Gorkha earthquake (Kargel *et al* 2016).

However other changes in surface water flows are observed that cannot be ascribed to such physical surface phenomena that are likely to be associated with changes in permeability, pore pressure and groundwater level as described above. These flows can be very large, for example an additional discharge of 0.8 km^3 was estimated following the M7.5 Chi Chi earthquake in Taiwan (Wang *et al* 2004) and a discharge of 0.5 km^3 following the M7.5 Hebgen Lake earthquake (Muir-Wood and King 1993). Other notable examples include the increase in discharge from the Alum Rock springs, California, USA following a nearby M5.5 earthquake in 2007 (Manga and Rowland 2009). Although the area over which these flows occurred is not stated, a similar response would be expected in mine flows, particularly where the mine intersects a major discharge route such as a fracture or fault zone.

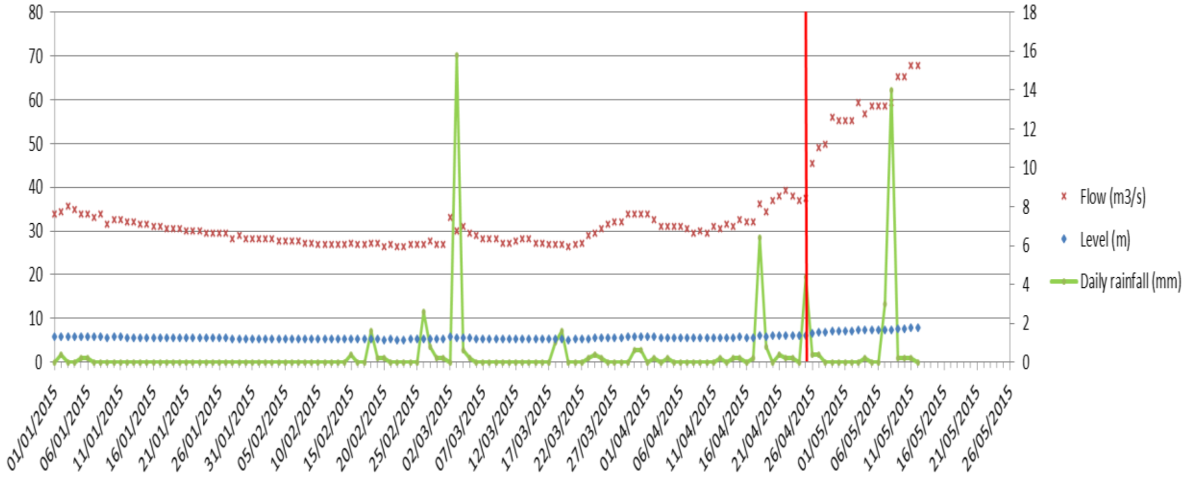

Figure 2 *River flow and level compared with daily rainfall at the Tamakoshi river gauging station at Bustie, Nepal (data from http://hydrology.gov.np/new/bull3/index.php/hydrology/basin)*

Similar increases in surface water flows were observed in Nepal following the Gorkha earthquake on 25th April 2015 (e.g. Figure 2), that occurred rapidly and are not directly ascribable to physical changes in surface hydrology/geomorphology.

Implications for Mine Water Management and Operational Resilience

Mine water management infrastructure is typically designed based on historic meteorological records and baseline monitoring of groundwater levels and surface water flows and levels. Inflow calcualtions are undertaken based on these datasets, integrated within an understanding of the conceptual hydrogeological model of the site and encompassed within a water balance, often supported by numerical models of groundwater flow and dewatering operations. At operational mines these estimates are typically refined based on operational records and experience. Should a significant change in the groundwater or surface water regime occur as a result of an earthquake, as might be anticipated in the event of a "major" (M7 – M7.9) or "great" (M8+) earthquake then the impacts on water management may be significant. It may be argued that in the event of a major or large earthquake other priorities such as the stability of the tailings dam, mine workings and process plant infrastructure may be of greater concern than water management, however should such structures be resilient to such events then ongoing water management will require consideration.

A major or great earthquake within a few hundred kilometres of a mine site could trigger increases in flow to the mine, based on the mechanisms outlined above, that may be of a sufficient rate to be a management concern (potentially many times the pre-quake inflow) as a result of:

- An increase in permeability due to fracturing in response to dynamic stress changes or dilation in extensional or strike-slip regimes;
- Increases in groundwater pore pressures in compressional stress regimes; and
- Increases in groundwater pore pressures as a result of compaction or liquefaction of overlying alluvial sediments.

Prediction of the volume of inflow as a result of each of these mechanisms is not possible due to the uncertainty regarding the type of earthquake which may occur and the static and dynamic stresses to which an area may be subject, uncertainty in the response of the rock beneath the mine site to dynamic stress changes, and uncertainty in the susceptibility of saturated soils at a particular mine site to liquefaction. With investigation and data collection, it may be possible to estimate the broad order of magnitude possible inflows for an earthquake on a particular magnitude as a response to for example liquefaction or elastic strain. However, large permeability changes have the greatest potential to influence mine water inflow, and these changes are not calculable.

As many of the impacts are not calculable it is recommended that mine water management plans at mine sites in areas of high earthquake hazard acknowledge the risk and that contingency management options are put in place. In addition to management measures contingency plans may include for the over-sizing of surface water drainage channels and ponds and or providing for additional pumping capacity to be installed as and when necessary.

Conclusions

Although oscillation of water levels in groundwater monitoring wells can occur at great distance from major earthquakes, this is a resonance effect of small changes in the aquifer and has limited implications for groundwater flow (though there may have implications for the integrity of instruments installed in the borehole). Although long term changes in groundwater level are sometimes observed in response to earthquakes at large distances from the epicentre and have the potential to be associated with increased groundwater flow due to increased pore water pressure or increased permeability, such instances are rare.

Compressional static coseismic strain can cause large changes in water level immediately following an earthquake (e.g. Manga and Wang 2007) but there is unlikely to be a significant impact on groundwater flow due to the relatively small volume of flow necessary to allow groundwater pressures to equilibrate. However major or great earthquakes can cause significant changes to groundwater levels and flows due to alterations to the permeability and changes in pore pressures. These changes will often result in changes to surface water flows.

Although earthquakes may cause significant changes to the groundwater and surface water regime at a mine site, it is acknowledged that many of the impacts are not calculable hence is recommended that mine water management plans at mine sites in areas of high earthquake hazard acknowledge the risk and that contingency management options are put in place. By way of example this could take the form of management measures or engineering measures such as over-sizing surface water ponds and or drainage channels as well as providing for additional pumping capacity to be installed as and when necessary.

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Mechanisms on Mine Water Loss Based on a Theory of Mining-Fractures Development Pattern

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Abstract

Longwall mining could inevitably induce the generation of fractures in the overlying strata, the dynamic development of which is believed to be one of the most primary factors controlling groundwater leakage. A hypothesis, triangle fracture arch theory, was proposed for the evolution law of mining-induced fractures, considering two cases of ignoring compaction of gob with successive weightings or not. A connection between the evolution of mining-induced fractures, triangle fracture arch and groundwater leakage was developed. In conjunction with practical experience the first two double-stage arches happening in first weighting and periodic weighting for the first time would be seemed as the key parts of the whole fracture development by means of this theory, which led the widening of some fracture pathways for water to flow. Insight into the development of mining-induced fractures can help us know when, where, and how the mining-induced fractures develop and determine key fracture pathways controlling groundwater leakage paths during longwall mining, providing important theoretical basis for safe mining.

Key words: Water loss, mining fractures, triangle fracture arch

Introduction

An increase of energy needs was mainly driven by growing world population and industrialization. However, we must reconcile this with other demands such as environmental quality and the protection of water resources for a better life (Gordalla et al. 2013; Gregory et al. 2011; Osborn et al. 2011). Severe conflicts of interests are especially noteworthy in the protection of water resources and the exploitation of energy resources, even worse in some water-stressed countries. Originally, the water resources are under immense pressure due to the needs of agriculture, industries and drinking of the local inhabitant (Howladar 2012; Bayram and Önsoy 2015). The exploitation activities further aggravate this situation with the direct impacts on the water resources in the mining area such as exhausted springs, well-water level lowering, water flooding/inrushing, water contamination and so on (Zipper et al. 1996; Howladar 2012; Molson et al. 2012; Bayram and Önsoy 2015). China, one of energy giants, is based on coal as its main source of energy, with coal production and consumption accounting for approximately 77% and 65% of the national ones, respectively (Chang et al. 2003; Wu et al. 2009; Yu and Wei 2012; Zhang 2014; Xu et al. 2015). Water resources are extremely scarce and its protection is of vital importance in the mining areas of China.

Generally, the distribution of surface water mainly depends on the topography, vegetation, climate, the conversion between surface water and groundwater and so on (Kollet and Maxwell 2006), which could be isolated from major mining-induced impacts by a less permeable layer and is extremely localized relating to the mining front same as the shallower aquifers (Hill and Price, 1983; Liu et al. 1997). On the other hand, a complex succession of hydrogeological changes occur in hydraulic properties (e.g. hydraulic conductivity, heads, gradients and so on), groundwater chemistry, groundwater flow and groundwater sustainability among the deeper aquifers during and after mining (Booth et al. 1998; Sukhija et al. 2006).

Through the past studies, the dynamic development of mining-induced fractures in the overlying strata is believed to be one of the most primary factors that control the groundwater flow patterns and that lead to considerable water loss into mined panels from the deeper aquifers (Zhang et al. 2010; Islam et al. 2009; Zhang et al. 2014; Poulsen et al. 2014), which poses a great challenge to the hydrogeologists, geophysicists, geochemists as well as to environmentalists and engineers (Sukhija et al. 2006). Currently, a variety of methods, ranging from analytical methods and field experiments to numerical and physical simulation, have been used and mainly focus on the mining-induced effects on water environment (e.g. water level and parametric analysis of water), subsidence (e.g. land and strata subsidence) and the fractures evolution of the overburden strata (e.g. natural and induced fractures propagation, closure and connection) (Peksezer-Sayit et al. 2014; Zhang et al. 2014; Howladar 2012; Panthulu et al. 2001). But very few detailed studies of mining impact on groundwater leakage paths have been reported, more particularly, for the deeper aquifers.

Main objectives of this study are to (1) know when, where, and how the mining-induced fractures develop on the basis of water analysis (2) determine some dominant or key fracture pathways controlling the initiation of an water-conducting way and groundwater leakage paths during longwall mining and (3) spatially and temporally characterize preferential paths in groundwater leakage.

Methods

Under natural conditions, groundwater resources go into coal seams by infiltration and by vertical movement through the surrounding rocks. Nevertheless, overburden desaturation and drainage into the mine caused by numerous upward propagating fractures may occur during and after mining (Islam et al. 2009; Booth et al. 1998). As we all know, nature will eventually seek the most stable configuration when a void is created by external force, which may be enlargement, connection or closure of fractures. Accordingly, coal mining inevitably causes the fracturing of overburden strata, and groundwater flow is controlled by some dominant fractures along which groundwater can preferentially flow towards the mine workings (Howladar and Hasan 2014; Yang et al. 2007). Repetitive operation of mining activities and regular re-distribution of the stress field may lead the dominant fractures to develop directionally, creating a regular or potential fracture face, fracture passage to provide pathway for water movement or leakage.

In this paper a hypothesis approach on evolution law of mining-induced fractures would be proposed, which is triangular fracture arch evolution. Insight into this mechanisim can provide preference for some phenomena about groundwater losses into the mine workings and water disasters during mining process combined with the past results such as field observations, numerical modeling, and physical analogs (Zhang and Shen 2004; Wang and Park 2002; Wu et al. 2004).

Conceptual Models for evolution law of mining-induced fractures

It is assumed that mining-induced fractures evolve in the mode of triangle under complex and variable stress which may make it possible for interconnected system of fractures to form some regular potential face or pathway for water to flow. When mining excavations are made, mining process can be simplified as one that coal is mined with one mobile end at an increasing distance from the other fixed end along the direction of face advance. In addition, one end is constrained less, but the other is changeable and constrained more because of the increasing volume of the extraction and the enlargement in scope. It can be seen as simple repetition of this pattern in disregard of local geological and structural differences and disturbance to fracture evolution caused by previous mining, which would cause the overlying strata above the gob to plunge towards the panel setup entry coupled with effects from the deformation and movement of rock mass. Moreover, assuming that these evolution models are mainly controlled by fractures development in the cross-section of face advance with by that of face length less affected, we just consider the case of flat-lying coal seam for subsequent analyses.

Triangular fracture arch disregarding compaction process

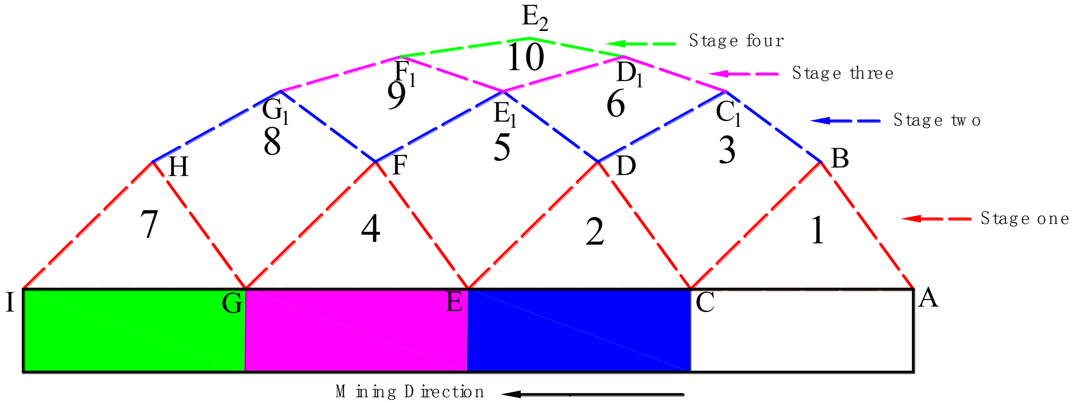

Figure 1 *The schematic diagram of triangular fracture arch illustrating evolution law of mining-induced fractures*

In this model we ignore closure phase of factures from compaction of gob with successive weightings for the moment. As we can see from Fig.1, along with the right-to-left advancing of face, there would eventually have a arch-like fracture arch created above the mined-out area. Moreover, its scope is also forward more than upward, and there is a tendency plunging towards the panel setup entry in overall shape of fractures. There exists criss-crossed potential fracture faces or pathways in its interior which conclude four or more stages of fracture development with nearly identical fracture porosity and permeability at the same stage, from the bottom up naming them as follows: stage one, stage two, stage three, stage four and so on. When coal face reaches a certain distance, the first triangular fracture arch at the first stage appears, namely, fracture ABC seen in Fig.1. And further advancing would cause the second fracture arch CDE.

We suppose that first weighting happens in location E after the formation of two triangular fracture arch at the first stage, fracture arches ABC and CDE, the effects of which can make these two adjacent fracture arches tend to close upward like arch and form the triangle fracture arch BC_1D of the second stage, and the fracture arch of double stage has gotten into shape. Meanwhile, it would widen the fracture pathways of AB and DE of at both sides of fracture arch AC_1E. On the other hand, locations G and I can be seemed as where periodic weighting occurs. Taking G for instance, when periodic weighting occurs the fracture arch EFG firstly emerges followed by DE_1F similar to BC_1D, then the tendency to close would cause it to evolve upward and form $C_1D_1E_1$ at the third stage. During this process, the fracture pathways of CD and GF of at both sides of fracture arch CE_1G would be widened likewise, and similar situations occur with further advancing. We can say that the effects on the evolution of fracture from weighting only cause the formation of triangle fracture arch of double stage, but the other stage evolution mainly depend on the tendency to merge between the neighboring arches. If the evolution of these triangle fracture arches can be classified in chronological order, we obtain a supposed collation in marked numerical order seen in Fig.1. In addition, it is under the influence of first weighting and periodic weighting for the first time where fracture arches develop well, that is, fracture arches AD_1G, AC_1E and CE_1G are the main parts of whole fracture development, because their distances to the panel setup entry are so close that initial deformation and movement of rock mass would give them enough chance to develop. And the fracture arches beyond these distances may be constrained by the interaction of surrounding rock and influence of initial mining. Among these important arches, fracture pathways AB, DE, CD and GF have been influenced and widened by first weighting and periodic weighting. This is the results in disregard of the compaction process after mining.

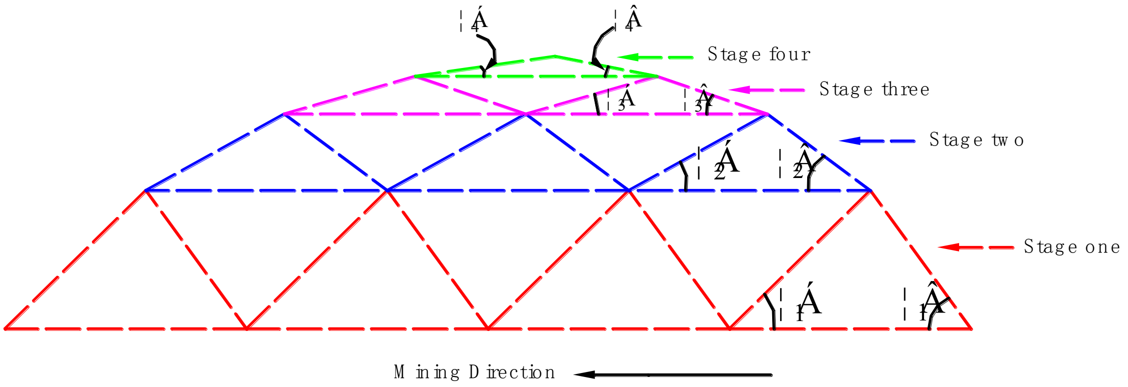

Figure 2 *The schematic diagram of triangular fracture arch illustrating fracture angles*

a) Lateral characteristics of triangle fracture arch

As mining advances, the highest point of every fracture arch moves forward and upward, and its front part grows in length and obviously longer than the rear one along the direction of face advance. These arches are getting so much more rounded with new triangle fracture arches constantly produced. As we can see from Fig.2, there has been an assumption that the fracture angles of every triangle fracture arch can be separated into two branches: front and rear crack angle, α and β , which are acute angles between the front part of every little triangle arch, the rear part and the horizontal line. In addition, some patterns can be concluded as follows: the front crack angle is smaller than the rear one among every little triangle fracture arch at every stage, which is caused by the tendency to the panel setup entry

b) Vertical characteristics of triangle fracture arch

From the vertical distribution of triangle fracture arch we can draw a conclusion that the nearer the triangle fracture arch get to goaf, the more the fracture develops and the larger the fracture angles are. That is, the front or rear crack angle at the first stage is respectively larger than that at the second stage, and so on. We can use triangle of tall and slim, triangle of short and stout to describe them more evocatively. Moreover, along with the upward development of fracture arches the spacing between fracture pathways above and below get smaller and smaller. When these fracture pathways of small spacing are connected, horizontal fractures would be created, then developing with an upward and forward trend.

Triangular fracture arch taking compaction process into consideration

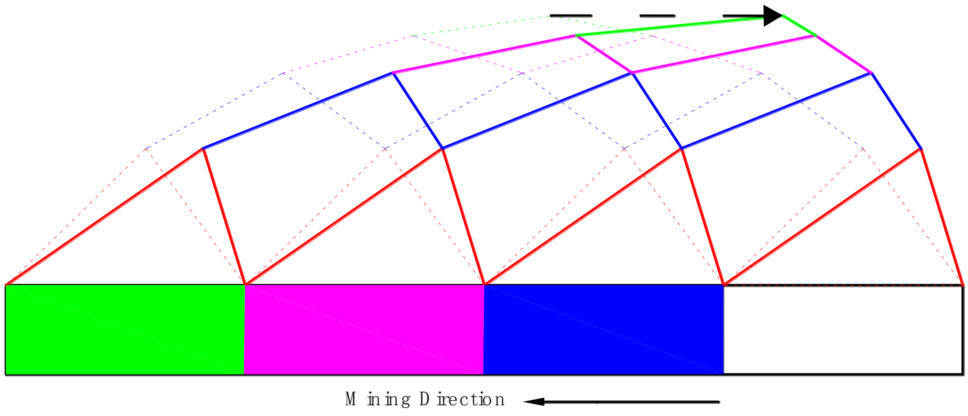

Figure 3 *The schematic diagram of triangular fracture arch considering compaction of of gob with successive weightings*

Based on triangle fracture arch, we can obtain another hypothesis of fracture arch evolution combined with the compaction of gob with successive weightings. It can be assumed that the rear compaction would constantly cause the established triangle fracture arches to incline towards the mined area as the distance of mining face from the panel setup entry increases, which can be seen in Fig.3. During this process, the fracture arches close to the panel setup entry (AD1G, AC1E and CE1G) have also been influenced, inducing fracture pathways C_1DE, D_1E_1FG and BC to widen, together with mining effects on the front strata of face advance. That is because the front part of these triangle fracture arches moving towards the mined space would be widened more than the rear one constrained by the adjacent strata. That fracture increases in the front of face advance and compacted in the back will make the probability of the front part of triangle fractures be extended more than the rear one.

All in all, we can know that whether in disregard of compaction or not would make the fracture pathways C_1DE, D_1E_1FG become the key parts of the whole fracture evolution.

Discussion and Conclusion

In this paper a hypothesis of triangular fracture arch about evolution law of mining-induced fractures has been proposed, which considered two cases: disregarding compaction process or not. This model put forward spatio-temporal evolution laws of mining-induced fractures charactering lateral and vertical development. According to the conceptual models for evolution law of mining-induced fractures, together with practical experience, we can obtain that as the mining advanced through the panel it would mainly create a series of triangle fracture arches in the cross-section of face advance, involving the fracture development of different stage vertically and the front part of every triangle fracture arch in length longer than the rear one with the rear crack angle more than the front one laterally. From Fig.2 we can get the results of fracture angles $\alpha_1<\beta_1$, $\alpha_2<\beta_2$, $\alpha_3<\beta_3$, $\alpha_4<\beta_4$, $\alpha_1>\alpha_2>\alpha_3>\alpha_4$, and $\beta_1>\beta_2>\beta_3>\beta_4$. During the process of first weighting and periodic weighting for the first time the first two double-stage arches would be seemed as the key parts of the whole fracture development, leading to the widening of fracture pathways AB, DE, CD and GF.

Moreover, if the compaction process of gob with successive weightings is taken into consideration, we can find that the established triangle fracture arches would incline towards the mined area, causing fracture pathways C_1DE, D_1E_1FG and BC to be widened seen in Fig.3. In accordance with the above both side, we can draw a conclusion that the fracture pathways C_1DE, D_1E_1FG would become the key fracture pathways of the whole fracture development under the role of two aspects.

On the other hand, during longwall mining groundwater could flow away through these key fracture pathways. It is assumed that the fracture arches possessing double stage, especially AC_1E and CE_1G, can exactly reach roof water-bearing zone. There is no doubt that water would move along the widened fracture pathways C_1DE and D_1E_1FG. That is why locations E and G where first weighting and periodic weighting for the first time happen would become the frequent site of water leakage, even water inrush.

Knowing when, where, and how the mining-induced fractures develop can give us a thorough understanding about key fracture pathways or groundwater leakage paths, providing theoretical basis and technical support for safe mining of coal seam.

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Can natural Stratification prevent Pollution by Acid Mine Drainage?

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Abstract

Acid mine drainage (AMD) from underground or open pit mines is considered one of the most problematic liquid pollutants in the mining environment. Therefore, it is crucial for mine operators to either prevent AMD or to purify the water once it emerges to surface water courses. Though a number of AMD prevention techniques exist, they are not as far developed as would be necessary for preventing AMD discharges regularly. Therefore, the standard method to eliminate pollutants, acidity and solids from AMD are active or passive treatment techniques. After mining ceases, it would be of importance to have methods available that can either prevent the discharge of AMD or the treatment is conducted *in-situ* of the abandoned mine. Various authors investigated or proposed to use the effects of natural stratification as a means to prevent AMD discharging from abandoned mines.

Natural stratification is the layering of water bodies, in this case in a flooded underground mine, by water of various chemical or physical properties. These physicochemical differences result in density differences which, consequently, may cause the stratification of mine water bodies. Stratification in flooded underground mines has long been known to occur under certain conditions, but a detailed study of its causes has not been conducted yet. This paper will present stratification investigations in flooded underground mines and investigate if natural stratification is able to prevent surface water courses from being polluted by AMD.

Based on the *Straßberg*/Germany, the *Georgi Unterbau*/Austria, the Frances Colliery/England and the 1B Mine Pool/Canada, the natural stratification and its causes will be described and the reasons for its breakdown be discussed. The presentation will describe the stratification pattern, the water chemistry and why the systems cannot be used as reliable options for long term *in-situ* remediation. It will not considered forced stratification which can be caused by manmade structures.

One of the key findings of this investigation is that natural stratification is not stable and can be broken down by a variety of external forces. Proposing to use natural stratification as a means for *in-situ* remediation or to prevent the discharge of AMD to the environment is therefore not feasible. In case of their breakdown, the polluted AMD will cause damages to the natural environment if no other means for water treatment are available. Consequently, for a full understanding of stratification in flooded underground mines, more work will be necessary and analogue laboratory as well as numerical models need to be conducted for a better understanding of the processes involved.

Key words: Mine water, stratification, pollution prevention

Introduction

Mine water pollution is a threat to nearly all areas in the world where mining played a substantial economic role in the past or today (Younger et al. 2002). This pollution can arise from tailings dams, waste rock deposits, soil contamination from using chemicals or from mine water *sensu stricto* (Wolkersdorfer 2008). In nearly all cases, where treatment or remediation measures are employed to eliminate this pollution, active treatment methods are the method of choice. Yet, these methods are costly and operators and authorities around the world are trying to identify methods to reduce the costs of site clean-up or water treatment (Zinck and Aubé 2010). Since the 1980ies, methods have been developed for polluted mine sites (Chapman et al. 1988) and are still under investigations in various mining regions around the world (Novhe 2012), *in-situ* methods being one of these passive methods being investigated (e.g. Elina 2009; Harrington et al. 2015). Though these *in-situ* methods for mine water treatment have been probed or where developed, they are currently not used to a grade that might technically be feasible.

Off the potential pollution arising from working or abandoned mine sites, acid mine drainage (AMD) is one of the most problematic pollutants (Blowes et al. 2014; Kelly et al. 1988), as it usually contains elevated acidity loads or potentially toxic elements (PTE). Yet, also circumneutral or alkaline mine drainage might pose problems and can severely pollute receiving water courses or the environment around a polluted mine site (Nordstrom 2011). Usually, the sources for this mine water pollution are the disulphides within the mined voids, i.e. in the open pit mines or underground mines (Stumm and Morgan 1996). It would therefore be favourable if the sources of this pollution could be eliminated or sealed off. One of the methods proposed by various authors is to use the natural stratification in underground mines to keep the more polluted water within the mine (Melchers et al. 2015; Wolkersdorfer 1996; Wolkersdorfer 2006; Wolkersdorfer 2008). Yet, the most common mine water treatment options to date are active or passive methods (Bejan and Bunce 2015).

Stratification is the layering of water into water bodies with distinct physicochemical characteristics, such as the temperature and electrical conductivity and can be stable for a long period of time (Zeman et al. 2008). The differences in theses physicochemical characteristics result in different densities of the water and once the density differences between the single water bodies exceeds a certain threshold, a more or less stable stratification will develop in the water body. In most cases, this stratification is a natural process, occurs without actively interfering with the water body and is referred to as “natural stratification”. “Forced stratification”, on the other hand, would be stratification that is actively promoted by the installation of manmade structures or the modification of water flows. The reason for a stable stratification is a large enough density difference between the two layers and a relatively small velocity difference between them Wolkersdorfer (2008). In general, temperature differences above 10 K ($\Delta\rho$ > 2 kg/m³), total dissolved solid differences of more than 3% ($\Delta\rho$ > 20 kg/m³) or large differences in turbidity ($\Delta\rho$ > 200 kg/m³) can cause stable stratification (Kranawettreiser 1989).

This effect of stratification is well known and has been thoroughly studied in lakes or the ocean (Blanc and Anschutz 1995; Geller et al. 2013; Voorhis and Dorson 1975). Researchers and mine operators also found stratification in flooded underground mines, the first known study dating back to 1961 (Stuart and Simpson 1961), and in some cases it was assumed that this stratification can be used to omit the discharge of polluted mine water from abandoned shafts. Though natural stratification in flooded underground mines is long know, systematic studies into the causes of this stratification and if it might be possible to use it as a passive remediation method are lacking in the mine water literature. The only more detailed studies known to date with dozens of measurements and tracer tests as well as chemical investigations have been conducted by Wolkersdorfer (1996) for the *Niederschlema/Alberoda* uranium mine and for several other sites by Wolkersdorfer (2008). Most other publications usually deal with only single observations without providing details about the observed stratification.

In the light of the pollution arising from the flooded underground gold mines in South Africa’s Witwatersrand, the discussion about natural mine water stratification and how it can be used as a remediation measure is emanating again (Sheridan et al. 2015). A downhole measurement in the West Rand Consolidated’s Deep Shaft, conducted in 2000, showed that the mine pool at this time was stratified into 4 distinct layers with better quality water on the top (electrical conductivity ± 1 mS/cm) and bad water at a depth of 1078 m (± 7 mS/cm). This paper will therefore take a look at the features of stratification and tries to indicate some of the causes for stratification by investigating already existing literature and non-published results.

Methods

Existing literature and unpublished data of the first author were studied to identify cases of stratification in flooded underground mines. A lot of data is published on stratification in flooded pit lakes and natural lakes (Geller et al. 2013), but as the initial reasons that cause stratification in lakes are different from underground mines, these cases will not be discussed further. All the identified cases of mine water stratification in the literature were compared against each other. Based on these similarities, the *Straßberg*/Germany, the *Georgi Unterbau*/Austria, the Frances Colliery/England and the 1B Mine Pool/Canada were chosen as these are the most thoroughly investigated sites know. Currently, there is not enough data available to validate if all flooded underground mines eventually show stratification and how stable that stratification might be.

Measurements in the flooded shafts by the first author were conducted with various dippers, some only measuring the temperature, others the temperature and electrical conductivity (Spohr-Messtechnik GmbH, Germany; Solinst TLC, Canada; Heron Instruments, Canada; Ott Gmbh, Germany). In addition, continuously measuring downhole probes (Login Gommern, Germany) were used to monitor the physico-chemical parameters in flooded shafts. To identify chemical parameters of the mine water, a large number of chemical and physicochemical parameters were measured on mine water that was sampled depth dependent in various shafts.

Results and Discussion

Unquestionable, one of the most extensive investigations into the stratification of flooded mine shafts was conducted at the German *Hope* salt mine with the aim of investigating the flooding of a radioactive waste disposal site (G. S. F. – Gesellschaft für Strahlen- und Umweltforschung 1985; Herbert and Sander 1987). Shafts and workings were equipped with 16 stationary monitoring stations located at 4 different working levels and physicochemical measurements with mobile downhole probes were conducted in the *Hope* and *Adolfsglück* shafts. The investigations started in 1984 and continued during the whole flooding process until 1988. Detailed physicochemical measurements and calculations resulted in an extensive database which was mainly used for interpreting seismic events, the chemical evolution of the brine and the developing stratification in the two shafts. It became obvious that water with higher temperatures and electrical conductivities, i.e. mineralization, which consequently results in higher densities collects in the lower parts of the mine. This development became obvious already during the initial stage of the flooding, but became more prominent at later stages. A comprehensive, English summary of the results is given in Wolkersdorfer (2008, 330 ff).

Another long term study of stratification in flooded mine shafts was conducted by Wolkersdorfer (1996) at the 2000 m deep Niederschlema/Alberoda, Germany uranium mine; at that time the deepest metal mine in Europa. These studies comprised of 200 physicochemical and 477 chemical studies in seven, 380 to 761 m deep mine shafts and a large scale tracer test. Water sampling and mobile downhole probes (temperature, electrical conductivity, pH, redox, water velocity) as well as dippers (temperature) were used during the investigations and a comprehensive, partly unpublished dataset was produced (the results discussed here are based on a re-examination of the dataset published together with the inaugural version of the before mentioned thesis). Without going into details, it could be shown that the deeper portions of the mine always contain water with a lower quality and that the water quality in the interconnected sections of the mine usually showed similar physicochemical and chemical properties. A total of 19 downhole redox measurements were conducted in the shafts when the on-site situation allowed lowering the probe. To protect the redox probe, continuous measurements were only possible up to a water depth of 167 m. Without exception, all measurements showed a decrease of the redox potential, with the lowest redox-potentials in the deepest parts of the shafts. Identical results were obtained by Snyder (2012), who measured redox potentials in seven shafts in Butte, Montana/USA up to 300 m water depths. These low redox potentials at the Niederschlema/Alberoda site were also connected to lower Fe_{tot}- and U-concentrations in the mine water. As-concentrations showed a positive correlation and SO_4-concentrations are not affected by the redox potential of the mine water. Based on the tracer test's results nearly the whole mine is well interconnected and the mean effective mine water velocity ranges between 1 and 20 m/min with an overall average around 1 m/min.

A large number of mostly unpublished depth dependent physico-chemical and chemical measurements were conducted at the flooded *Straßberg*/Germany fluorspar mine. These data were compiled by DMT (Rüterkamp and Meßer 2000) and are partly published in various articles (Kindermann 1998; Kindermann and Klemm 1996; Klemm and Kindermann 1996) with an English compilation in Wolkersdorfer (2008, 318 ff). This mine has four day-shafts of which three were used for man and material haulage, and the three sections of the mine are joined by two adits on the 5th and 9th working level. Two of these shafts (*Überhauen* 539 and *Hauptschacht*) have been easily accessible for *in-situ* measurements and showed the development of a stratification between the start of flooding in 1992 and 1997 (Kindermann 1998). This stratification consisted of two layers with water of distinctive chemical characteristics: highly contaminated water in the deeper parts and less contaminated water in the shallower parts of the mine. Both layers showed a water quality improvement over time. It was therefore decided to stop pumping and treating the mine water from the *Hauptschacht* (main shaft) and construct three dewatering adits into the less contaminated upper layer. The idea was to discharge the less contaminated water into the receiving streams and treat the water only until the water quality improves even more as the less contaminated layer gets less contaminated. Yet, immediately when the three dewatering adits were completed in 1998, the stratification broke down, the discharging water quality substantially worsened and the total annual flow increased by 2 Mm^3. This was caused by the fact that the newly constructed adits allowed for open convection loops, resulting in a complete mixing of the mine water pool. Eventually, a full scale mine water treatment plant was constructed and treats the polluted mine water before it is discharged in to the receiving Uhlenbach stream.

One of the main differences between the three before mentioned mines and the *Georgi Unterbau*/Austria is the fact that the latter has only one main shaft, where the mine water discharges into the 320 m long dewatering adit (Wolkersdorfer 2008, 325 ff). This blind shaft, constructed in 1900, is 100 m deep and connects to the 20, 40, 70 and 100 m levels of the mine (Pirkl 1961; Schmidegg 1953). Between 2000 and 2002, several depth dependent measurements of the temperature and electrical conductivity as well as discrete chemical measurements of the mine water were conducted. In addition, two tracer tests took place. The physico-chemical and chemical measurements identified two distinct layers of mine water with only small differences in their chemical and physico-chemical properties. Though these differences resulted only in minor density differences of the mine water layers, the stratification remained consistent throughout the whole time of investigation. Yet, it was damaged instantly, when 200 kg of a NaCl tracer was injected into a small connecting blind shaft, but was naturally restored half a year later. A tracer test with a solid tracer showed no tracer from the lower layer of mine water at the point of discharge of the shaft, which also could be proven by a numerical model of the flooded mine (Unger 2002).

Nuttall et al. (2002) conducted investigations in the Frances Colliery/England. During a pump test in one of the flooded shafts, they encountered a substantial deterioration of the water quality and a scaling of the equipment within 4 hours (Croxford et al. 2004). Subsequent depth dependent measurements in the shaft identified a stratification with water of higher electrical conductivities in the lowermost parts of the shaft and water with better quality overlaying this highly contaminated mine water body. While SO_4-concentrations in the upper layer were in the range of several hundred mg/L, they reached 4000 mg/L in the lower layer. This increase is accompanied by a decrease in pH from around 7 to 5. Later electrical conductivity measurements in this shaft by Wyatt et al. (2014) showed that the stratification still persisted in 2012 with electrical conductivities around 4 mS/cm in the uppermost layer and 14 – 15 mS/cm in the lower one. It was also observed that the redox potential increased from 50 to 150 mV during the initial phase of the pump test but decreased to 0 mV once the deep water was pumped. During the course of the pump test the mine water's redox potential increased again to 100 – 150 mV (Elliot and Younger 2007) indicating a mixing with less reducing water.

A different case compared to the before mentioned mines is the flooded 1B Mine Pool on Cape Breton Island/Canada. No single shaft exists, but a number of inaccessible inclines and adits and many boreholes into the mine water pool (Shea 2009). In 14 boreholes, the water temperature and the electrical conductivity was measured with downhole probes between 2009 and 2010 (Secka 2010). Instead of discrete depth dependant samples, mine water samples were taken after pumping clear a selection of these wells. It became obvious that a layering of the mine water exists. Part of that layering might be a result of the hydrodynamics in small diameter wells and does not represent the overall layering in the whole mine. Yet, the mine water chemistry clearly indicates that there is a stratification in the mine pool with a lower water quality in the deeper parts and a better water quality in the shallower parts of the mine pool (Chimhanda 2010). Fe_{tot}-concentrations in these deeper layer can reach up to 300 mg/L while the upper layer has Fe_{tot}-concentrations of 30 mg/L and less. No correlation of the redox potential and the contamination load could be show, which might be due to the sampling procedure.

Conclusions

All the above mentioned cases of stratification are a result of natural processes occurring in a flooded underground mine. In none of these mines, the mine layout was modified such as to promote the build-up of layers with different water qualities. It can therefore concluded that many mines develop a more or less stable natural stratification. In all cases discussed above, the water quality in the deeper water body of the mines is worse than the water quality in the shallower parts of the mine, which is obvious, because the fresh water infiltrating into a flooded underground mine as groundwater or surface water is usually unpolluted and has a lower density than the mine water. It therefore "floats" on top of the higher contaminated mine water which, consequently, has a higher density. Yet, the *Georgi Unterbau* case shows that mines with only one shaft develop a less stable stratification as the stratification broke down when a NaCl tracer was injected into the shaft.

As has been shown in the *Straßberg* fluorspar or the Francis Colliery mines, the stratification immediately breaks down when the water is pumped from depth or when a convection loop is allowed to build up. In the case of the Western Pool of the flooded Witwatersrand gold mines, pumping from deeper depths, as suggested by Sheridan et al. (2015), would therefore continually cause a forced flow and mixing in the deepest sections of the mine pool where the water quality is always bad. This would result in low quality, possibly acidic mine water that has to be treated until perpetuity. Yet, if the mine water is allowed to rise as high as possible, a layer with a better water quality will very likely develop on top of the less quality water. Consequently, if the water pumped from this layer does not exceed the mine water recharge, which means that no forced flow between the higher and lesser contaminated mine water is caused, it is possible to use natural stratification to lower the treatment costs of polluted mine water. More tracer tests, *in-situ* measurements in shafts and analogue mine models are necessary, to understand the detailed reasons behind building up of natural mine water stratification and how this knowledge can be used in the future to force stratification in mines.

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The progress of the mine water prevention and control on basic principles in China

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Abstract

Water disasters occur during coal mine construction and production in China and account for many of the nation's mine disasters and casualties. However, China has made major strides in preventing these major water inrush disasters during the last decades. Based on the comprehensive summary of the theory and method, application technology, practical engineering and technical standard currently used in coal mines of China, this paper analyzed systematically the latest research progresses and achievements on the basic theory, hydrogeology (supplement) exploration, advanced detection and monitoring as well as early warning of the water disaster, prevention and control technologies in the field of the mine water prevention and control as well as utilization.

Key words: prevention and control of mine water; utilization of mine water; research progress; China

Introduction

China ranks the third around the world in geological reserves of coal resources, but is the first coal-producing country from the beginning of 21st century. China' land is composed of multiple tectonic plates reworked by sequential geological tectonic movements. As a result, the geological structures are very complex. China is one of the countries in which the most serious mine water disasters occur. According to statistics by Chinese State Administration of Production Safety Supervision and Management, the water inrush disasters are second only to the gas explosion disasters in coal mines in the serious and extraordinarily serious accident categories. Mine water inrush disasters not only cause heavy casualties, but also are the most serious of mine accidents in terms of economic losses, accident emergency rescue, and mine restoration effort. In addition, the water disasters occur widely. All the mine enterprises, especially underground mines or underground excavation engineering works, generally face with these problems. So the social impact of water disasters is serious, and the attention degree is high in China and abroad.

With the exhaustion of shallow and upper group coal resources, water disasters in mining deep and lower group coal resources are increasingly serious because of progressively complex mine water-filling hydrogeological conditions, additional control factors over water disasters, and complicated water inrush mechanism and type. Many mines not only face with roof water inrush threat from gob water because of the water pooling in the shallow closed mines, but also face with the floor water inrush threat from high confined groundwater in carbonate rock. Meanwhile, gas explosion, gas outburst and water inrush coexist in the coal seam, i.e., the working face and development face are in the environment of "roof threat, floor inrush, and middle burst".

Mine water inrush disaster control continues to keep decline and continuous improvement in the case of strong growth production and increasing mining intensity recently. The national coal production increased from nearly 1 billion t in 2000 to 3.7 billion t in 2013. The output turned over 3.7 times in 13 years. At the same time, the accident total number and total death toll induced by water inrush disasters in China have decreased to 21 and 89, respectively in 2013 from 104 and 351, respectively in 2000, falling by almost 80% and 75%, respectively (Fig.1).

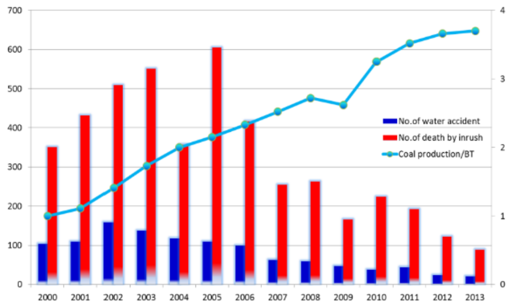

Figure 1 *Relationship of national coal production and water inrush disasters*

According to the surveys and statistics by State Administration of Coal Mine Safety in 2012, the national mine water discharge was up to 7.17 billion m^3/a in recent years; there were 61 mines in which the normal water inflow was more than 1,000 m^3/h; and mine water resources utilization rate increased year after year. These data showed that China had made great progress and research results in recent years in the field of water inrush prevention and control and resource utilization[6-8]. But water disaster prevention and control is still a daunting task and face with many challenges because of various hydrogeological condition type and complex structure and changeable hidden water inrush factors and various mechanism, especially with the large-scale development of deep level resources. Mine water inrush disasters control and resource utilization will be still one of the important research topics in safety production and scientific mining in China.

1. The new basic principle of water prevention and control

The research results have improved the basic principle of water prevention and control, put forward the new basic principle that is summarized with 16 Chinese words and its corresponding comprehensive measures, i.e., prevention, plugging, dewatering, drainage, and interception. The previous basic principle used in China for mine water inrush prevention and control was summarized with “8 Chinese words”, i.e., “when in doubt, exploration must be done in advance; excavation occurs only after the exploration.” The “8-words” principle has played a positive role in recent years, as the state emphasized the great importance to the safety production and implemented a series of policies and punishment regulations. The mine enterprises improved safety production consciousness and management, and miners also paid attention to the safety.

If suspicious symptoms of water disaster had been found at the scene, engineering technicians and professional workers will immediately investigate the situations and dewater in advance if needed. The doubtful position or hidden danger of water inrushes must be identified before mining. The questions are how to find the doubtful position? How to judge water disasters risk in advance? These are much more in demand to resolve the important issue for mine enterprise and field engineering technician at present. To answer these questions, *Coal Mine Water Prevention and Control Regulation* article 3 presents the new “16-words” principle, i.e., “first forecasting; when in doubt, exploration must be done; excavation occurs only after exploration; control should be in place before mining.” First of all, we should find doubtful position of disasters through scientific forecasting methods, followed with detection and discharge of water in advance. We then excavate after detection and water discharge. We finally mine coals after any necessary control measures are in place. The “16-words” basic principle forms a complete technical route. In correspondence with the “16-words” principle, *Coal Mine Water Prevention and Control Regulation* article 3 puts forward five comprehensive prevention measures in prevention, plugging, dewatering, drainage, and interception.

2. The new mine hydrogeology classification

The achievements have supplemented and improved the basic principle of mine hydrogeology classification and the main influence factors, put forward the mine hydrogeology classification based on scientific methods and analysis of the new water disasters features in China in recent years. The purpose of mine hydrogeology classification is to analyze the mine hydrogeological condition, direct hydrogeological supplement exploration and water disasters prevention and control. Due to high proportion of coal resources under water disasters threat and various water hazards types caused by complex mine hydrogeological condition, the hydrogeology classification plays an important role in safety production. Considering the wide distribution of gob water with fuzzy scope, location and shape, and the continuous water inrush disasters induced by the gob water in recent years, at the same time considering the factors (whether water inrush occurred or not in the process of construction, production and water inflow) are associated with the complex degree of mine water filling hydrogeological condition, the mine hydrogeology classification incorporated two new factors of gob water distribution and mine water inflow based on the original four factors.

3. The new safety requirements and technical standards of mining under water and surroundings

With the increase in mining intensity and exhaustion of shallow level resources in China, development of the deep level resources is inevitable. In addition, the coal resources that are not be commonly developed under or around of the sea, lakes, rivers, reservoirs, gob water area and strong rich water aquifer and other large water body in the past are increasingly exploited. First of all, all kinds of water sources which threaten safety production should be dewatered in advance. Mining can be done only after the water is drained and hidden dangers are eliminated. If dewatering is not feasible and the coal seams to be mined are inclined or gently inclined, the regulation *Coal Pillars Setting and Coal Mining Regulations of Building, Water, Railway and Main Shaft* must be followed. We must understand the water filling hydrogeological conditions, compile special mining design, and organize relevant technical discussion in order to determine the safety and reliability of water prevention coal (rock) column and make safety precautions. Mining can occur only after approval by the chief manager of the coal mining enterprise. In addition, dynamic monitoring should be in place. Producing should stop and withdraw of miners must be in order immediately if abnormal situations are discovered. Due to lack of theories and engineering technology problems induced by mining such as caving mechanism, the caving development regularity and height, caving control, mining of steep coal seams is still a task to be solved effectively and is strictly prohibited in China.

4. The platform construction of mine water filling 3D visualization analysis of hydrogeological conditions

Traditional water filling hydrogeology analysis method was based on point, line, plane, section, etc. By forecasting, we understood and cognized the 2D space of mine water filling hydrogeological condition. These methods could not reflect and depict the complex 3D water filling condition and phenomenon, lacking dynamic space-time processing and analysis ability, and having big limitations. The 3D hydrogeology visualization modeling and simulation analysis method solve these problems to some extent, can provide a uniform 3D display channel, and support comprehensive and integrated display as well as management of data such as the hydrogeological exploration, test and underground exploration and mining engineering. The method can also analyze arbitrarily stratigraphic profile, query a variety of hydrogeological parameters, and realize stress-strain analysis, groundwater flow simulation, water inrush risk evaluation, water inflow forecast and optimization of water prevention and control design, etc. The 3D water filling hydrogeology visualization analysis platform will become an effective tool for the ground and underground hydrogeological exploration and test data processing, physical concept model analysis of water filling condition, water flow simulation evaluation, water disaster prediction, water prevention and control plan formulation, etc.

5. Mine water disaster forecast theory and the different disaster forecast evaluation methods

Hydrogeology exploration provides a very important geological information for mine structure, the relations of main coal seam and sedimentary structure, the water filling source, water channel and gob. But the local discrete information is limited, and using the information directly to analyze water disaster is very preliminary, and unable to give full consideration to the potential value contained in the hydrogeological exploration results. If we use the advanced scientific evaluation method and model to analyze, simulate and process the original information, the results can be evaluated and predicted in zoning characteristics and water hazards risk levels from the roof, floor, gob and geologic structure in the process of mine production. The prediction results can be effectively used to make prevention measures for different types of mine water disaster. We presented the comprehensive evaluation method of the vulnerability index method which considers more factors than those based on water inrush coefficient method for floor water inrush. For roof water disaster, we put forward three maps - double prediction method which can solve the key technical problems of roof water filling source, channel, and the intensity at the same time.

6. Rapid recognition technique of water inrush

Any water inrush points of underground mining engineering happened in most cases by accepting different types of water supply such as atmospheric precipitation, surface water, groundwater, or gob water and discharging into underground mines. Due to different types of water source in the process of formation, runoff and discharge influenced and interfered by different geological environment and human factors, the hydrogeochemical characteristics, water temperature and water level (pressure) of water source are all different. These large number of sample points collected at the scene in different aspects and the various parameter such as water chemistry, water temperature and water pressure (level) can provide an extremely important water source information and form the foundation database. Mathematical models can then be established for rapid recognition of underground mine water inrush supply source. Inputs of water pressure (level), the measured water temperature and water chemistry analysis results in underground water inrush point into the mathematical models will help quickly and accurately recognize the water supply sources of the water inrush point. The main used equipment with better application effect at present in China include intrinsically safe YSYF6 mine water inrush source rapid recognition instrument researched and developed jointly by Wuhan Long Sheng An Ke Technology Co., Ltd. and China University of Mine & Technology (Beijing), and HA-W600 mine filling water source rapid recognition instrument researched and developed jointly by Beijing Hua An Ao Te Science and Technology Co., Ltd.

7. Conclusion

This paper systematically analyzes the latest research progress and achievements in China including the current basic theory of mine water prevention and control, the hydrogeology exploration and water disasters forecast, the advanced detection and the monitoring and early warning, main prevention and control technology of mine water disasters.

Acknowledgements

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Stable Isotope Techniques as a Tool in Hydrogeological Conceptualisation of Ayazmant Mine Site (NW Turkey)

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Abstract

Ayazmant mine site is situated in the near vicinity of a dam reservoir being utilized for drinking and irrigation purposes. The mine is planned to be extracted by combination of two methods: open pit mining followed by underground mining. Most part of the operations will take place below the groundwater level. Preliminary hydrogeological assessment has revealed that the groundwater system is in connection with the dam reservoir. Prediction of groundwater inflow to both the open pit and the underground galleries and calculation the ratio of reservoir water in the inflow were the major questions. Numerical modeling was the methodology selected to be followed to achieve these objectives. Reliability of the numerical model is based on the accuracy of the hydrogeological model of the site. Hydrogeological conceptualization requires detailed geological hydrological and hydrogeological information. These studies give sufficient information on the occurrence, potential, availability and flow of groundwater systems. However, knowledge of interactions with different water bodies requires information on the flow path and velocity of a particle in the system. Isotopic constituents of water bodies provides this information. Particularly, stable isotopes are very useful in tracing the origin of the waters, mixing processes and interactions. This technique was used in conceptualization of the hydrogeological system in the mine site. The hydrogeological conceptual model suggested that the groundwater system is recharged mainly from highlands but also in connection with the dam reservoir. The water level fluctuation in the reservoir affects the interaction between the groundwater system in the mine site and the reservoir.

Key words: Ayazmant mine, conceptual model, hydrochemistry, stable isotope

Introduction

Occurrence of groundwater in mine sites is of major concern due to its two opposing impacts on mining activities. Particularly in arid and semi-arid areas, groundwater in most cases is the major source that can be used to meet the need for water at mine sites for different purposes such as process water and site water supply. On the other hand, mining commonly requires large excavations below the water table where groundwater inflow to excavations may cause serious problems of dewatering and depressurization (Kumar Deb 2014). Regardless of type of the problem, whether related to shortage or excess of groundwater, construction of a representative conceptual hydrogeological model has an essential role in achieving practical and effective solutions (ASTM 2000). However, conceptualization and characterization of groundwater systems, particularly in geologically complicated areas is not straightforward and various techniques need to be applied in combination with conventional methods. The combined use of hydrogeochemical and isotopic techniques is proved to provide an effective tool in this regard (Yurtsever 1995, Geyh 2000). The value of this tool stems from the fact that it contributes to the understanding of how the groundwater occurs and circulates by tracing the water starting from the recharge area until it reaches a point of interest in the flow domain (Clark and Fritz 1997, Aggrawal et al 2005). This knowledge is of significant importance in construction of a representative conceptual model of the site. This technique was applied in a mine site located in northwest of Turkey (fig.1). The area where the mine is located is environmentally sensitive because the mine site is bordered by a dam reservoir utilized also for drinking purposes. Mining operations, therefore should be planned to minimize if not remove its impacts on quantity as wells quality of water resources that exist in the area of influence of the mine.

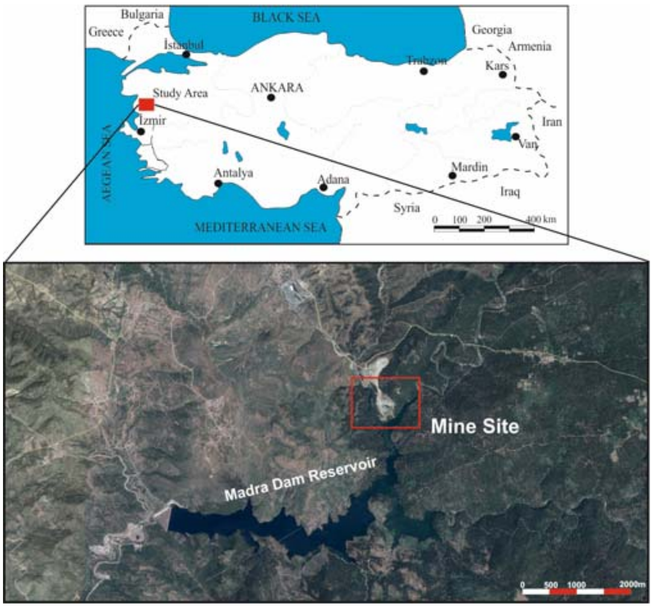


Figure 1 *Location Map of the Study Area.*

Hydrogeological Characteristic of Lithological Units

The Ayazmant iron-copper mine is of contact-metasomatic/scarn type mineralization within plutonic rock mass [Jeopark 2011]. Geologically, the site is located on the edge of the Kozak Pluton which has been intruded during Late Oligocene-Early Miocene in one of the ten horst-graben systems that have been developed as a consequence of intensive tensional tectonics affected the region during Neogene (Oyman 2010). The pluton has been intruded through the Kınık metamorphic basement. The basement is composed of metabasitic complex including limestone and sandstone blocks of Permian age. The mine site is dominated by hornfels, granatfels, granodiorite prophyry, arenaceous granodiorite, split and endoscarn. The ore constitutes hematite, magmatite, chalcopyrite and limonite (fig.2)

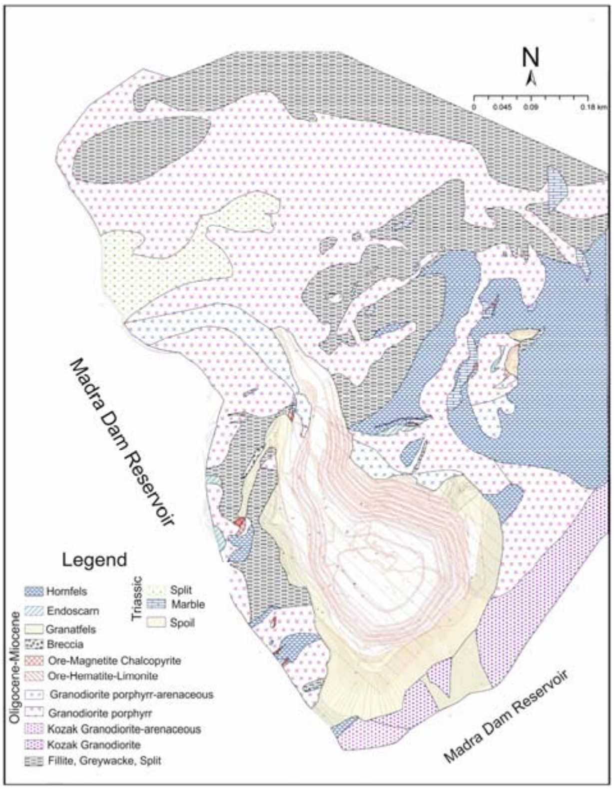
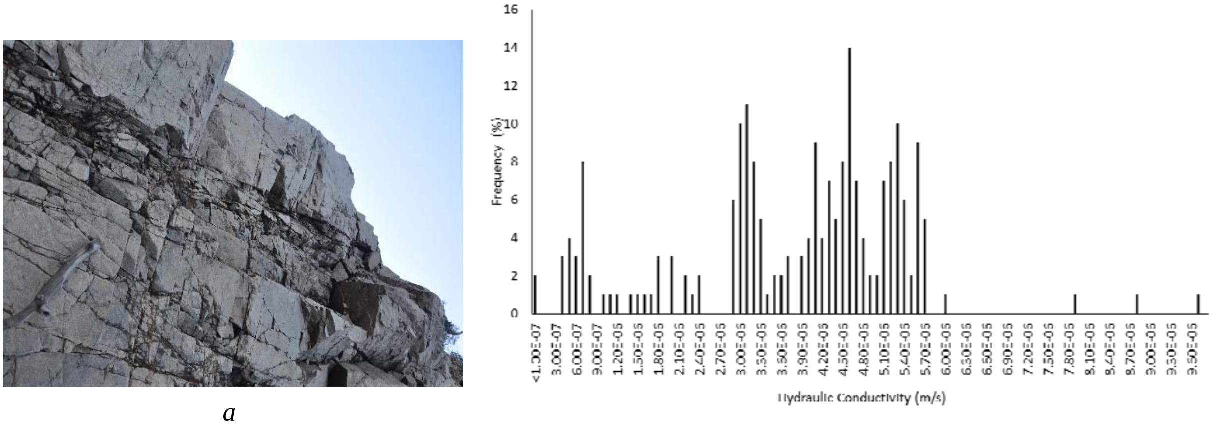


Figure 2 *Geological Map of the Mine Site (after Jeopark, 201)*

The intrusive magmatic rocks in the area are intensively fractured (fig.3a) and in some places are weathered, particularly along major faults intersecting the mine site. The rocks have gained secondary porosity and permeability owing to the intensive fracturing, forming a fractured hard rock aquifer. Hydrogeological characterization of the hard rock aquifer was achieved by a) fracture analysis and b) insitu well tests. Four fracture systems were identified on outcrops in the site. Based on fracture spacing and aperture measurements the total porosity of the hard rock aquifer was calculated as 0.018. The effective porosity was estimated as 0.010 on the basis of annual change of groundwater level in piezometers installed around the pit. The high effective porosity is due to fact that the intersecting fractures create a high degree of connectivity in the domain. The recharge in this calculation was obtained from water budget calculations as explained below. More than 140 packer tests were performed in 6 boreholes to characterize the rock for permeability and hydraulic conductivity. Although changed spatially, the hydraulic conductivity found to concentrate between $3x10^{-6}$ m/s ile $5.9x10^{-6}$ m/s (fig. 3b), with a geometric average of $3.2x10^{-6}$ m/s. This value suggests that the hard rock aquifer may yield significant groundwater flow into the pit and galleries.



a

b

Figure 3 *a) Frcature Systems b) Distribution of Hydraulic Conductivity in the Mine Site*

Hydro-Meteorology

Northern Aegean (Mediteranean) climatic conditions prevail in the Ayazmant mine site. Hydrographically, the site is located on the ridge separating two major tributaries of the Madra dam reservoir. The drainage areas of the tributaries at the mine site are 19.4 km^2 and 90 km^2, respectively. The shape of the basin and the drainage network pattern is controlled by the position of the Kozak Pluton and the permeability and erodibility of lithological units. The basin is rectangular in shape with 15 km length and 7.5 km width.

The long-term average annual precipitation onto the area is calculated as 635 mm. Precpitation is mainly rainfall and it occurs mostly in winter months from November to February. The rest of the year is dry (fig. 4). More than half of the rainfall was found to return to the atmosphere by evapo-transpiration. The water budget calculations showed that more than half (51 %) of the rainfall was found to return to the atmosphere by evapo-transpiration, 41 % of the rainfall makes the surface runoff which ultimately flows to the Madra reservoir and the rest (0.08 %) infiltrates to form recharge the hard rock aquifer.

Occurrence and Flow of Groundwater

Relatively high fracture permeability of the hard rock mass allows significant occurrence and flow of groundwater. Groundwater level measurements were performed in 9 piezometers installed at the site along two water years to cover dry and wet periods. The coefficient of variation of groundwater levels in the piezometers did not exceed 5 %, suggesting no significant seasonal effect. Based on this fact, a groundwater contour map was prepared to demonstrate the areal distribution of the hydraulic head and the direction of groundwater flow in the site. The map is given in Figure 5.

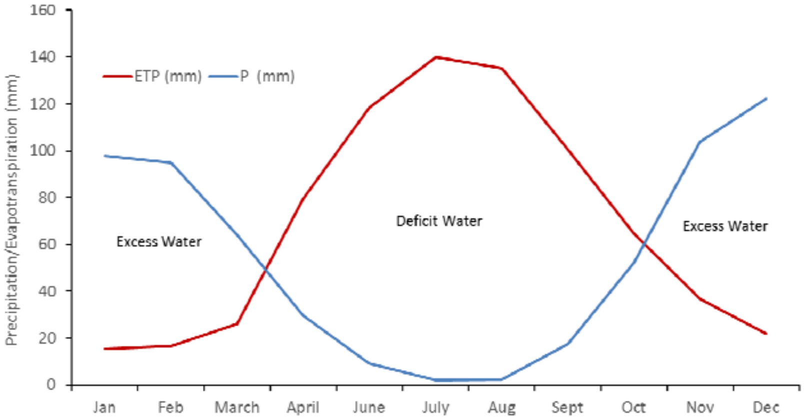


Figure 4 *Monthly Variation of Precipitation and Potential Evapotranspiration in the Study Area.*

As seen in figure 5, there is a prominent groundwater divide passing through the open pit, and the general groundwater flow direction occurs from north to south, to the reservoir. The groundwater contours bend and make a "v" in the southwest, indicating a higher permeability zone along anortheast-southwest line. This line was found to correspond exactly to one of the major fault lines.

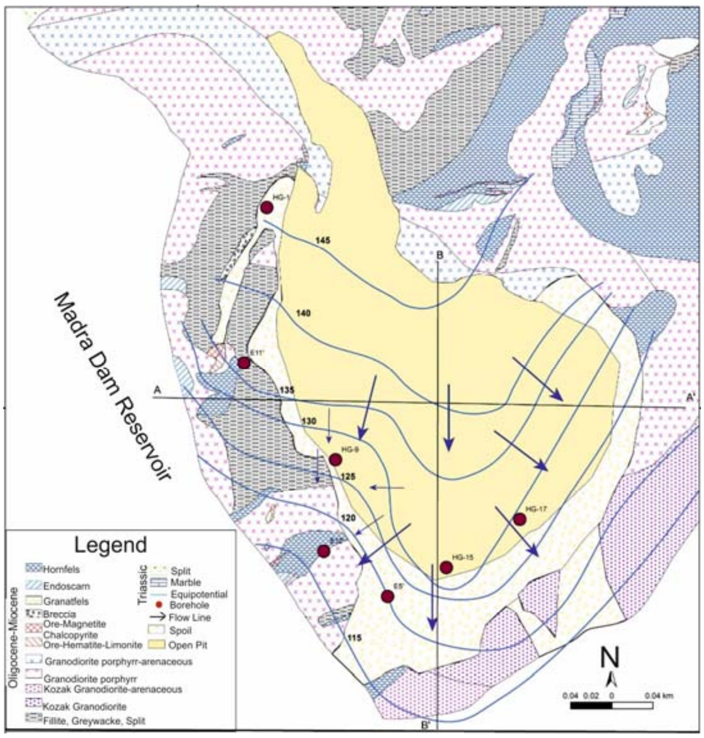


Figure 5 *Distribution of Hydraulic Head in the Site.*

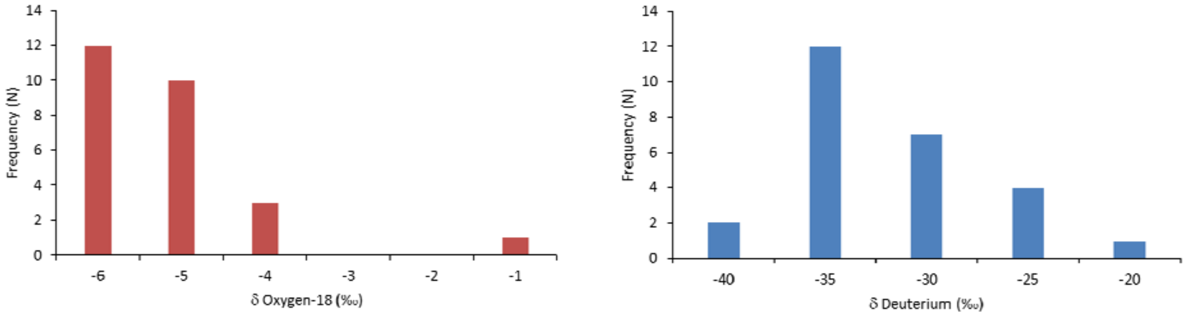
In addition to groundwater level measurements and the hydraulic conductivity variation with depth, hydrochemical measurements and analyses have indicated that the hard rocks form a single and unconfined aquifer, and the aquifer is in connection with the dam reservoir at the periphery of the open pit. This finding is important to consider for safe mining operations.

Need for a Representative Hydrogeological Conceptual Model

The ore deposit is to be mined at two major phases; first as open pit mining to a certain elevation of pit bottom and by underground galleries excavated from the ultimate pit bottom. The plutonic (dominantly granodiorite and hornfels) rocks are fractured and jointed such that they have gained moderately high secondary permeability. The mine site is surrounded by surface water bodies from the east, west and the south. Two streams in the east and west of the site join the dam lake in the south. The elevation of the ultimate bottom of the open pit will be about 90 meters below the maximum level of the dam lake. The mine site is situated on a secondary groundwater divide where the groundwater level is about 30 m higher than the lake, which makes the groundwater flow to the streams and the lake in natural (pre-mining) conditions. The galleries will also be excavated below the groundwater level and the dam lake level. Thus, the major concern was to estimate the groundwater flow into the open pit and the ingress to the galleries at different stages of mining to prevent any probable adverse impact. Analytical and/or numerical methods are applied to predict the groundwater inflow to excavations. For both methods, construction of a representative hydrogeological model is essential. A hydrogeological appraisal was performed based on hydrostratigraphic definition of litohological units, core drilling and in-situ tests, and hydraulic head observations. A preliminary hydrogeological conceptual model was constructed to explain the occurrence of groundwater at the site. However, this study could not produced all information required in conceptualization of the groundwater system in terms of recharge-discharge relations and surface water-groundwater interactions; an essential knowledge for definition of the boundary conditions needed in analytical and/or numerical analyses. Hydrogeochemical and stable isotope techniques were used to obtain this information.

Stable Isotope Hydrology

Various water points representing surface waters and groundwater were sampled for hydrogeochemical and stable isotope analyses. Some basic physio-chemical properties such as temperature, specific electrical conductivity, total dissolved solids, dissolved oxygen, pH and oxidation-reduction potential of waters were also measured on site by a multi-probe. Samples were analysed at registered laboratories for some trace elements as well as major ions and for stable isotopes, namely oxygen-18 (δ^{18}O) and deuterium (δD). In addition to samples collected from the site and its near vicinity, seasonal springs located at different altitudes were also sampled to quantify the altitude effect on stable isotopes. δ^{18}O in water samples was found to vary between -1.91 and -6.95 permil, concentrating around -5 and -6 permil (fig 6a). Similarly, δD ranges between -22.06 and -40.91 permil with a concentration around -35 permil (fig. 6b). The relationship between oxygen-18 and deuterium forms a regression line whose slope is 8 with an interception of y-axis (deuterium) known as the deuterium excess (DE) (Craig 1961). The DE indicates the evaporation kinetics in the source area of the precipitation, but also changes when the water is subjected to evaporation. The deuterium excess in the water samples collected at the site varies between -6.81 and 16.98 with a representative value around 15.7 (fig.7). The negative DE of the sample from the sump in the pit, indicates excessive evaporation.



a b

Figure 6 *Distribution of a) Oxygen-18 and b) Deuterium in Water Samples.*

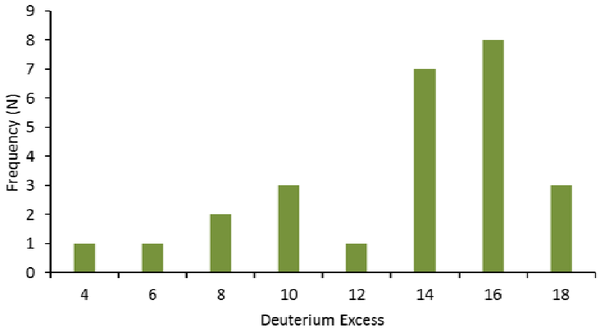


Figure 7 *Distribution of a) Oxygen-18 and b) Deuterium in Water Samples.*

The regression equation representing the global precipitation is given as $\delta D=8O^{18}+10$. The equation for the site, known as local meteoric line is found as $\delta D=8O^{18}+16$. The surface waters and the water collected from the sumps at bottom of the pit, plot on a evaporation line (fig.8).

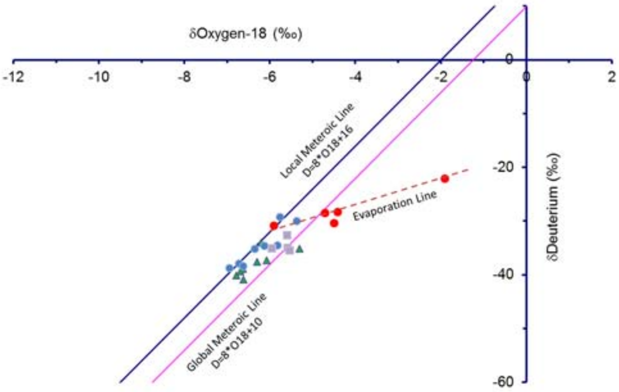


Figure 8 *Meteoric Lines Obtained from Isotopic composition of Water Samples.*

A plot of $\delta^{18}O$ vs altitude suggested that the precipitation is depleted with respect to this isotope at a rate of 0.33‰ per 100 m of change in altitude (fig.9). Using this information, the recharge area of the groundwater at the mine site was found to be located at higher elevations (450-480 m amsl) and at a distance of about 8 km from the mine site. The direct recharge from precipitation over the mine site was found insignificant compared to the regional recharge. Based on this information the hydrogeological model of the mine site was completed with a clear definition of the site-specific water balance and boundary conditions.

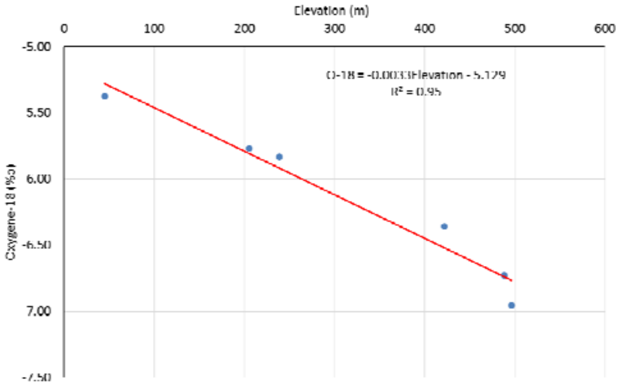


Figure 9 *Change of Oxygen-18 of Precipitation With Elevation.*

Hydrogeological Conceptual Model

Based on the information obtained from hydrological, hydrogeological and evaluation of isotope data, a hydrogeological conceptual model was constructed for the mine site. According to the model, an unconfined, fractured hard rock aquifer exists in the mine site. The aquifer is mainly recharged from the highlands and the recharge from direct precipitation is insignificant. The annual recharge from highlands is about 5.5 x 10^6 m^3. This amount is less than 10 % of the total precipitation. More than 40 % of the precipitation is direct runoff at the surface and contributes to the dam reservoir. The dam reservoir forms the southern, southeastern and southwestern boundaries of the flow domain at the mine site. A block diagram illustrating the hydrogeological conceptual model is given in Figure 10.

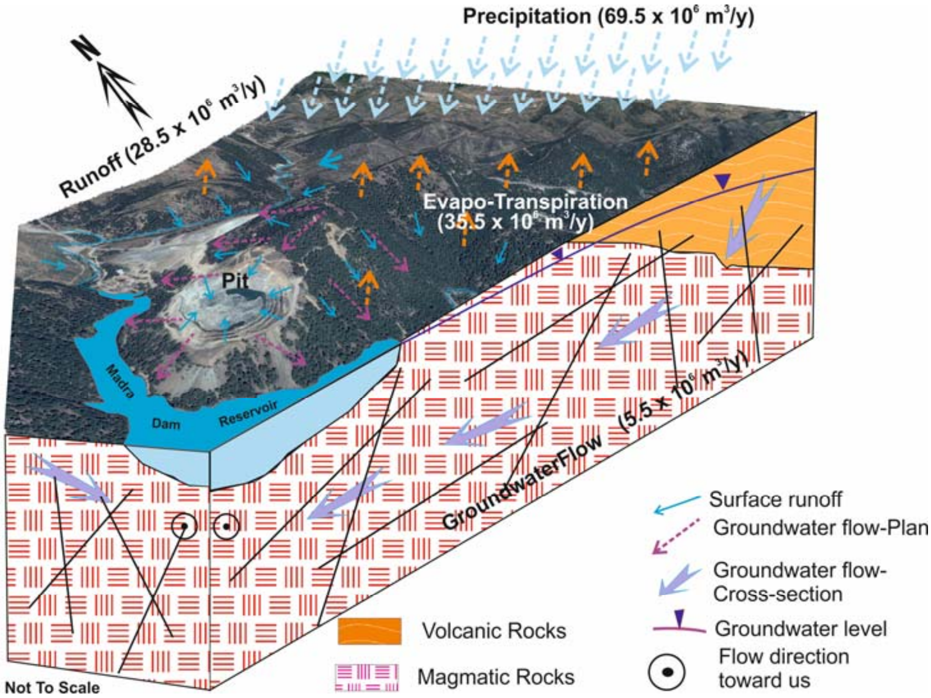


Figure 10 *Block Diagram Illustrating the Hydrogeological Coceptual Model at the Mine Site.*

Conclusions

Mining commonly requires large excavations below the water table where groundwater inflow to excavations may cause serious problems of dewatering and depressurization. Regardless of type of the problem, whether related to shortage or excess of groundwater, construction of a representative conceptual hydrogeological model has an essential role in achieving practical and effective solutions. However, conceptualization and characterization of groundwater systems, particularly in geologically complicated areas is not straightforward and various techniques need to be applied in combination with conventional methods. The use of isotopic techniques is proved to provide an effective tool in this regard. The value of this tool stems from the fact that it contributes to the understanding of how the groundwater occurs and circulates by tracing the water starting from the recharge area until it reaches a point of interest in the flow domain. This knowledge is of significant importance in construction of a representative conceptual model of the site.

Having been bordered by a dam reservoir, the Ayazmant mine site was studied in detail to construct a hydrogeological conceptual model that is required for further numerical analyses. The magmatic rocks were found to form a single, unconfined aquifer that may yield significant groundwater inflow to the mine site. Stable isotope analyses of water samples collected from the mine site and the surrounding area revealed that the recharge of the aquifer occurs at highlands at a distance of about 8 km from the mine site. In some of the sampled piezometers, the mixing with reservoir water was detected, suggesting that the water ingress should be expected from the bordering dam reservoir.

Acknowledgements

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Investigations in a closed mining area in China – challenges of limited datasets and understanding of hydraulic behaviour

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Abstract

A coal mine named Pangzhuang in Xuzhou, China was recently closed and the groundwater hydrogeochemical evolution process will be studied. The groundwater system has a very complicated structure, that so much work has to be done (parameter estimation, permeability measurements), before chemical analysis for the transport modelling. There are four main aquifers, named Q, 7S, C, O, in the area. Because of the partly lack of data the numerical model has to be simplified.

To solve this problem, onsite sampling work and laboratory tests were conducted. Core samples from a nearby coal mine were transported to Germany for laboratory tests. Multi-Chamber Testing Method (Mohammed 2015) was used to measure both permeability and porosity of the cores.

From the results of the above work, comparisons among different datasets are addressed including investigations reports from other coal mines in this large mining region. It can be concluded that there are huge differences between the permeability values from lab tests and the literature values. Some may differ to several orders of magnitudes. The lab tests results show a significant feature which indicate some aquifer cores are not homogeneous, but heterogeneous media. While the values from literatures are obtained by pumping tests and field drillings, the differences indicated that, groundwater in even limestone aquifers in this area is somewhere driven by fissure flow. The values of porosity also prove this conclusion in some of the samples.

Research work in this paper may indicate that groundwater flow in those target aquifers are multiply controlled by different mechanics not only by porous and karst structures but also by fissures. It is helpful for the further investigation work in this area and more accurate scenarios for further-on transport modelling.

Key words: Data shortage, hydraulic conductivity, Multi-Chamber Testing Method, fissure driven flow

Introduction

In the recent few decades, coal mines in China are having closure problems (Liu 2011). Pangzhuang coal mine which locates in Xuzhou, Jiangsu, was one of the closed mine in this large coal producing area. The whole mine was closed in 2013 with some shafts (Dongcheng Shaft) shut down in 2010. However, there are four active mines around and the closure may have impacts on the regional groundwater system. Therefore, a subject about mine closure groundwater evolution is settled. The groundwater system has a very complicated structure with four main aquifer groups named Q, 7S, C(L_4 and L_{12}), O(O_2) included. Much of basic work such as parameter estimations should be finished before transport modelling. Unluckily, the subject is suffering from a partly shortage of data, for example, important hydraulic parameters-permeability is only a range of values according to local investigation reports. To solve the data shortage problem, this paper employed some methods and tests. And significant results and new clues are found to improve further modeling set up.

Laboratory test method

The saturated hydraulic conductivity of water in soil and sediments can be measured both by onsite and laboratory tests. Onsite tests may include pumping test, slug tests, DPIL, DPST and so on. For laboratory tests, this paper used a new method named Multi Chamber Testing developed by Drilling and fluid mining Institute, Technische Universität Bergakademie Freiberg (Mohammed 2015).The method is designed to determine the permeability of tight rock samples and the interpretation of data using this method allows the permeability, effective porosity and Klinkenberg effect (Klinkenberg 1941) to be quantified by means of a single measurement run. In an operating transient two chamber method test rig porosities and permeabilities of up 10-24 m^2 can be determined on cylindrical samples.

The test rig is shown schematically in Figure 1. It consists of two stainless steel pressure chambers for the test gas (Vinlet and VOutlet) and one core holder for the test samples. The maximum test pressure may afford maximum 200 bars. The volume of the pressure chambers is about 165 ml each including the line volume. The pressure sensors at the measuring chambers have a measuring range of 0-250 bars, the maximum error of the display is smaller than 0.1 %. In addition, it is desirable to perform the tightness test on fresh core samples when possible (Mohammed 2015).

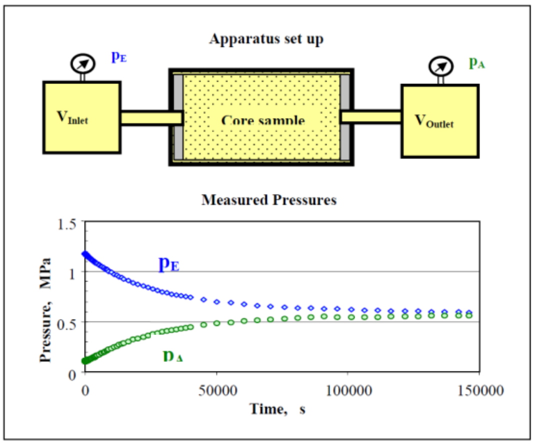


***Figure 1** Set up of Multi-Chamber Testing Method and the resulted chart (Mohammed 2015).*

Core samples preparation

As described, the data shortage is restricting the topic for gathering useful parameters. In the target closed coal mine, it is however now very difficult to operate new drilling work or boreholes to get cores since it has been abandoned. Thus, a nearby coal mine named Sanhejian was chosen as a substitute to get core samples. It is feasible because the two coal mines are both in the same regional geological unit with very similar geological structures and layers. Figure 2 shows the location of the coal mine which is only 70km away.

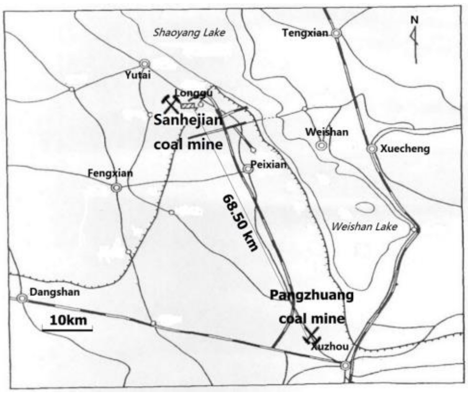


***Figure 2** Location of the substitute coal mine site for cores sampling*

In Aug, 2014, 5 core samples were collected from this coal mine with different labels representing different aquifer layers-7S, L_4, L_{12} and O_2 as well as an clay layer-7C. 7S is a sandstone aquifer while 7C is claystone. They are both the direct roof strata of coal seam 7. L_4 and L_{12} are key floor limestone aquifers of the mined layer. O_2 is supposed to be the largest and thickest limestone aquifer in the whole large region. Table 1 shows the detailed information about these layers.

***Table 1** Profiles of the core samples from Sanhejian coal mine (Regional close to Pangzhuang)*

Label number	Core rock property	Depth (m)	Formation Name	Stratum thickness(m)	Description	K(m/s) (Literature)
7C	Clay and mudstone	-300--400	P_1s_1 (Permian)	-	Aquitard, Low permeability and the layer is the direct roof rocks for coal seam 7	-
7S	Sandstone	-300--400	P_1s_1 (Permian)	Ave:35.64 Min:0.79	Low permeability and the layer is the direct roof rocks for coal seam 7	3.472e-8~7.963e-6
L_4	Limestone	-370--470	C_3t (Carboni-ferous)	5.65-15.88 Ave:10.7	The thickest and most karst fracture developed limestone aquifer in Taiyuan Formation, floor aquifer of coal seam 7 and 9	3.172e-5~2.13e-4 ave:1.445e-4
L_{12}	Limestone	-450--600	C_3t (Carboni-ferous)	2.69-9.98 Ave:6.07	Karst fracure developed, thin but is the direct roof and floor aquifer for coal seam 20 and 21	4.514e-7~9.166e-5 ave:4.605e-5
O_2	Limestone	-500--650	O_2 (Ordo-vician)	450-530 ave:484	Thickest, strongest aquifer in the region. Karst fracure very developed	5.243e-12~0.0010677

*The core samples are listed according to the order of the depth increase (from shallow to deep).

*Label name is defined due to the naming regulation of Chinese coal mining rock layers.

*Depths showed above are illustrated from the regional cross section diagram which is only a range, not so accurate as well as the thickness. Other parameters are also from regional geological investigation reports.

Results and discussions

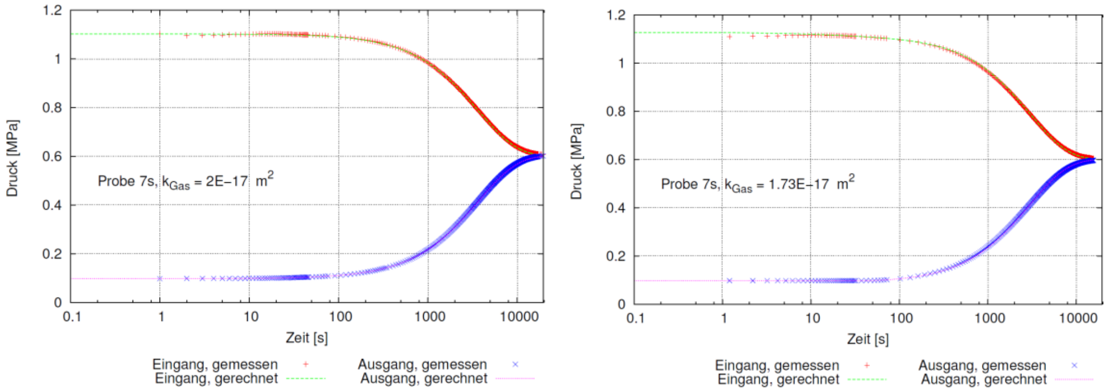


***Figure 3** Test results of core sample 7S and 7C*

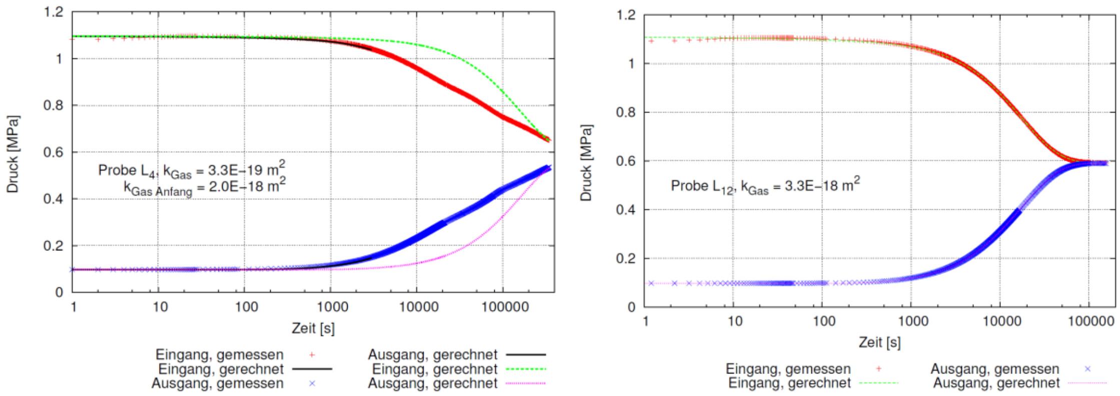


Figure 4 *Test results of core sample L_4 and L_{12}*

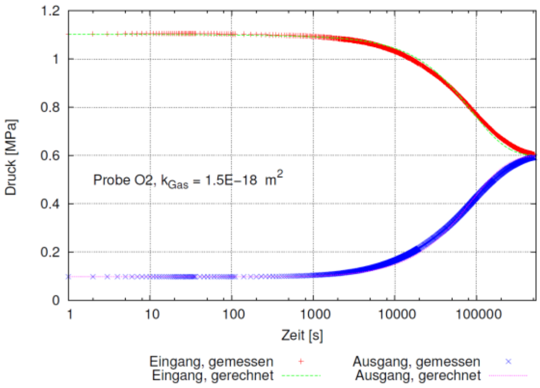
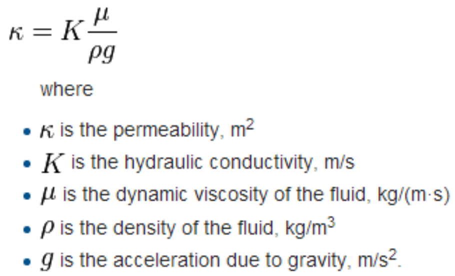


Figure 5 *Test results of core sample O_2*

Figure 3-5 show the tests results of the permeability values. Then, the equation below (Frieder, et al. 1985) was used to transfer the $k_{gas}(\kappa)$ value to K. After calculation, the results are compared with other local coal mines literatures and some geological investigation reports which are shown in Table 2.



$$\kappa = K\frac{\mu}{\rho g}$$

where

- κ is the permeability, m^2
- K is the hydraulic conductivity, m/s
- μ is the dynamic viscosity of the fluid, kg/(m·s)
- ρ is the density of the fluid, kg/m^3
- g is the acceleration due to gravity, m/s^2.

Table 2 *Permeability values Comparisons between lab tests and literatures**

Core label	Lab Measured results(m/s)	Literatures Pangzhuang(m/s)	Literatures Zhangshuanglou(m/s)	Literatures Wanbei(m/s)
7S	1.73E-10	3.47E-8~7.96E-6	1.62E-8	7.64E-8~1.68E-5
7C	2E-10	-		
L4	3.3E-12	3.17E-5~2.13E-4 ave:1.45e-4	6.92E-5~1.51E-4	1.88E-4
L12	3.3E-11	4.51E-7~9.17E-5 ave:4.61E-5	8.66E-6~1.33E-4	5.47E-5
O2	1,5E-11	5.24E-12~1.07E-3	3.72E-6~5.6E-5	2.73E-5~6.97E-4

*Literature values collected from several different related reports listed in references

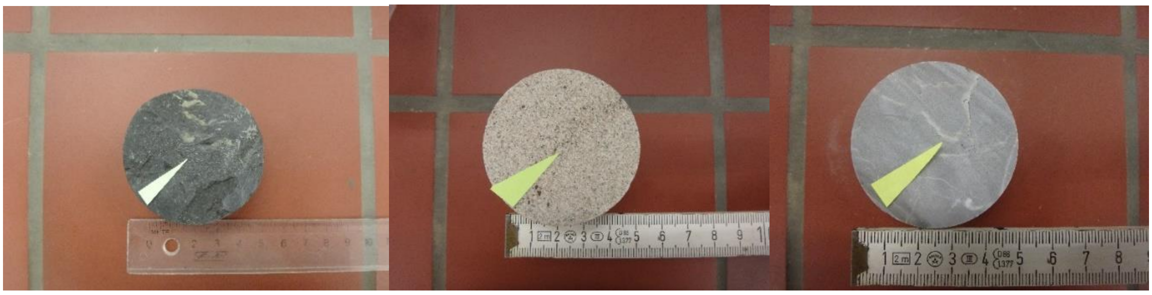


Figure 6 *Cross section surface of core sample 7C(left), 7S(middle) and L_4 (right)*

Figure 7 *Cross section surface of core sample L_{12}(left) and O_2(right)*

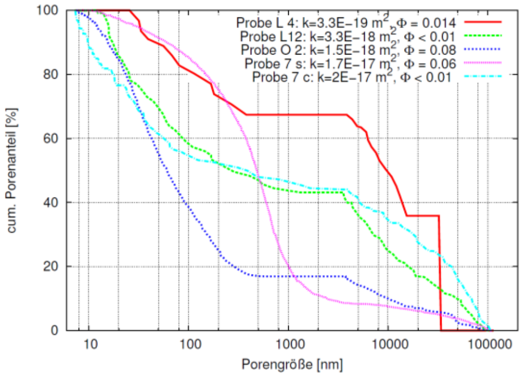


Figure 8 *Porosity test results of each core*

The table 2 shows clearly that there are huge differences of the lab obtained permeability values compared with those from literatures and reports. Some of the samples may differ from several magnitudes, for example, L_4 and L_{12}, literature values are 10^5 or even 10^8 times larger. Only 7S and O_2 have relatively similar values but still too small as aquifers.

Additionally, those cross section surface pictures also indicate, most of the matrixes collected from the nearby coal mine are to some extent heterogeneous with very compact properties. This could be verified from the Figure 8 which demonstrates all of the cores' porosity measured values. These values range from 0.01 to 0.08 are all not typical or representable for aquifers because normally a permeable aquifer should have a much higher value.

Therefore, the possible reasons why there are such differences between lab tests and literatures may lie on several different points:

1) The mine site is not exactly the right coal mine those literatures described although they are all in the similar region, the characteristics of the hydrogeology may vary locally.
2) Lab test method is generally used for matrix measurements while those literatures values were obtained mostly from a site pumping or slug tests. They have different scales and represent various aspects of the strata properties.
3) Another reason that could be spoken is that the groundwater hydraulic behavior in those layers are also driven by fissure flow or fractures flow not only porous and karst flows. This could be a conclusion for this paper and the proof may also be seen from both tests results and pictures

of the cross section surfaces. Most of the cores are not homogeneous but heterogeneous. The large ranges of K values from the literatures may also indicate this.

4) Those core labels may not be so accurate since these cores samples were not collected from the very drilling scene or sites. Thus they may be not so reliable to measure with.

Conclusions

To overcome the data shortage difficulty, this paper adopted several different methods, some of them are developed by TU Freiberg. This Multi Chamber Testing is a reliable and accurate method to measure the permeability values of the cores which is feasible to avoid some technical errors and influencing effects. However, the measured values of the tests showed a large difference with those written in related reports and literatures, some may differ to certain magnitudes. Together with the analysis of the core samples cross section surface pictures, the matrixes appearances seem to be more heterogeneous instead of homogeneous. All of the comparisons, values of permeability themselves and matrixes surfaces pictures lead to one conclusion: the hydraulic behavior may be not only driven by karst or porous power, but also to some extent by fractures and fissures which is contained in those aquifer rocks. On the other hand, the huge differences between literature and lab tests may result from several potential reasons: distance from the target coal mine, the incorrect labels written in the cores and so on.

To summarize, this paper has investigated the closed coal mining area with some of the lab tests and analysis to solve the data shortage problem encountered in the topic and the conclusion is showing a special properties of the aquifers in this region. The aquifers are to some extent a heterogeneous structure and the hydraulic behavior inside may not only be driven by normal porous or karst media but also by lots of fissures and fractures. This information is of great importance for further modelling process. And the investigation has also given critical comments on the rock cores sampled from the nearby mine site. It is therefore quite beneficial for future research work even to set up a more reliable and more representative groundwater flow model.

Acknowledgements

Cores samples were collected with the help of Prof.Sun Yajun of Chian University of Mining and Technology as well as Prof. Chen Zhongsheng of Xuzhou Coal Mining Group Co., Ltd. The lab tests and rock cutting work were done by the support of Dr. Carsten Freese in Institute of drilling and fluid mining, and Mr. Gert Münzberger, Dr. Frühwirth in Institute of Geotechnik, Technische Universität Bergakademie Freiberg. All of their kind support are appreciated. The pictures of the cores were from the support of our own water lab in Institute of Mining and Civil engineering. Moreover, Dr. Nils Hoth and Prof. Drebenstedt helped with corrections and revise of the paper writing. Their supervisions are also sincerely appreciated.

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Integrated Mine Water Management: Innovative Design to address Challenging Environments

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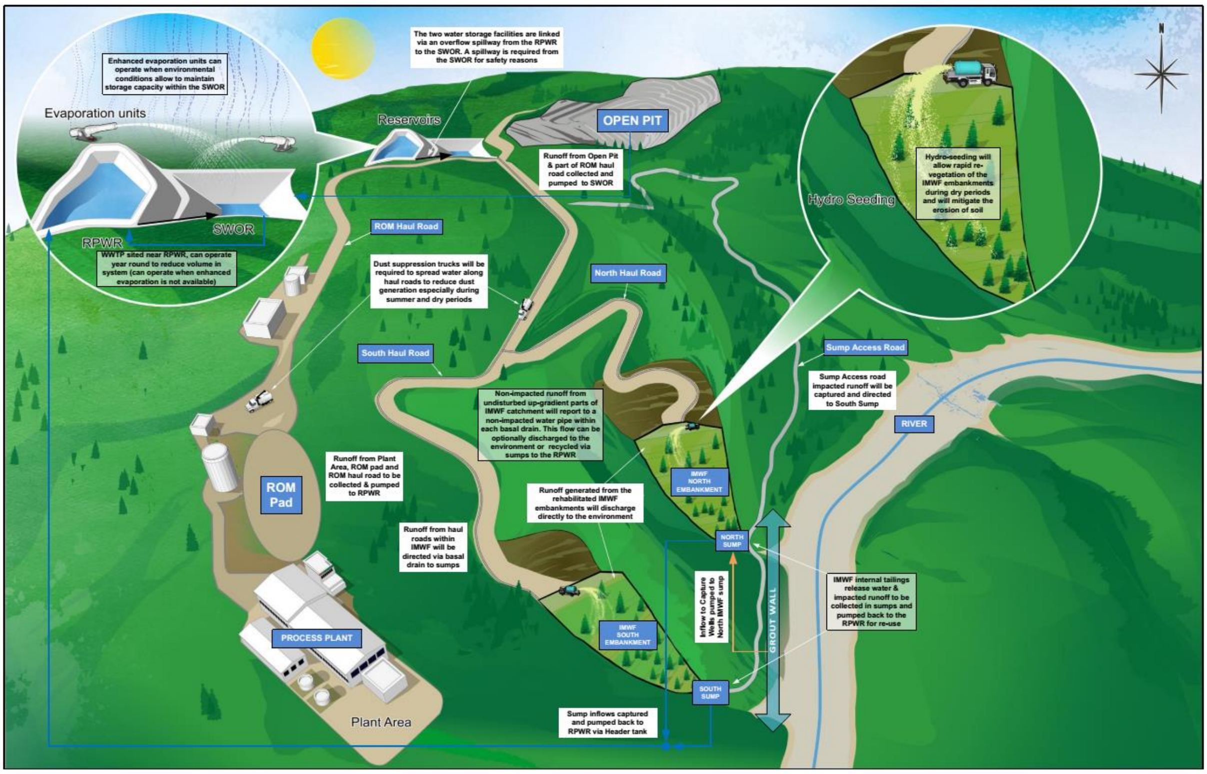
Extended Abstract

Extreme geophysical and water environments found at many mine sites can present unique challenges in controlling the quantity and quality of mine impacted water. Our poster will explore the difficulties presented in designing a complex water management system at a mine site (open pit, process plant and tailings management facility) proposed for the extraction of a low grade auriferous deposit. Issues which had to be overcome included a steeply sloped site with limited natural water storage areas; operating in close proximity to a superficial aquifer used for potable water supplies; operating adjacent to a protected river; challenging regulations; and patterns of extreme rainfall events.

The Feasibility level design of the water management facilities had been based on a high level understanding of the annual water balance at the site and did not allow for the temporal separation of high evaporation and high runoff generation periods. Resolving this issue at the detailed design stage required expansion of water storage facilities despite the steep topography and limitations imposed by European dam regulations; this required a novel approach tailored to the local restrictions. In parallel to the volume management issue, water quality regulations limited the ability to remove excess contact water from the system. In order to address these restrictions, the relative hydraulic performance of lining and capping systems had to be interrogated, and the likely environmental impacts assessed. A sophisticated, probabilistic water management model of both water quantity and water quality throughout the water management system was built to drive the design with the model results predicting "zero operational discharge" for the life of mine.

Some of the key improvements in Mine Design included:

- Water Management Dam embankment height was reduced while increasing overall capacity through the adoption of a dual storage approach;
- Careful separation of mine water streams (contact vs non-contact) meant that a large proportion of the contact water generated on site could be utilised for operational and environmental purposes and not just constrained to supplying the process plant;
- A thorough understanding of the system performance across a wide range of likely operating conditions was gained through use of probabilistic water balance modelling;
- Enhanced evaporation techniques:
- Critical design parameters of a mandated water treatment plant was optimised using the probabilistic model.



Enhanced evaporation units can operate when environmental conditions allow to maintain storage capacity within the SWOR

The two water storage facilities are linked via an overflow spillway from the RPWR to the SWOR. A spillway is required from the SWOR for safety reasons

Runoff from Open Pit & part of ROM haul road collected and pumped to SWOR

Hydro-seeding will allow rapid re-vegetation of the IMWF embankments during dry periods and will mitigate the erosion of soil

WWTP sited near RPWR, can operate year round to reduce volume in system (can operate when enhanced evaporation is not available)

Dust suppression trucks will be required to spread water along haul roads to reduce dust generation especially during summer and dry periods

Sump Access road impacted runoff will be captured and directed to South Sump

Non-impacted runoff from undisturbed up-gradient parts of IMWF catchment will report to a non-impacted water pipe within each basal drain. This flow can be optionally discharged to the environment or recycled via sumps to the RPWR

Runoff from Plant Area, ROM pad and ROM haul road to be collected & pumped to RPWR

Runoff generated from the rehabilitated IMWF embankments will discharge directly to the environment

Runoff from haul roads within IMWF will be directed via basal drain to sumps

Inflow to Capture Wells pumped to North IMWF sump

IMWF internal tailings release water & impacted runoff to be collected in sumps and pumped back to the RPWR for re-use

Sump inflows captured and pumped back to RPWR via Header tank

Figure 1: *Schematic illustrating the challenging site water management*

Some of the techniques used during the detailed design stage of the mine have clear applications within the wider mining industry. The particular approach taken to dual storage and judicious separation of water streams increases the efficiency of operational water management while optimising the cost of water treatment, providing both financial and environmental incentives for developers. The application of Monte-Carlo [1] simulation tool allows for transparent and sensible risk assessments to appraise differing water management strategies under a wide range of conditions. The integrated approach to mine water management focused on water recycling whilst limiting the volumes of generated mine impacted water and its release to the environment under normal operating conditions. Operators should be encouraged to develop sophisticated water management tools much sooner in the mine design process to avoid unnecessary regulatory restrictions and reduce costs.

Key words: Mine water, modeling, water balance, mass balance

References

[1] GoldSim Technology Group LLC (GTG).2011. GoldSim Pro Version 11.1.

CHAPTER 3

Mine Water Impact on River Systems

How does Salinisation of Running Waters Affect Aquatic Communities? Answers from A Case Study

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Abstract

The introduction of brines from salt mining into nearby running waters is still a prevalent method of disposal. These salt waste waters often originate from processing of salt-containing rocks and drainage of the residue heaps. Hereby salt waste waters may still accumulate for a long time after shutdown of the mines.

Indeed it has early been reported that elevated salt concentrations as caused by this disposal method may damage the aquatic communities of the running waters afflicted. The question in which way salinisation of running waters affects aquatic communities was answered by means of a case study. It was performed along the Wipper river (Central Germany) where salt inputs from 4 residue heaps along the river cause an increase in salinity thus forming a salt gradient (95 km stretch). Monitoring data of 7 sampling sites (31 – 1,286 mg Cl^-/l) of the period 2008 to 2014 were analysed for salts, nutrients and changes in the benthic macroinvertebrate and diatom communities. Benthic macroinvertebrates responded to elevated salt concentrations with decrease in species numbers and diversity. Development of r-species and spreading of neozooa was favoured, whereas salt-sensitive groups declined. Freshwater species were replaced by more salt-tolerant forms. Similar effects were observed in view of benthic diatom assemblages. Numbers of reference species decreased, and shifts in the diatom assemblages took place whilst the proportion of salt-tolerating (meso- and polyhalobic) taxa increased.

Key words: diatoms, macroinvertebrates, salinisation, Wipper river,

Introduction

Salinisation may affect running waters seriously. A number of reasons are in line for anthropogenic salinisation, among them salt mining (Canedo-Argüelles et al. 2016). In this case, salt brines from mining and/or production are often discharged into nearby rivers, causing elevated salt concentrations here which may influence structure and function of the afflicted aquatic ecosystems distinctly (Canedo-Argüelles et al. 2013).

The catchment area of the Wipper river (Northern Thuringia, Germany) forms an example for this. Here salt brines are especially rich in single ions such as potassium which is reported to have toxic effects on aquatic organisms (Ziemann & Schulz 2011) and magnesium. Besides this anthropogenic salinisation saline tributaries of geogenic origin join in. This paper presents a case study of the Wipper river catchment area. It focuses on the question in which way aquatic communities are influenced by salinisation by special reference to benthic macroinvertebrates and benthic diatoms.

Methods

Sampling area and locations

The catchment area of the Wipper river is situated in Northern Thuringia (Central Germany, fig. 1). It

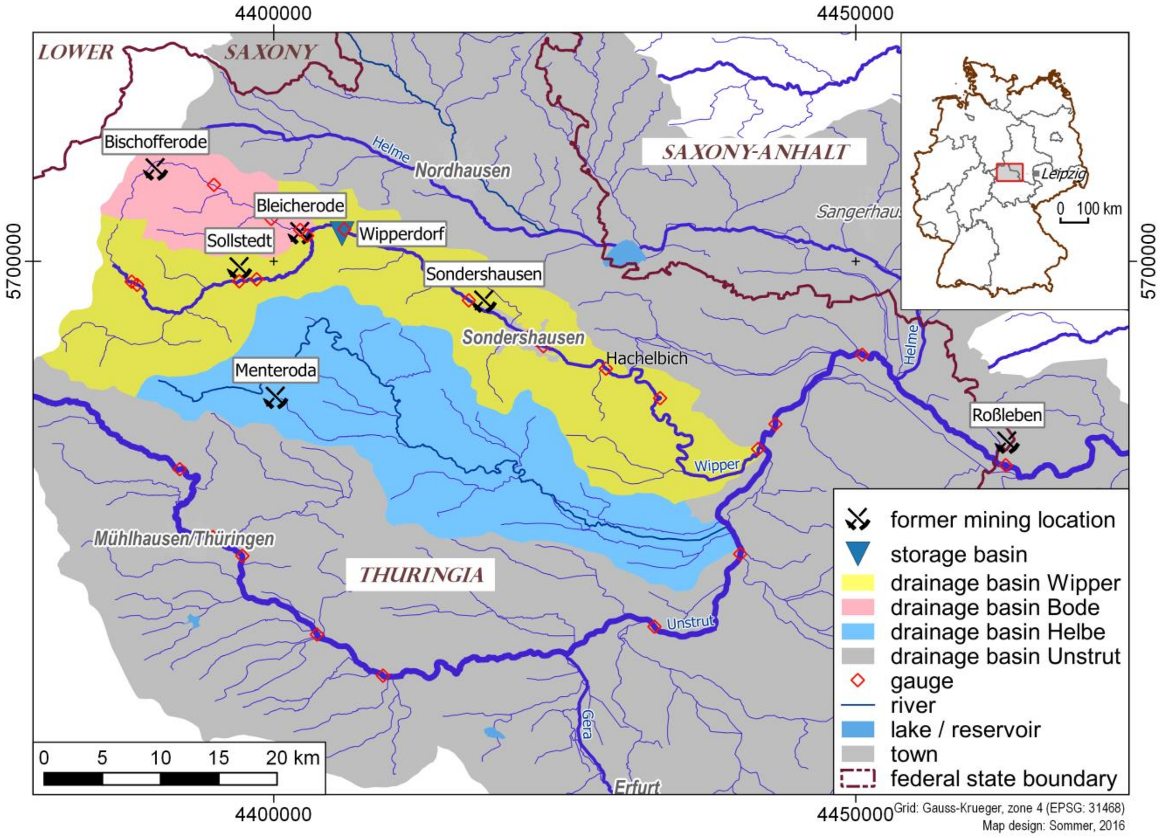

Fig. 1: *Catchment area of the Wipper river. Map design: Thomas Sommer, Dresden (Germany)*

is a tributary river of the Unstrut river (rivers Saale, Elbe). Its total length is 95.3 km, the catchment area is 649.1 km^2, mean discharge 3.5 m s^{-1} and average low discharge 1.1 m s^{-1}. The headwater is a small coarse substrate dominated calcarous highland river (German WFD classification: type 7), the lower course is a mid-sized fine to coarse substrate dominated calcarous highland river (type 9,1, all data; Thuringian State Institute for Environment and Geology, Jena, Germany).

Four potash mines and their affiliated factories (Sollstedt, Bischofferode, Bleicherode and Sondershausen) discharged their salt brines into the Wipper river and its tributary creek Bode during the potash mining period from 1893 to the early 1990s. Since shutdown in the 1990s, still drainage waters from the stockpiles left behind accumulate, are stocked up in two storage basins (near Wipperdorf and Sondershausen) and are and discharged into the river Wipper during periods of sufficient runoff. Salt springs below the river bed and a few tributaries rich in electrolytes cause an additional increase in salinity (Thuringian State Institute for Environment and Geology, Jena, Germany).

Sampling and sample processing

Data presented in this case study were collected as part of the governmental sampling to fulfil the monitoring requirements of the EU-Water Framework Directive. The sampling period considered in this study involved the years from 2008 to 2014. Chemical sampling was performed once a month. Water samples were taken, preserved if necessary, cooled and transported to the laboratory where analyses were conducted. Involved were salts (ions: K^+, Mg^{++}, Cl^-, SO_4^{--}), nutrients (NO_3, total phosphorous TP) and carbon (TOC).

Biological samples were taken once a year. Samples of benthic invertebrates were taken by means of substrate-specific multi-habitat kick-sampling, preserved in EtOH (96%) and stored at 4°C in the dark in the laboratory until processing according to Meier et al. (2006). For evaluation the ASTERICS/PEROLODES software was used. The following metrics were used for interpretation: No.

of taxa, diversity (Shannon-Weaner-index), r/K ratio, proportion of neozoa, proportion of EPT and EPTCBO taxa, percentage of freshwater, oligo- and mesohaline species, resp.

Sampling and evaluation of the diatoms followed the PHYLIB procedure by BayLfU (2006ff). For the calculation of the final result the metrics proportion of reference species, trophy index according to Rott and Halobion index are necessary which at once give valuable insights into structure and loads of diatom assemblages.

Statistical calculations followed Sachs (1982).

Results and Discussion

Chemical parameters

Concentrations of carbon, nutrients and salts are compiled in table 1 and illustrated in fig. 2 and 3.

Table 1: *Carbon, nutrient and salt concentrations of 7 sampling locations along the Wipper river. Values given are average concentrations and corresponding standard deviations of the sampling period 2008 – 2014 (12 samples/a).*

serial no.		1	2	3	4	5	6	7
location		Worbis	Wülfingerode	Sollstedt	Bleicherode	Großfurra	Hachelbich	Sachsenburg
river km	km	85.6	73.2	68.7	62	43.8	29.2	0.4
TOC	mg/l	2.45±0.93	4.63±0.50	4.58±0.55	4.64±0.32	4.83±0.47	4.83+0.50	4.49±0.51
TP	µg/l	60±10	400±60	400±50	300±30	230±30	220±30	180±20
NO_3-N	mg/l	6.11±0.34	5.76±0.39	5.59±0.51	5.29±0.31	5.17±0.67	4.95±0.58	4.59±0.70
K^+	mg/l	2.1±0.30	7.3±0.43	20±2.31	30±3.23	67±7.32	75±4.47	61±5.77
Mg^{++}	mg/l	20±0.53	23±0.52	28±2.45	56±6.37	94±4.42	110±5	101±3
Cl^-	mg/l	31±9.68	84±3.99	196±20	471±60	1004±365	1286±107	1024±113
$SO4^{--}$	mg/l	90±5.64	213±8	222±12	305±21	351±18	370±16	455±33

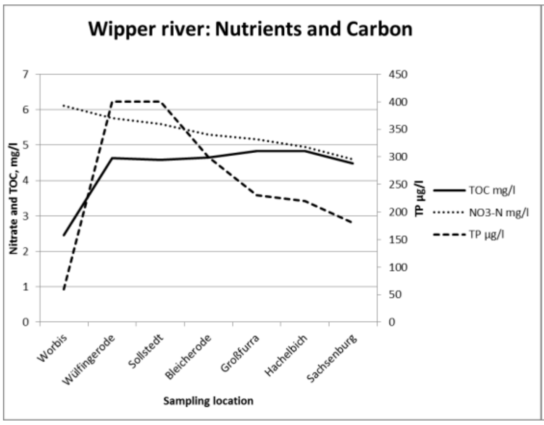

Fig. 2 *Nutrient and carbon concentrations Average means of the years 2008 – 2014.*

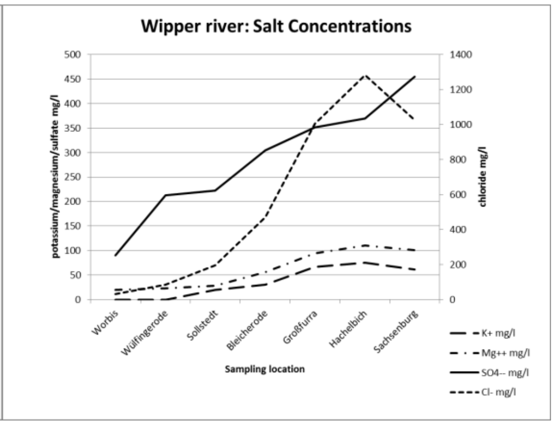

Fig. 3 *Salt concentrations. Average means of the years 2008 – 2014.*

The data show that TOC concentrations are lowest below the source near the village of Worbis. Further down they increase and remain comparatively stable afterwards. In contrast to this, NO_3-N concentrations are highest near the source and decrease slightly furthermore. Regarding the phosphorous concentrations they are lowest below the spring, leap distinctly between Wülfingerode and Sollstedt and drop beneath.

Salt concentrations show different patterns. Regarding the concentrations of potassium, magnesium and chloride, three sections may be distinguished: A slightly salanised section extends until the village of

Sollstedt where the first heap is situated. Here the moderately salanised part begins where the Wipper river receives salt waste waters from (i) the abandoned mine of Sollstedt, (ii) the dead mine near the city of Bleicherode, (iii) the tributary creek Bode polluted with waters from the disused mine of Bischofferode and (iv) geogenic sources emitting below the river bed (Sommer and Stodolny 2012). Further down between the sampling locations Bleicherode and Großfurra (situated just above the city of Sondershausen, fig. 1) brines of the storage basin near the village of Wipperdorf are discharged causing a strong increase in salinity. This is the third section being strongly salanised that extends up to the oulet near the village of Sachsenburg. Along this section salt concentrations decrease only slightly due to the freshwater dilution by a few creeks flowing in. – Sulfate concentrations increase from spring to outlet over the whole transect. The reason for this are mostly geogenic inputs (76%) whereas mining inputs are less important (24%, Sommer and Stodolny 2012).

Based on the effects of elevated salt concentrations on aquatic communities, sensitivity groups can be distinguished. From field data Coring et al. (2016) identified 5 chloride classes for benthic macroinvertebrates (< 200; 200 – 600; 600-1,100; 1,100 – 2,000; > 2,000 mg Cl^-/l, annual mean). A comparison of these concentration ranges with the values from table 1 suggests that impacts of salinisation on the aquatic communities are to be expected whereas the threshold value above which changes take place is probably considerably < 200 mg/l (Halle and Müller 2013, Pohlon and Schulz 2016).

Biological parameters

Results of the macroinvertebrate metrics are given in table 2 and figure 4. The metrics no. of taxa and diversity indicate the integrity of a biocoenosis, unaffected invertebrate communities being characterised by high species numbers and low abundances. Numbers of macroinvertebrate taxa were highest at the freshwater-marked sampling location near the city of Worbis. In the following section numbers dropped slightly, a distinct decrease was found for the strongly salanised section below the storage basin near Wipperdorf between Großfurra and Sachsenburg. At Hachelbich, macroinvertebrate numbers increased a little (fig. 4, top left). An explanation for this may be that the creek Hachel flows in somewhat above the sampling location and transports animals into the Wipper river. Number of macroinvertebrate species were inversely correlated with chloride (r= -0.7912) and moreover sulfate (r=-0.9370). These findings are in contrast to the observation that slightly salanised river sections often display enhanced species numbers probably due to a faciliated osmoregulation of many aquatic insect species (Kefford et al. 2016 and observations of the author). However, this pattern can be observed with regard to the diversity (Shannon Weaner Index): The index showed increased values in the moderately and dropping ones in the strongly salanised section (fig. 4, top right).

Table 2: *Macroinvertebrate metrics. Values are given as average means of the years 2008 to 2014 and the corresponding standard deviation. Parameters are number of taxa, diversity (SWI, Shannon Weaner Index), percentage of neozoa, percentage of sensitive species (EPT=Ephemeroptera, Plecoptera, Trichoptera, EPTCBO= Ephemeroptera, Plecoptera, Trichoptera, Coleoptera, Bivalvia, Odonata), r/K proportion, percentage of freshwater, oligo and mesohaline species.*

serial no.		1	2	3	4	5	6	7
location		Worbis	Wülfingerode	Sollstedt	Bleicherode	Großfurra	Hachelbich	Sachsenburg
river km	km	85.6	73.2	68.7	62.0	43.8	29.2	0.40
no. of taxa		29.7±3.5	26.6±5.0	26.7±3.3	26.5±3.2	22.7±2.8	24.3±3.8	19.3±1.3
SWI		2.17±0.40	2.11±0.42	2.22±0.27	2.57±0.18	2.17±0.24	1.99±0.59	1.41±0.36
neozoa	%	0.68±0.76	1.2±2.25	1.42±1.73	3.35±3.55	8.14±6.64	9.41±7.64	4.18±3.48
EPT	%	39.6±6.34	33.0±14.11	39.2±7.29	43.6±5.01	23.4±5.19	11.8±9.92	15.8±5.14
EPTCBO	%	14.00±3.63	13.29±1.83	13.00±1.93	14.00±1.53	9.86±. 2.17	11.00±2.78	7.00±1.31
r/K ratio	%	0.13±0.03	0.15±0.03	0.16±0.03	0.14±0.03	0.17±0.05	0.18±0.06	0.24±0.03
freshwater	%	41.1±13.9	50.2±10.2	51.2±8.8	33.3±3.9.	27.8±8.3	42.1+18.9	23.8±13
oligohaline	%	0.5±0.3	0.5±0.5	0.5±0.4	0.9±0.9	5.2±3.3	4.2	1.3±1.0
mesohaline	%	0.1+0.1	0.5±0.5	0.3±0.3	0.7±0.7	0.3±0.3	1.2+1.49	0.8±0.6
no data	%	56.6±14.2	49.1±10.2	48±8.5	65.1±4.2	66.7±10.5	51.2+23.8	74.1±13.9

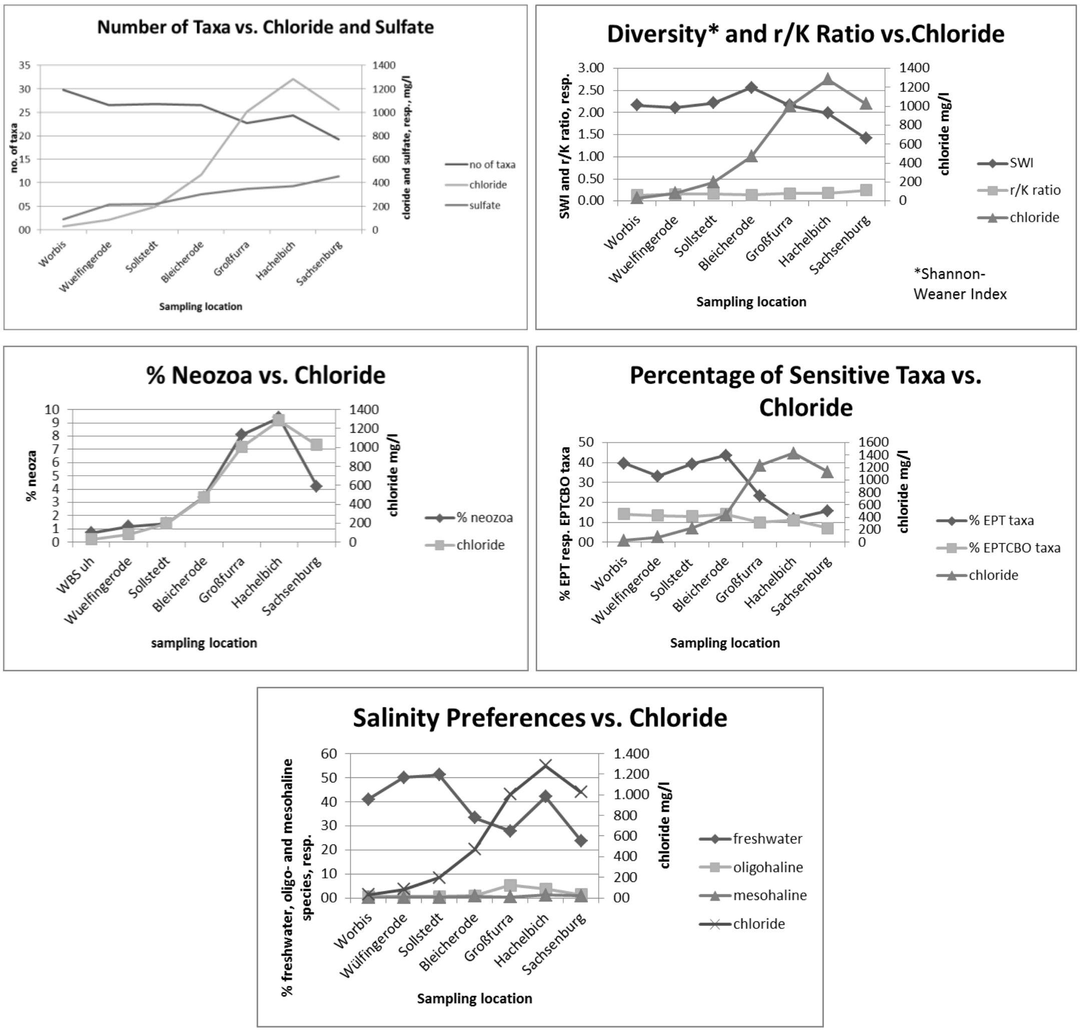

Fig. 4: *Macroinvertebrate metrics: Total number of species (top left), diversity/Shannon Weaner Index and r/K ratio (top right), percentage of neozoa (middle left), percentage of sensitive (=EPT and EPTCBO taxa, middle right) and salinity preferences.*

The r/K proportion describes the ratio between pioneer and climax species. Data show that r-species increased with rising salt concentrations, namely sulfate. They benefit the occurrence of species characterised by short generation times, small body sizes and high indivudual numbers ("r-species").

A suppression of the authochtonous fauna by increasing salt concentrations favours the spreading of neozoa due to their tolerance of salinity and further environmental parameters (Canedo-Arguelles et al. 2015). The proportion of neozoa is usually low in unaffected, stable communities. This is consistent with the observed distribution of neozoa species: Except for the last sampling location their percentage increases continually (fig. 4, middle left), thus following the concentrations of potassium, magnesium and chloride.

Aquatic macroinvertebrates may differ considerably in their salt sensitivity. Especially among the mayflies, stoneflies and caddis flies (Ephemeroptera, Plecoptera, Trichoptera) being typical for near-natural running waters ecosystems, are many sensitive taxa. A high proportion of EPT taxa indicates undisturbed conditions. In reference to the Wipper river low values were found in the strongly salinised section (Großfurra – Sachsenburg). Here salt conctrations obviously exceed the salt thresholds tolerable for many species. Percentage of EPT taxa was inversely correlated with the concentrations of potassium, magnesium, chloride and sulfate (r=- -0.8495, -0.8620, -0.8720, -0.7448, resp.). Interestingly the percentage of EPT taxa of the moderately salanised section exceeds that of the unsalanised reference site Worbis in at least one case (Bleicherode). Here a pattern similar to the above mentioned becomes visible: Slightly elevated salt concentrations may favour the occurrence of EPT species on the whole although it must be taken into account that a number of strongly salt sensitive species may have been eliminated already. Even though beetles, mussels and dragonflies (Coleoptera, Bivalvia, Odonata) are included (→ % EPTCBO) higher vales of the un- and slightly salanised section were opposed to lower values of the strongly salinised part (fig. 4, middle right). In this case also negative correlations between macroinvertebrates and salts are given (potassium r=-0.7727, magnesium r=-0.7995, chloride r=-0.7688, sulfate r=-0.8345).

The PERLODES software designates the macroinvertebrates to one of the following salinity groups: freswater, oligohaline, mesohaline, polyhaline and euhaline species. The proportion of freshwater, oligo- and mesohaline species indicates the salt tolerance focus of a given invertebrate community. In the present evaluation neither poly- nor euhaline species were found. The percentage of freshwater species was highest in the un- and slightly salanised part and lowest in the strongly salanised section. Increasing salinities were followed by a decrease of freshwater species and elevated proportions of oligo- and mesohaline species (fig. 4, bottom). This means that salt sensitive freshwater taxa were replaced by more salt resistant forms.

Table 3: *Diatom metrics. Values are given as average means of the years 2008 to 2014 and the corresponding standard deviation.*

serial no.		1	2	3	4	5	6	7
location		Worbis	Wülfingerode	Sollstedt	Bleicherode	Großfurra	Hachelbich	Sachsenburg
river km	km	85.6	73.2	68.7	62	43.8	29.2	0.4
no.of ref. species	%	53.0±17.1	35.7+4.6	26.7±8.1	29.2±9.1	15.8±3.8	16.8±11.1	25.5±11.8
Trophy Index (Rott)		2.67±0.2	3.01+0.1	3.05±0.1	2.99±0.1	3.04±0.1	3.07±0.1	3.06±0.1
Halobion Index		2.6+2.1	6.5±2.6	14.3±4.4	18.0±6.7	28.1±7.3	34.5±6.8	33.4±6.0

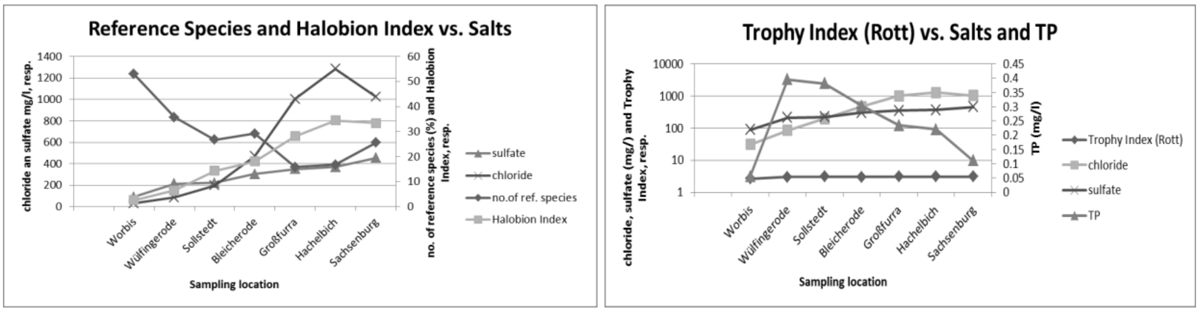

Fig. 5: *No. of reference species and Halobion Index vs. salts (left) and the Trophy Index according to Rott vs. salts and total phosphorus (right)*

Results from the diatom metrics are presented in table 3 and fig. 5.The proportion of reference species gives a measure for the conformance of a given diatom assemblage with type-specific reference assemblages and was highest by far at the salt-free sampling location near the city of Worbis. This indicates that under conditions free of anthropogenic salt inputs the composition of the diatom assemblages were most similar to that of reference conditions. Further down (section Wülfingerode to Bleicherode) the proportion of reference species dropped to values between 35.7 and 26.7%. A further increase of salt concentrations (sampling locations at Großfurra, Hachelbich and Sachsenburg) coincided with another decline of reference species reflecting changes in the composition of the diatom communities. There was a distinct negative correlation between the proportion of reference species and concentrations of chloride (r=-0.7985), sulfate (r=-0.8108), potassium (r=-0.8234) and magnesium (r=-0.7495) visible. The opposite pattern occurred with respect to the Halobion index which indicates the biological impacts of salinisation, especially osmotic pressure and relative ion composition, on benthic diatom communities (Ziemann & Schulz 2011). Values around 0 indicate freshwater, values from +10 to +30 indicate elevated salt concentrations, values > +30 ibdicate moderate and > +50 strong salinization (Ziemann 1999, BAYLfU 2006). The Halobion Index values increased nearly continually over the total transect. They were lowest at the unsalanised locations near Worbis and Wülfingerode (2.6/6.5, resp.), slightly elevated near Sollstedt and Bleicherode (14.3 and 18.0. resp.) and peaked at Großfurra and below (28.1 to 34.5). Values were strongly correlated with the concentrations of potassium (r=0.9796), magnesium (r=0.9824), chloride (r= 0.9749) and sulfate (r=0.9419). Data suggest that increasing salt concentrations led to shifts in the species structure whilst haloxenic taxa were replaced by halophilic, meso- and polyhalobic forms.

The trophy index according to Rott describes the trophic condition of a running water, In contrast to the reference species metric the trophy index remained rather balanced over the transect and did hardly reflect changes in nutrient concentrations. This is a surprising result and the reasons are still not understood. Probably elevated salt concentrations overlay the effects of other stressors.

Conclusions

As demonstrated by the case study salinisation may affect the aquatic communities of running waters in several ways. In general, benthic macroinvertebrates responded to elevated salt concentrations with a decrease in species numbers and diversity. Development of r-species and spreading of neozooa were favoured, and salt-sensitive groups declined. Freshwater species were replaced by more salt-tolerant forms.

Similar effects were observed in view of benthic diatom communities. Numbers of reference species decreased, and shifts in the diatom assemblages took place whilst the proportion of salt-tolerating (meso- and polyhalobic) taxa increased.

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Iron-Hydroxide-Removal from Mining Affected Rivers

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Abstract

Oxic and ferric iron hydroxide rich river waters are evolving in the Lusatian mining district due to discharge of ferrous iron rich ground waters. These river waters are characterized by small hydroxide flocs which show a very slow sedimentation. To stop pollution of downstream ecosystems flocculation and sedimentation of the hydroxides has to be accelerated. Addition of flocculants like polyacrylamides into the rivers is effective but shall be avoided because of unknown ecological consequences. Liming is also effective but demands technological infrastructure and ongoing supply with lime milk. To reduce technical infrastructure and to integrate ferric hydroxide retention in the river systems, alternative technologies are being developed. It is the aim to supply the stakeholders with easy to maintain techniques for the years to come to protect the downstream parts of the rivers from severe iron hydroxide pollution.

Key words: iron hydroxides, polluted rivers, remediation technology, groundwater discharge

Introduction

The Lusatian mining district is one of the three large lignite mining districts in Germany. After reunification a large part of the mines was closed due to economic and ecological reasons. The remaining mines are still in operation. After closing the mines in the nineties the pitlakes were flooded and the former groundwater level is currently being reestablished in and around the abandoned mines. Today the groundwater level has reached its natural level in many parts of the mining area and the groundwater starts to discharge into the local river systems again.

The mining dumps but as well the surrounding unworked sediments contain sulfides, which have been partly oxidized during the period of groundwater drawdown. The oxidation products partly remained in the unsaturated zone and were dissolved in the rising groundwater. Sulfide-rich but temporarily aerated swamps release additional amounts of ferrous iron to the groundwater. The groundwaters thus became rich in ferrous iron showing concentrations up to 400 mg/L even outside the dumps [3].

By discharging into the rivers the ferrous iron rich anoxic groundwaters mix with the oxic river waters. The ferrous iron loads oxidize in the presence of oxygen and form iron hydroxides. Iron hydroxide formation releases protons by hydratation of ferric iron. Due to the natural buffer capacity of most river waters of the region of 1 to 1.5 mmol/L most waters keep their neutral pH. Nevertheless it takes several hours up to several days to completely oxidize the whole iron load [1]. Thus the river waters in the mining area are characterized quite often by a combination of ferrous and ferric iron, total iron loads reaching more than 100 mg/L.

Hydroxide formation results in an elevated turbidity of the river water and high sedimentation rates which impair the living conditions of the Macrozoobenthos. The sludge reduces photosynthesis and oxygen uptake as well as food supply for the fish population. The riverbeds are clogged by the sludge. Last but not least the optic impression of the surface waters is considered to be a major drawback for the evolving tourism in the region.

It is the common aim of the mining industry and the authorities to prevent the deterioration of large parts of the rivers by iron hydroxide loads. Two strategies are currently tested and implemented:

1) The iron loads are stopped downstream of the sources right in front of areas which have to be protected from the iron sludge. A well known example is the Spreewald area, an alluvial forest of high touristic and ecological value downstream of the mining region. The advantage of this

strategy is that a few “core areas of hydroxide retention” next to the dominant zones to be protected would be sufficient to stop the hydroxide load. The disadvantage is that many of the upstream rivers will stay polluted with the iron hydroxide sludge, will suffer under low ecological conditions and just serve to transport iron hydroxide loads. Iron hydroxide sludge has to be removed from these parts of the rivers periodically to avoid clogging of the river beds [2]. This is why the local population and authorities demand the retention of the iron “at its source”.

2) So a more desirable strategy might be the retention of the iron loads next to their sources still in the underground (Hildmann et al. 2015) or at least in the upstream parts of the rivers next to the areas of exfiltration. In this way the downstream rivers could be protected from the iron loads. However ferrous iron release from groundwater into the rivers occurs in a diffuse manner and is distributed widely along large parts of the riverbanks. Therefore it is difficult to detect and to treat the “hot spots” of exfiltration. Local measures, like pumping wells and ditches next to the rivers are tested to keep the iron rich groundwaters away from the rivers. Many of these local measures would have to be taken to stop the overall iron load.

State of the art technologies for iron removal rely on the control of the flocculation process by liming, by catalysed ferrous iron oxidation in contact with already existing flocs at elevated pH-values between 8.0 and 9.0 and by the use of flocculants. By creating large flocs in technical plants fast sedimentation of the produced solids within 1 to 2 hours is possible (Bilek, 2013). Yet the conditions in the river waters differ from those in classic treatment plants which treat water which is typically rich in ferrous iron:

- The river waters are already oxidized and the pH is still in the neutral range in most cases even after complete iron oxidation due to their natural buffer capacity and the low groundwater/river water mixing ratio.
- Neutral pH-values and abundant oxygen result in fast iron oxidation kinetics at least in summer. Hydroxide formation is more or less completed within a few hours.
- The flocs stay small due to pH-values below 7.5, low density of solids and no artificial flocculants present. Therefore their sedimentation rate is rather slow. Field observations show that sedimentation may take several days up to two weeks even in still water [1].
- Conditions for sedimentation are bad due to the tractive forces of the rivers and due to the constantly changing flow velocities and fluxes during the year.

This shows that the possibilities to influence the flocculation and sedimentation process by classic technical means are limited. Iron hydroxides stay in suspension for many kilometers and pollute large parts of the rivers.

Liming the rivers and even adding flocculants can increase the sedimentation of the iron hydroxides. However out of ecological considerations, local large pH-increases and addition of flocculants in natural environments should be avoided. Besides that application of flocculants leads to sludges with rather high water contents which rapidly clog the riverbeds and are not favorable for further sludge processing. By creating rather dense iron hydroxide sludges their volume can be kept low and removal intervals from the river beds can be kept larger.

Sometimes artificial basins next to the rivers are available which can be used as sedimentation ponds for the whole river. Due to the large retention times of several days large basins or stillwater areas are required to guarantee permanent ferric iron hydroxide sedimentation.

Currently new technologies are under development to accelerate the sedimentation process and to minimize the size of additional sedimentation pond volumes which have to be provided along the affected rivers even without adding large amounts of chemicals. It is the aim to provide methods to retain and remove the iron hydroxide loads which need less technological effort and should be applicable also for small rivers. They should be better integrable into the natural environment of the affected river systems than classical treatment plants.

One way to intensify the flocculation is to temporarily increase the turbulence of the water by applying mixing energy. This technique serves to intensify the contact between the already existing flocs. The probability of coagulation is increased that way. On the other hand turbulence does not have to be too large. Otherwise already existing flocs will be disintegrated again.

Another technique which may be applicable to intensify sedimentation and increase sludge density is the high density sludge technique, which is well known in mine-water treatment [Aube´, Coulton, 2003]. Iron-hydroxide sludge, which already settled, is pumped back into the reaction zone to serve as a reactive surface for the oxidation and coagulation reactions. The presence of hydroxide solids in turbulent water in combination with additional liming is used to accelerate ferrous iron oxidation and coagulation of already existing small flocs. Sedimentation of the larger flocs now is faster and a much more dense sludge can be created. This process is currently adopted to river waters and its potential to increase the flocculation and intensify the sedimentation process is tested.

Methods

In a first step **laboratory tests** have been performed to identify various combinations of pH-control, mixing energy input and sludge recirculation. In these tests the river water was firstly mixed with various amounts of lime, stirred with various velocities and then was transferred to settling vessels to examine the settling process. The sedimentation process was observed for about 1.3 days. After certain time intervals the supernatant water of each batch was sampled repeatedly for the remaining total iron content. The iron hydroxides were completely redissolved in nitric acid and analyzed in aqueous phase with ICP-OES.

A **bench scale treatment plant** (*figure 1; left*) consisting of two reactors was set up to test various combinations of liming, application of mixing energy and increased floc density. In the first reactor lime, air and mixing energy could be added. In the second reactor also mixing energy could be applied and higher sludge densities were achievable by adding sludge. The settling process was observed in column-like vessels, which were filled with the runoff from the reactors after a steady state flow through process was established.

A **pilot plant** next to a river is currently set up to test the most promising combinations in the field (*figure 2*).

Natural river water was used for all tests because also other suspended components besides iron hydroxides like clay and organic particles are found in the water and may influence the flocculation and the precipitation process.The water shows a pH between 6.6 and 7.0 and a total iron concentration of 3 to 20 mg/L. Its total solids content ranges between 20 and 50 mg/L, its electric conductivity lies between 900 and 1100 µS/cm. The used river water is representative for many mining influenced waters of the region.

Results

The laboratory tests showed that increase of the pH helps to increase the size of the flocs and thus improves the settling process even if all iron is already present as ferric hydroxide colloids (Koinzer, 2014). Even a small pH-increase from 6.7 (original river water) up to 7.0 allows for a significantly faster removal of total iron from the water column (*figure 3*).

In a second test the influence of turbulence was tested. At first the influence of the duration of mixing with a propeller mixer (2, 5 and 15 minutes; 300 rpm) was investigated at various pH-values. *Figure 4* shows the remaining total iron concentrations in solution of pH 7.5 at various times after stopping the mixing process. It can be seen that also mixing leads to a faster removal of iron. Iron removal is faster when mixing 15 minutes instead of 5 minutes whereas mixing for 30 min did not improve the settling process any further (results not shown). This result was confirmed for all pH-values between 6.7 and 8.5.

In bench scale air injection, a propeller mixer with 450 r.p.m. and a paddle mixer 20 r.p.m. were tested as a means of crating turbulence (*figure 1 and 5*). Mixing energy input was higher with the propeller mixer than with the paddle mixer (Moritz, 2015). The tests showed that better results were achieved with the fast working propeller mixer than with the slow working paddle mixer. Air injection showed comparable results to the propeller mixer. Increasing the pH improved the sedimentation rate in any case and under any combination of propeller mixer and paddle mixer. Increase of energy input improved flocculation and sedimentation in any case.

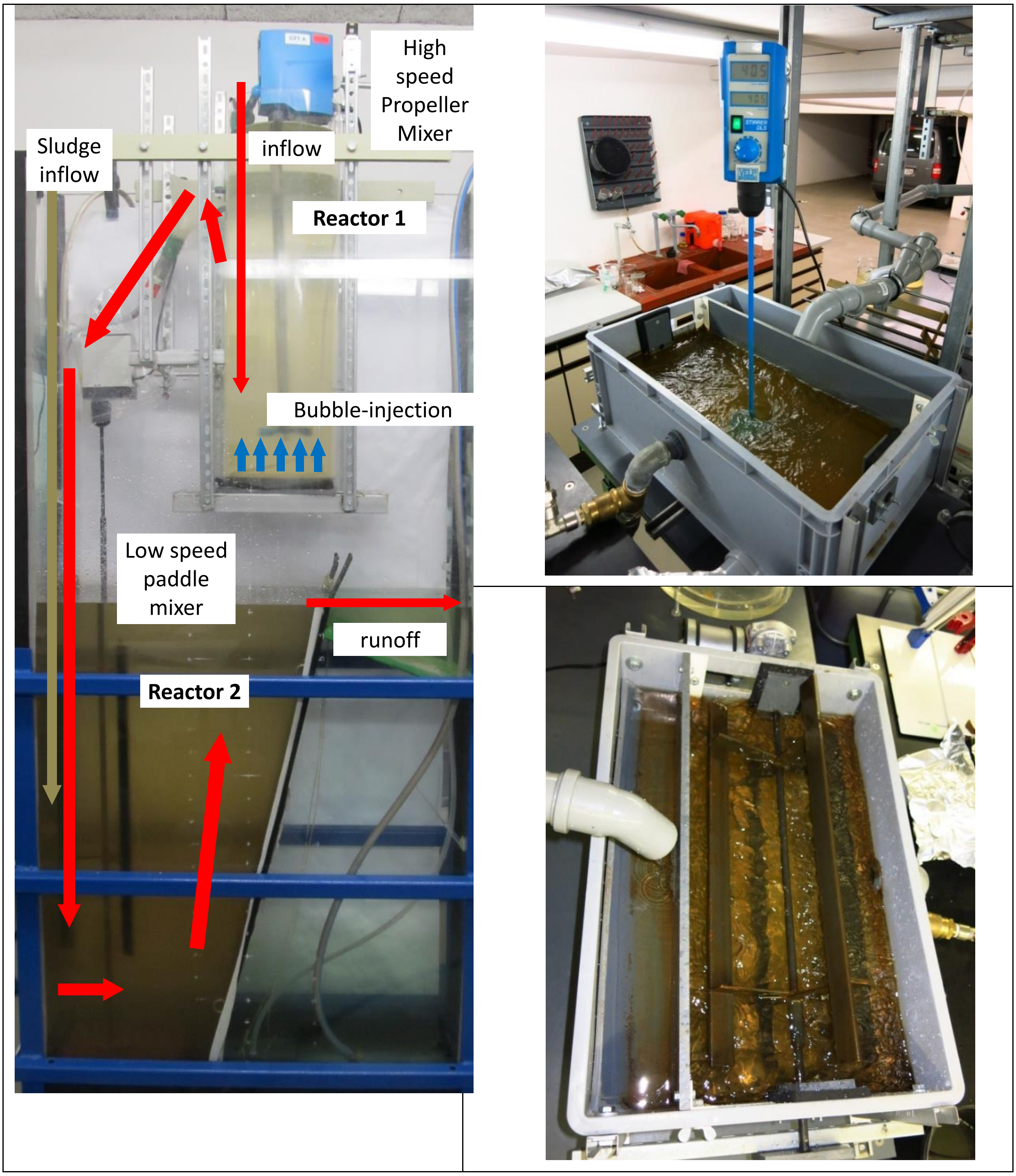


Figure 1 *Left: Bench scale plant with two coupled reactors to test the sequential influence of mixing energy input on flocculation process. Right top: Propeller mixer (405 r.p.m.). Right bottom: horizontal paddle mixer (8 r.p.m.)*

***Figure 2** Pilot plant in the field to test various combinations of mixing, liming and sludge recycling.*

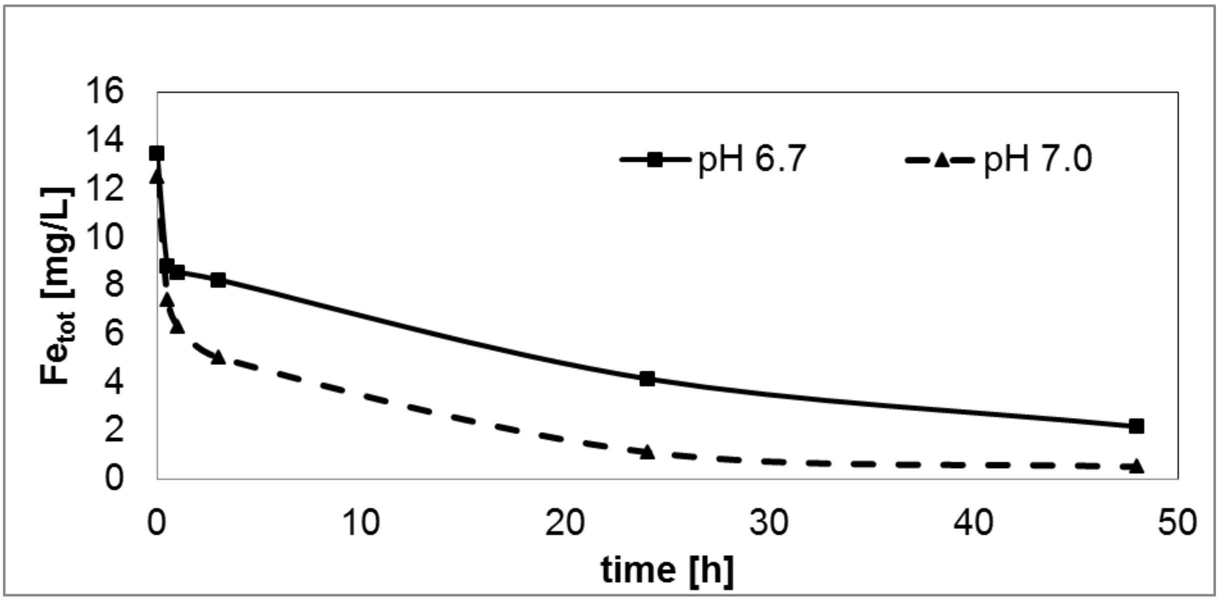


***Figure 3** Investigation of sedimentation at different pH-values. Change of total iron concentration with time.*

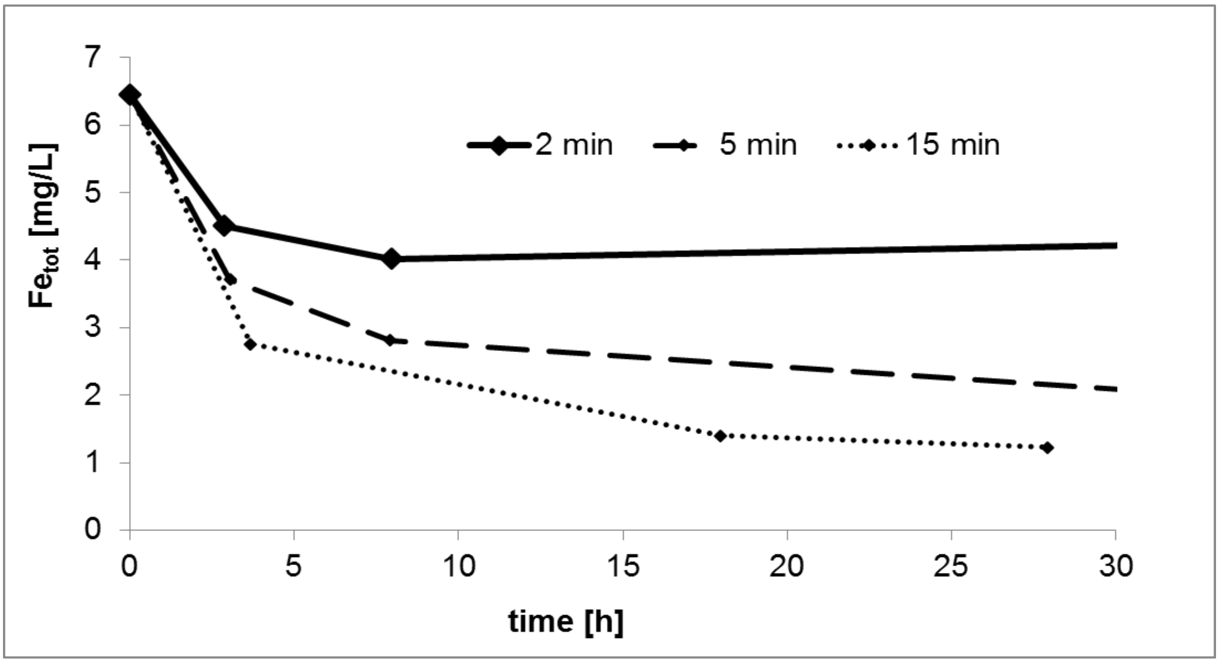


Figure 4 *Investigation of influence of stirring duration. Raw river water (pH 6,7) without lime addition was used.*

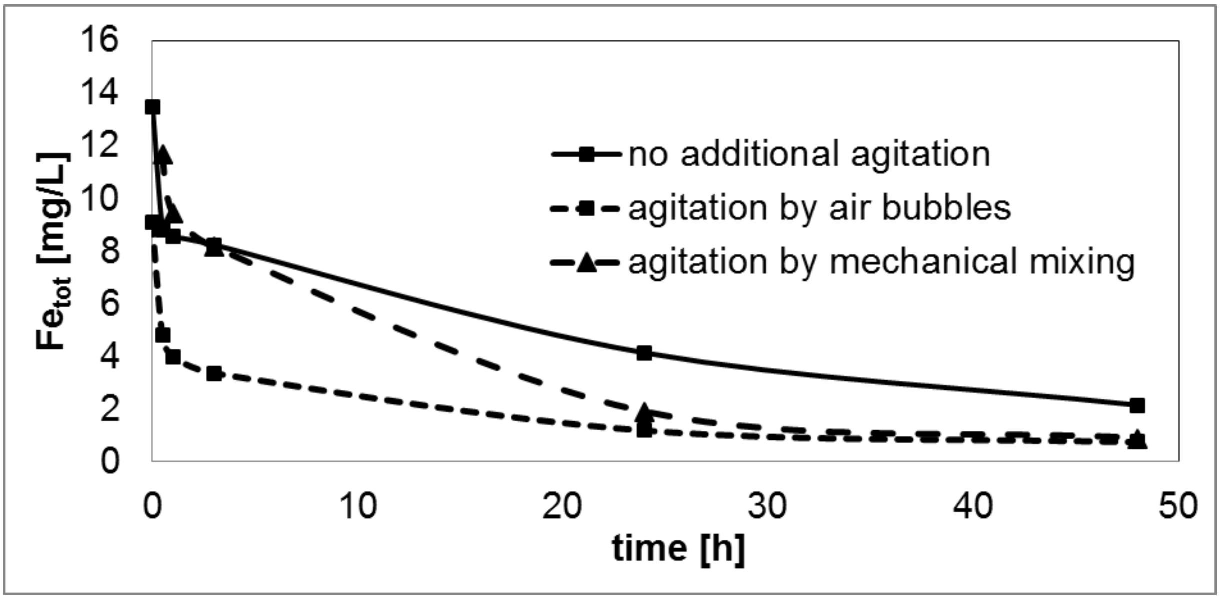
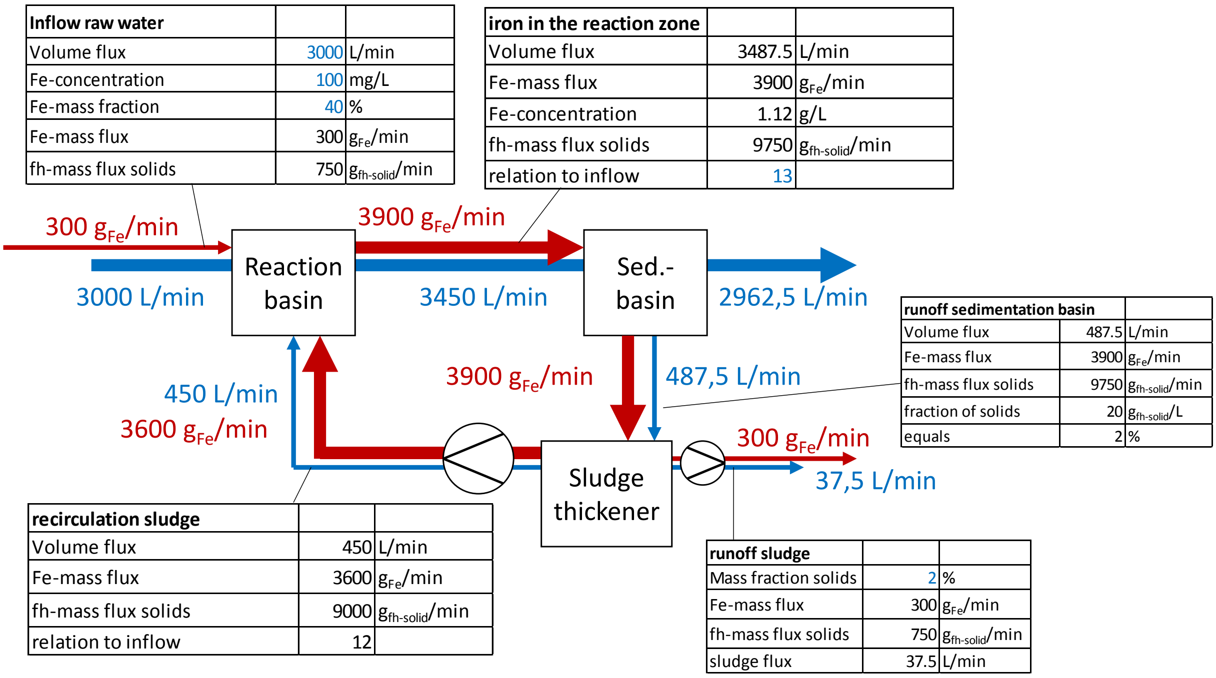


Figure 5 *Investigation of different ways of energy input. Change of total iron concentration with time.*

The bench scale plant was also used to test sludge recycling using mining affected raw waters with high ferrous iron contents up to 100 - 160 mg/L. A large improvement was achievable by sludge recycling in combination with liming. The flocs became much larger (diam. 2-3 mm) and settled within 30 min. *Figure 6* shows the mass balance calculated for the field application.

However, sludge recycling without liming did not improve total iron removal for the low concentrated river waters (Fe(III) ~16 mg/L). No growth or coagulation of the existing flocs was observable. The addition of lime proved to be a prerequisite to support coagulation. It is assumed that the change of the surface charge of the hydroxides due to pH-change is the prerequisite for further floc growth.

The remaining total iron concentration could not be lowered below 1.0 to 0.5 mg/L with any of the tested techniques in all laboratory and bench scale tests. After having reached an iron concentration of 1.0 to 0.5 mg/L only very little additional concentration decline was observable in all tests (*figure 3 to 5*). It is assumed that further reduction of the total iron concentration is only possible with filtration techniques. Yet it is not necessary to lower the iron concentration below this concentration because all current regulatory limits for discharge are met with these concentrations. Furthermore total iron with this concentration is not visible any more.



Inflow raw water		
Volume flux	3000	L/min
Fe-concentration	100	mg/L
Fe-mass fraction	40	%
Fe-mass flux	300	g_{Fe}/min
fh-mass flux solids	750	$g_{fh-solid}$/min

iron in the reaction zone		
Volume flux	3487.5	L/min
Fe-mass flux	3900	g_{Fe}/min
Fe-concentration	1.12	g/L
fh-mass flux solids	9750	$g_{fh-solid}$/min
relation to inflow	13	

runoff sedimentation basin		
Volume flux	487.5	L/min
Fe-mass flux	3900	g_{Fe}/min
fh-mass flux solids	9750	$g_{fh-solid}$/min
fraction of solids	20	$g_{fh-solid}$/L
equals	2	%

recirculation sludge		
Volume flux	450	L/min
Fe-mass flux	3600	g_{Fe}/min
fh-mass flux solids	9000	$g_{fh-solid}$/min
relation to inflow	12	

runoff sludge		
Mass fraction solids	2	%
Fe-mass flux	300	g_{Fe}/min
fh-mass flux solids	750	$g_{fh-solid}$/min
sludge flux	37.5	L/min

Figure 6 *Example of volume and mass fluxes of iron using the high density sludge technique (fh: Ferric hydroxide)*

Conclusions

Sedimentation of iron hydroxides in natural environments has to be accelerated to facilitate the maintenance of ferric hydroxide polluted rivers. To increase floc size and reduce sedimentation time liming is even useful for fully oxidized waters, which are characterized by ferric iron hydroxide colloids and neutral pH-values. Flocculation and sedimentation are intensified by increased pH. Application of mechanic energy can also be used to accelerate flocculation and sedimentation. Flocculation is increasing with higher energy input.

Mixing energy can by applied to the water by different methods (among them stirring with propeller and paddle mixer and air injection). Sludge recycling does very much improve ferric hydroxide retention as long as it is combined with lime addition. Otherwise no improvement was detectable so far. The most effective and energy saving technique will be identified in pilot tests in the field.

It seems that ongoing growth of flocs is inhibited by their surface charge which repels other particles. It is assumed that changing the pH results in a change of the surface charge of the hydroxides and thus enables further coagulation. This is why increase of pH is not only helpful to accelerate ferrous iron oxidation but also to coagulate already existing ferric iron hydroxide flocs.

The results imply that distinct zones of turbulence (e.g. created by rapid of cascade like structures) in the riverbeds could be used to agitate the river waters to increase flocculation. Sedimentation of these flocs could be focused in stillwater areas. Maintenance of the river beds could be limited on zones of iron hydroxide sludge formation. The pilot tests in the field will serve to investigate this approach in more detail.

Acknowledgements

The authors are grateful to the LMBV for funding and supporting this study.

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Open cast mines as river sediment and pollutant sinks. The example Mulde Reservoir (East Germany)

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Abstract

Since 1975, the Mulde River has flown through the abandoned open-cast lignite mining pits at Muldenstein near Bitterfeld (Germany) forming a lake named Mulde Reservoir. Ever since, the Mulde Reservoir has built up a sediment and pollutant deposit protecting the downstream water bodies and sediment quality in the lower Elbe stretch extending to the port of Hamburg area and the North Sea. Therefore, the Mulde Reservoir is an example for beneficial effects of riverine flow-through of pit lakes.

Core drillings have revealed that the sediments currently deposited in the Mulde Reservoir still have to be regarded as highly polluted as to their contents of As, Cd, Cr, Hg, Ni, Pb, Zn, according to the classification of the Pollutant Sediment Management Concept (PSMC) of Elbe River. Arsenic and the mentioned metals originate from former metal mining and processing in the upper part of the catchment of the Mulde River. However, a decrease in pollutant inflow since 1990 has been documented, correlating with the long-term changes observed in the upper course of the Mulde River. As far as organic pollutants are concerned, the lake sediments do not show any excessive concentrations, apart from a few exceptions.

From a geochemical and hydraulic point of view, there is presently no need to remove the contaminated sediments from the Mulde Reservoir. Main activities in sediment management should focus on further improving stabilization and efficiency of the Mulde Reservoir sedimentation zone and its transregionally vital ecosystem services. Given the present retention capacity of the Mulde Reservoir, it will continue to serve as an important sediment trap of supra-regional significance for the downstream water courses for at least another 770 years.

Key words: pit lake, Mulde Reservoir, sediment deposit, sediment management, sediment quality

Introduction

Open cast lignite mining released a lot of pit lakes in Germany (Schultze et al. 2013). Further lakes will form in future when currently operated mines are abandoned and remediated. Like natural lakes and also reservoirs (Wetzel 2001; Knoll et al. 2013; Frings et al. 2014), pit lakes are basically sinks for many kinds of matter in the landscape and in river systems. They act as big sediment traps. Biogeochemical processes inside the lake may produce additional sediment, e.g. via sedimentation of dead plankton or precipitation of calcite due to high photosynthetical activity in the lake (Wetzel 2001). In the Island Copper Mine pit lake (Vancouver Island, Canada), this is used to remove and deposit metals from acid rock drainage as technology to protect the environment (Wen et al. 2015).

Regions with long lasting metal mining activities often experienced contamination of river water, river sediments, floodplain soils and even estuaries with metals (Macklin et al. 1997; Krüger et al. 2005; Olias et al. 2006; Foulds et al. 2014), in extreme dimensions in case of breaches of tailings ponds (e.g. Hudson-Edwards 2016). The legacy of mining and related smelting and industrial activity often lasts long in aquatic sediments and floodplain soils (e.g. Coulthard et al. 2003; Förstner 2004; Resongles et al. 2014). Managing such sediments is complicated due to resuspension by floods and since dredging (e.g. in harbors) causes resuspension and high effort for treatment and safe deposition of the dredged material (Detzel et al. 1998; Förstner 2004).

The so called Mulde Reservoir (Germany) is basically a pit lake which is used as a reservoir. The Mulde River is flowing through it. Much of the inflowing suspended matter load is deposited in the Mulde Reservoir. We present the results of sediment investigations and the cleaning of the river water caused by sedimentation of the suspended matter. The focus is on arsenic and metals.

Study site

The Mulde Reservoir (fig. 1) is one of the pit lakes resulting from lignite mining in the northern part of the Central German lignite mining district (Schultze et al. 2010; Eissmann and Junge 2015). As indicated by the pit lakes shown in panel A of fig. 1, Mulde Reservoir is embedded in a region which was heavily impacted by lignite mining. Mulde Reservoir originated from the mine Muldenstein which was operated from 1955 to 1975. During this time, $126 \text{x} 10^6$ t of lignite were produced and $439 \text{x} 10^6$ t of overburden were excavated (Liehmann et al. 1998). When mining ceased, the remaining mining void was filled with water from Mulde River (initially 3-10 m^3/s, beginning at April 30, 1975; Liehmann et al. 1998; Böhme et al. 1994). Eventually the complete Mulde River was diverted into the new lake at March 4, 1976. In this way, the no longer used natural stretch of Mulde River and the accompanying floodplains were included into mine Goitsche which was operated a few kilometers to the west of mine Muldenstein since 1949 and which ended up in the two pit lakes immediately west of Mulde Reservoir in fig. 1 (Liehmann et al. 1998; Eissmann and Junge 2015).

In order to use the new lake as a reservoir, a dam was constructed at the outflow. It allows for a maximum water level of 82 m above sea level (a.s.l.) in case of high flow in Mulde River. The water level can be controlled between the minimum water level of 76.1 m a.s.l and the normal goal of water level management at 79.25 m a.s.l. (Böhme et al. 1994). At the latter level, the Mulde Reservoir has a surface area of about 6.1 km^2 and a maximal depth of 32 m (Junge 2015). The maximum storage volume is $135.5 \text{x} 10^6$ m^3 containing an exceptional storage volume for flood protection of $17.5 \text{x} 10^6$ m^3 and a normally managed storage volume of $18.0 \text{x} 10^6$ m^3 (Böhme et al. 1994). In 2009, a fish pass was added to the outflow dam to allow for re-colonization of the upper stretches of Mulde River and its tributaries by salmon (Wouters 2010).

Panel C of fig. 1 shows a bathymetric map of Mulde Reservoir. The lake basin consist of two sub-basins, Main Basin and Friedersdorf Basin which are connected by a channel-like part of the former mine void. There is a ridge-like structure crossing the Main Basin from south west to north east (fig. 1, panel C). It is the remnant of a paleo-beach-dune-system from the time when the lignite forming peat was deposited about 20 million years ago (Eissmann 2002).

In the upper part of the catchment, Mulde River has two branches, Freiberger Mulde and Zwickauer Mulde. Downstream the confluence of both branches, the full name is Vereinigte Mulde (fig.1A). However, we use only Mulde River for simplification.

The catchment size of Mulde Reservoir is 6,709 km^2 and the long term average annual inflow is $2{,}097 \text{x} 10^6$ m^3/a (Böhme et al. 1994). The highest elevation of the catchment is 1,243 m a.s.l. (Peak Klinovec, Czech Republic)., The nearest gauge upstream the Mulde Reservoir with a long term hydrological record is located in Bad Düben, about 15 km upstream (fig. 1, panel A). For the period 1961 to 2012, the average low flow was 15.8 m^3/s, the average flow was 64.7 m^3/s and the average high flow was 487 m^3/s (all data for hydrological years; LHW 2015). The highest daily average flow of the period 1961-2012 was 2,200 $m/^3$ at August 14, 2002 (LHW 2015). A further exceptional flood occurred in June 2013 with a maximum daily average of 1,720 m^3/s (Junge 2015).

Active mining in the upper part of the catchment area of Mulde River began in 1168 and basically ending in the 1990s (Hösel et al. 1997; Greif 2015). It was mainly metal mining with some hard coal mining around Zwickau. Panel A of fig. 1 shows the major centers of the mining in the Ore Mountains where the headwaters of Mulde River are located. However, there were also smaller mining activities between the marked centers. Mining in the Ore Mountains was almost exclusively underground. It started with silver and went on with tin and a second boom of silver mining (beginning in the 13th century). In the 18th century, also bismuth, cobalt and nickel became relevant while in the 19th century lead, zinc, fluorite and barite were in the focus of the mining activities. Hard coal and in particular uranium were the main targets of mining in the 20th century (Hösel et al. 1997). All the time, mining was accompanied by smelting and in the last two centuries also by diverse metal using industries (Greif 2015).

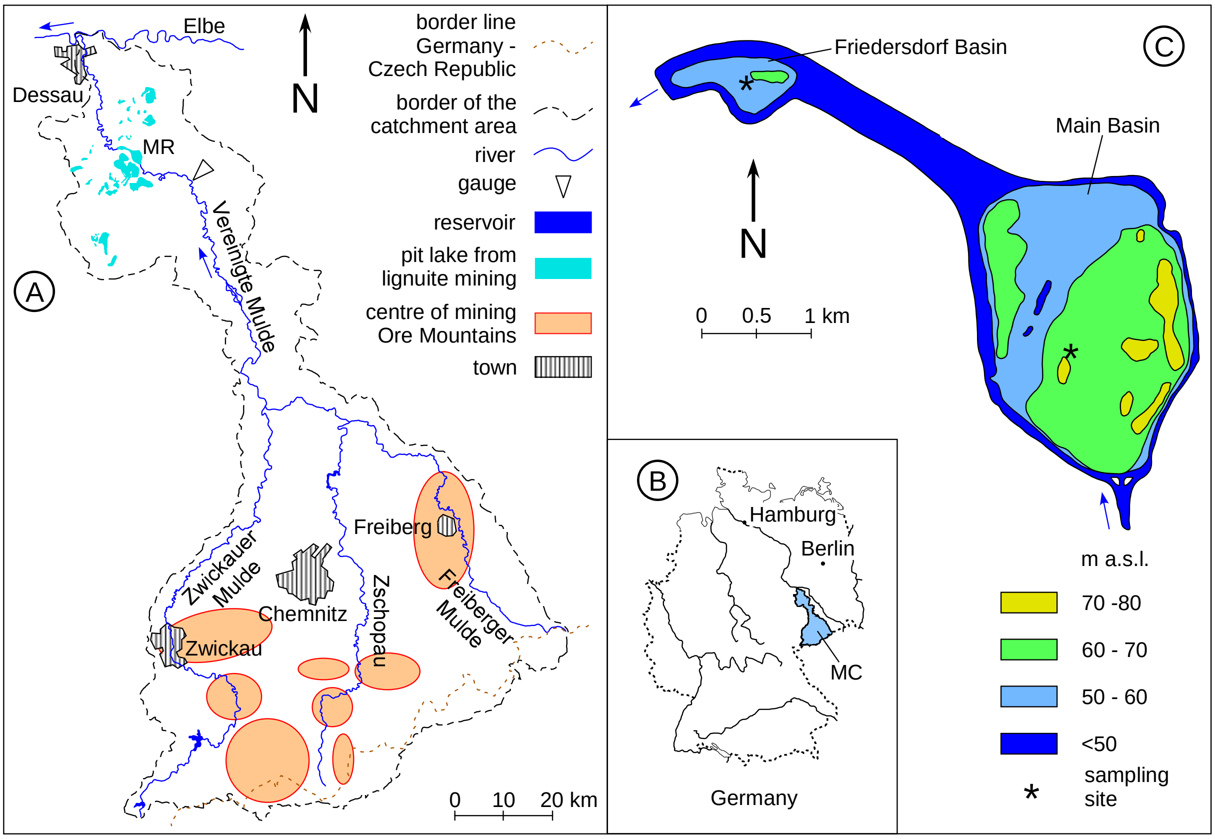

Figure 1 *Location of the study site. Panel A: Catchment area of Mulde River including Mulde Reservior (MR). Panel B: Location of the catchment area of Mulde River (MC) in Germany. Panel C: Bathymetric map of Mulde Reservoir*

Methods

Sediment cores were extracted by gravity coring (UWITEC, Mondsee, Austria) from the Main Basin and from the Friedersdorf Basin (fig. 1, panel C) in April 2002, September 2002, July 2012 and July 2013. Samples were taken from the cores according to the visible layers.

Samples were prepared according to Junge et al. (2004) and Klemm et al. (2005), i.e. only the fraction <20 µm was analyzed. Analyses were performed by the laboratories of the group Pollutant Dynamics in Catchments of the Saxon Academy of Science (Leipzig, Germany) and of UFZ Department Analytics (Leipzig, Germany) for samples from 2002 and by Labor Eurofin (Freiberg, Germany) for samples from 2012 and 2013 according to standard methods (DIN EN ISO 17294-2, DIN EN 1483, DIN ISO 10382, DIN EN 11308, DIN 38414 S24). Organic pollutants were analyzed only from cores taken in 2012 and 2013, i.e. only in the uppermost about 30 cm of sediment. For more details see Junge et al. (2004), Klemm et al. (2005) and Junge (2013).

Results and discussion

Concentrations of contaminants and their evaluation

Collected sediments showed clear layering (fig. 2). Light colored layers were separated by dark colored layers rich in organic material. The light colored layers were identified as originating from floods and the dark colored layer as representing periods between floods. Together with the detection of the Tschernobyl peak by ^{137}Cs activity, reliable dating of the layers was possible (Junge et al. 2004). Based on the found concentrations and knowledge of changes in the catchment area regarding treatment of waste water, handling of wastes in mining and industry and the general development of industrial activities in eastern Germany after German reunification in 1990, four different periods of sediment deposition can be distinguished in Mulde Reservoir: the period of highest contaminations from the time before 1990, a first period of decreasing contamination from 1990 to 2002, the deposits of the exceptional flood in August 2002 and a second period of decreasing contamination after 2002. Arsenic and metals concentrations are presented in tab. 1 according to these periods. Fig. 2 shows the results for a core taken in the Friedersdorf Basin in July 2013, including the fresh deposits of the exceptional flood in June 2013.

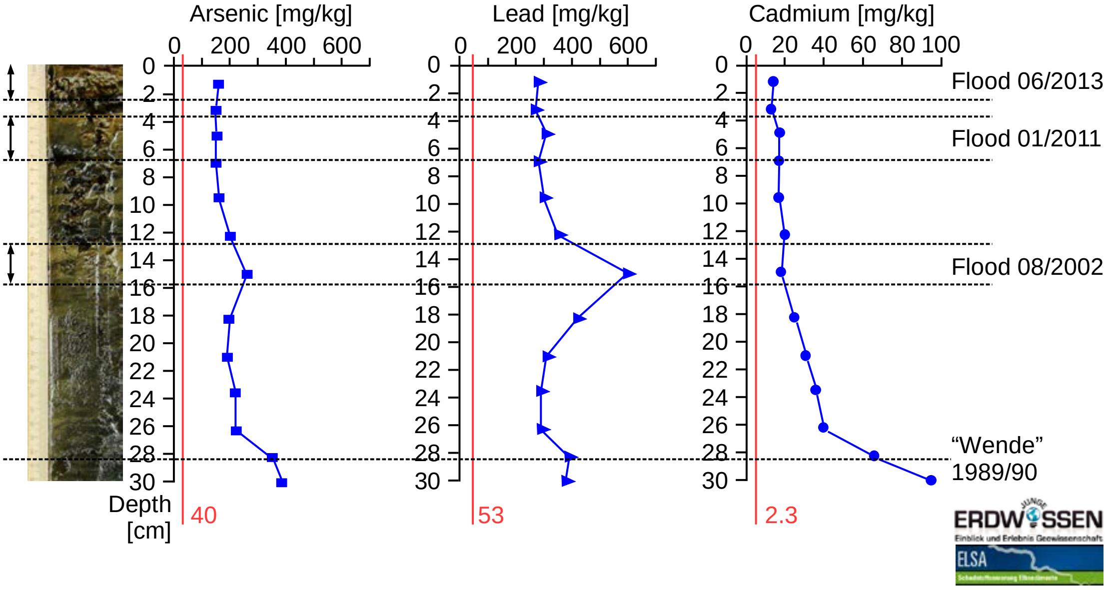

Figure 2 *Sediment characteristics of a core taken in Friedersdorf Basin in July 2013. From left to right: Photograph of the sediment core, concentrations of arsenic, lead and cadmium in mg/kg versus depth in the sediment (in cm). Vertical red lines and red numbers indicate the upper thresholds of the PSMC in mg/kg (ICPE 2014). "Wende" is the common German term for the crash of the former German Democratic Republic and the German reunification 1989/90.*

Three relatively thick light colored layers are visible in the photograph (fig. 2. They result from the three flood events in August 2002 (peak flow at gauge Bad Düben 2200 m^3/s), in January 2011 (peak flow at gauge Bad Düben 730 m^3/s) and in June 2013 (peak flow at gauge Bad Düben 1720 m^3/s). They represent the ranks 1, 2 and 6 in the ranking of daily average peak flows of floods in the data series 1961 to 2013 (LHW 2012). Concentrations of arsenic, lead and cadmium show a general decreasing trend with the highest decrease rate at the beginning of the 1990s, linked to the stop of mining and many industrial activities in the catchment. Later on, remediation of former mining and industrial sites and implementation of adequate waste water treatment became the most relevant reasons for improvement of the sediment quality (e.g. Greif 2015). The flood event of 2002 caused a considerable temporal increase in the concentration of lead which was much less pronounced for arsenic and cadmium and for the other two flood events. The background is the considerable erosion of mining and smelting wastes by the flood in 2002 which were deposited immediately at the banks of the Mulde River near Freiberg (Klemm et al. 2005).

In order to asses sediment quality and the extent of sediment contamination as well as to develop measures for improvement of sediment quality and prioritize such measures in the framework of a polluted sediment management concept (PSMC) according to the EU Water Framework Directive (EU 2000), the International Commission for the Protection of the Elbe River (ICPE) developed thresholds for a set of 29 contaminants which were identified to be most relevant for sediments in the catchment of Elbe River (ICPE 2014). These thresholds are included into tab. 1 for evaluation of the measured concentrations. While concentrations below the lower threshold indicate that good sediment quality can be reached without problems, exceedance of the upper threshold indicates the need for a source-related assessment of the risk (ICPE). All analyzed metals except chromium exceeded the upper threshold (tab. 1). Sources of metals and of arsenic are known and diverse measures were already undertaken or underway to reduce the contamination of the suspended matter in Mulde River and, thus, the concentrations of contaminants in the sediments deposited in Mulde Reservoir (Paul et al.

2013; Greif 2015). However, the work is not finished yet and widespread diffuse contaminations of soil exist around historical smelters or in aquatic sediments in the tributaries of Mulde River, which may be mobilized during floods and can hardly be fully controlled in future (Förstner 2004).

Table 1 *Concentrations of metals and arsenic in the sediment of Mulde Reservoir (averages of all analyses available for the different deposition periods) and thresholds of PSMC. Depth ranges mean depth below sediment surface. MB – Main Basin, FB – Friedersdorf Basin, data in parentheses - range from minimum to maximum; n – number of available analyses.*

	As mg/kg	Cd mg/kg	Cr mg/kg	Cu mg/kg	Hg mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
Lower threshold of PSMC	7.9	0.22	26	14	0.15	3	25	200
Upper threshold of PSMC	40	2.3	640	160	0.47	3	53	800
Period 2002-2012 Depth ranges MB: 0-50 cm FB: 0-12 cm	188 (130-300) n=32	21 (16-27) n=32	77 (62-87) n=32	140 (110-170) n=32	0.8 (0.46-1.1) n=32	78 (67-100) n=32	292 (210-370) n=32	1593 (1200-2060) n=32
Flood 2002 Depth ranges MB: 50-55 cm FB: 12-15 cm	230 (220-240) n=3	24 (15-32) n=8	88 (82-93) n=3	175 (160-187) n=8	1.0 (1.0-1.0) n=3	82 (78-90) n=8	549 (313-866) n=8	1685 (1240-2103) n=8
Period 1990-2002 Depth ranges MB: 55-110 cm FB: 15-30 cm	286 (170-440) n=14	45 (17-136) n=59	122 (74-220) n=14	198 (73-400) n=59	0.82 (0.57-1.4) n=14	99 (59-160) n=59	309 (88-477) n=59	2044 (527-3450) n=59
Period 1975-1990 Depth ranges MB: 110-200 cm FB: 30-50 cm	471 (260-620) n=13	104 (38-230) n=47	237 (150-380) n=13	372 (159-600) n=47	1.5 (0.9-2.6) n=13	136 (89-220) n=47	386 (243-590) n=47	2847 (1595-5000) n=47

Organic pollutants were investigated in the sediment of Mulde Reservoir first time in 2012 and 2013. Concentrations were highest in the old sediments originating from the period before 1990. The majority of concentrations were well below the upper threshold of the PSMC (ICPE 2014), in particular in surface layers of the sediment. Only DDT (1,l,1-trichloro-2,2-bis(p-chlorophenyl)ethane), some of its metabolites and fluoranthene considerably exceeded the PSMC thresholds(ICPE 2014), slightly even in the surface sediment. DDT and its metabolites certainly have two sources: widespread remnants of DDT use in the past and known contaminations resulting from a production site of DDT and other chlorinated organics in Delitzsch. The Lober-Leine-Kanal, a creek draining the area around Delitzsch, enters the Mulde River only about two kilometers upstream the inflow of the Mulde Reservoir.

Retention of contaminants in Mulde Reservoir

Zerling et al. (2001) summarized the results of investigations of the metal and arsenic content of suspended matter entering and leaving the Mulde Reservoir in the period 1992 to 1997 (tab. 2). The most important finding was that the deposition of suspended matter in the Mulde Reservoir considerably contributes to the limitation of the contamination of Elbe River, its sediments and flood plains downstream the mouth of Mulde River and also the North Sea (tab. 2). This is even more important as the Mulde River is one of the main contributors of metals and arsenic for Elbe River (e.g. Pepelnik et al. 1997). Only for mercury, the Mulde Reservoir is not such a relevant sink. The mercury introduced into Elbe River by the Mulde River almost completely originates from the former chlorine production in Bitterfeld and related contaminations, located downstream the Mulde Reservoir (Hintelmann and Wilken 1994; Brandt 2003). Our sediment investigations (fig. 2, tab. 1) confirm the results of Zerling et al. 2001.

***Table 2** Load of arsenic and metals trapped in Mulde Reservoir (averages for the period 1992-1997) related to total input as suspended matter by Mulde River and to total load of Elbe River at Schnackenburg(Germany) (Zerling et al. 2001).*

	Cu	Pb	Zn	Cd	Cr	Ni	Co	As	U
Trapped load [t/a]	22	35	192	4.1	12	12	3.2	19	5.0
Trapped load [% of input]	71	84	50	72	71	32	56	52	39
Trapped load [% of load of Elbe River]	23	51	16	90	21			27	

An important aspect regarding sediment quality evaluation and trapping of contaminants is the long term stability of the binding of arsenic and metals in Mulde Reservoir sediments. Conditions in the sediment are reductive and neutral. Accordingly, the formation of sulfides of very low solubility can be considered. There is no evidence of mobilization of contaminants like the decrease of their concentration in deeper layers over time when comparing results from 2002 with that of 2012 and 2013. In addition, the length of diffusion paths to the sediment surface is permanently increasing due to the deposition of new sediment, in particular for the most contaminated sediments in deeper layers. Close to the inflow, older sediments are gradually covered by sand and gravel which are deposited there and already filled up a small part of Mulde Reservoir and formed the two small islands in the inflow part (fi. 1, panel C). Since no changes in redox state or acidification have to be expected and sediment resuspension can be excluded at the lake bottom (the main potential causes for re-mobilization of contaminants from sediments according to Förstner (2004)), there is no considerable risk that the sediments turn from being a sink to being a source of contaminants within timescales relevant for planning in river basin management. Gradual covering of contaminated sediments by sand and gravel is even comparable with artificial capping, one of the options for in situ treatment of contaminated sediments (Förstner 2004).

The deposition of sediments, sand and gravel will fill up the Mulde Reservoir gradually. This raises the question “How long will Mulde Reservoir remain a considerable trap for contaminants from the catchment of Mulde River?” Estimates of sediment accumulation based on the sediment investigations and considering the dynamics of sedimentation in the Main Basin and the Friedersdorf Basin result in a period of about 650 years for continued sedimentation in the Main Basin and additional about 120 years of continued sedimentation in the Friedersdorf Basin, i.e. in summary about 770 years (for details of the applied methodology see Junge 2013).

Conclusions

Mulde Reservoir as an example demonstrates the potential beneficial effect of riverine flow-through of pit lakes. In this case, the effect is even relevant for part of the North Sea. Valente et al. (2015) support our findings and their evaluation: Considerable retardation of metals and arsenic in reservoir sediments was identified in the Rio Tinto basin which is also highly contaminated by long lasting mining and source of contaminations of global relevance (Olias et al. 2006). This is in line with evaluation of river flow-through of pit lakes by McCullough and Schultze (2015). Basically, reservoirs or natural lakes can have comparable effects. However, this finding and the resulting management option to mitigate environmental adverse impacts of mining via riverine flow-through of pit lakes, reservoirs or natural lakes does not allow for being less strict in preventing contaminations already during mining and as close as possible to the mining sites. Not only the river stretches downstream of pit lakes like Mulde Reservoir need to be protected, but also the ones upstream of them.

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Modelling pH and alkalinity in rivers impacted by acid mine drainage

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Abstract

A model that simulates pH and alkalinity when a river stream is impacted by acid mine drainage or other acidic discharge was developed using the theories of alkalinity and pH in natural waters. The main assumption of the model is that the mixing of the water from the river and acidic discharge is instantaneous. The main principles used in the modelling are that, the total inorganic carbon and total alkalinity are conservative with respect to mixing. Two approaches are used to do simulation using the model: considering the change of volumetric flow of acidic discharge assuming constant pH and considering the change of pH of acidic discharge assuming constant volumetric flow. The modelled results capture clearly the buffer effect of carbonic acid in water.

Furthermore, the model was applied to simulate possible acidification of the main stream of Zambezi River due to acid mine drainage from coal mining. From simulated results it was concluded that the pH of the main stream of Zambezi River will drop to values below 6 if the pH of the water of tributaries coming from the mining area goes below 3.The model is developed to be used to simulate the resulting pH and alkalinity in rivers impacted by acidic discharge but it can be extended to simulate acidification of lagoons or other similar processes. In practice, the model can be used as a decision support tool by authorities for granting new mining licenses, and by different industries that produce acidic wastewaters to manage their discharges to the environment.

Key words: Modelling, alkalinity, river, water quality, acid mine drainage

Introduction

Nowadays, mining activity is common in most developing countries and it brings revenues to the governments (Nhantumbo, et al. 2015). However, mining is also linked to severe impacts to the environment and the water resources can be seriously affected by acid mine drainage (AMD) (Ochieng, et al., 2010; DPLF, 2014; Mishra, et al. 2012). Developing countries lack water quality monitoring programs to assess the impact of mining on the water resources (Nhantumbo, et al. 2015). Financial and other resources limit the possibility of improving the water quality monitoring programs, if such programs exist.

Therefore, the use of indirect methods such as modelling is an alternative avenue to predict water quality changes without extensive sampling and analysis required in the water quality monitoring programs. However, the existing water quality models are not appropriate to simulate rivers impacted by AMD with limited data, and they were not developed to simulate acidification of rivers, which has additional complication (Mosley, et al., 2015; Mosley, et al. 2010).

In this paper we develop a model to simulate the pH and alkalinity in rivers impacted by acid mine drainage or other acidic discharge at the mixing zone. The model can be used to simulate the minimum flow or the high pH of the acidic discharge that would cause a potentially detrimental drop of the pH of the recipient river. The model can also be applied to simulate the discharge of acidic wastewater into lakes, lagoons or similar. The model can be used by water quality monitoring agencies to define limits and standards for acidic wastewater discharges, as well as by mining companies to manage their discharges in terms of flows and acidity.

Methods

Theories of alkalinity and pH in natural waters were combined to develop a model which is easy to apply since it minimizes the input data. The model uses as input pH, alkalinity, flow and average temperature of both, the river water and the acidic discharge, see (fig. 1). When simulating the discharge of a certain volume of water into a body of water such as a lake or lagoon the volumetric flows Q_1, Q_2, and Q_R in m^3/s are replaced by volumes V_1, V_2, and V_R in m^3.

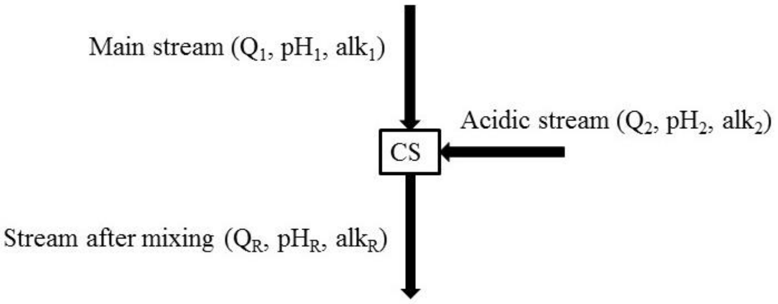

Figure 1 *Schematic representation of the simulated conditions. Q_1, pH_1, alk_1 are the volumetric flow, pH and alkalinity of the main stream. Q_2, pH_2, alk_2 are the volumetric flow, pH and alkalinity of the acidic stream. Q_R, pH_R, alk_R are the volumetric flow, pH and alkalinity of the stream resulting from mixing of the main stream and acidic stream. CS = completely stirred.*

In the development of the model it is assumed that when the streams merge, complete mixed conditions are instantaneously obtained. This is reasonable assumption when dealing with small streams at high velocity. When the streams are large the assumption is less accurate since it might take quite a long distance to have the two streams completely mixed.

There are also two main principles used in the modelling. These principles state that, the total inorganic carbon and total alkalinity are conservative with respect to mixing (Wolf-Gladrow, et al. 2007; Munhoven 2013). The total inorganic carbon (*TIC*) used in the model development is defined by (eq. 1). Carbon acid alkalinity (*TA*) is the only alkalinity considered in the modelling and it is defined by (eq. 2).

$$TIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \qquad (1)$$

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (2)$$

The concentration of ions in the main steam and in the acidic discharge are calculated using the protolithic water theory and carbonic acid equilibrium theory by (eq. 3, 4, 5, 6 and 7). alk is the alkalinity of the main stream or acidic discharge according to (fig. 1). The equilibrium constants k_w, k_{a1} and k_{a2} are temperature dependent and calculated using empirical equations (Appelo C A J 1999).

$$[H^+] = 10^{-pH} \qquad (3)$$

$$[OH^-] = \frac{[H^+]}{k_w} \qquad (4)$$

$$[CO_3^{2-}] = \frac{alk - [OH^-] + [H^+]}{2 + [H^+]/k_{a2}} \qquad (5)$$

$$[HCO_3^-] = \frac{[H^+] \cdot [CO_3^{2-}]}{k_{a2}} \qquad (6)$$

$$[H_2CO_3]=\frac{[H^+]\cdot[HCO_3^-]}{k_{a1}} \tag{7}$$

Total inorganic carbon and total alkalinity in the resulting stream from the mixing of the main stream and acidic water are calculated based on the two main principles of the model as expressed in (eq. 8, and 9) respectively.

$$TIC_R=\frac{TIC_1\cdot Q_1+TIC1_2\cdot Q_2}{Q_1+Q_2} \tag{8}$$

$$TA_R=\frac{alk_1\cdot Q_1+alk_2\cdot Q_2}{Q_1+Q_2} \tag{9}$$

Concentrations of carbonate ions in the resulting stream can be written as a function of $[H^+]$ only, (eq. 10, 11 and 12).

$$[H_2CO_3]=\frac{[H^+]^2}{[H^+]^2+k_{a1}\cdot[H^+]+k_{a1}\cdot k_{a2}}\cdot TIC_R \tag{10}$$

$$[HCO_3^-]=\frac{k_{a1}\cdot[H^+]}{[H^+]^2+k_{a1}\cdot[H^+]+k_{a1}\cdot k_{a2}}\cdot TIC_R \tag{11}$$

$$[CO_3^{2-}]=\frac{k_{a1}\cdot k_{a2}}{[H^+]^2+k_{a1}\cdot[H^+]+k_{a1}\cdot k_{a2}}\cdot TIC_R \tag{12}$$

(Eq. 13) is obtained replacing the concentrations of $[OH^-]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ using (eq. 4, 11 and 12) in (eq. 2). The only unknown in (eq. 13) is $[H^-]$.

$$TA_{R'}=\frac{k_{a1}\cdot[H^+]+2k_{a1}\cdot k_{a2}}{[H^+]^2+k_{a1}\cdot[H^+]+k_{a1}\cdot k_{a2}}\cdot TIC_R+\frac{k_w}{[H^+]}-[H^+] \tag{13}$$

(Eq. 13) can be written in the form $f(x) = 0$, where x is the hydrogen ions concentration $[H^-]$, and solved numerically using the Newton-Raphson method. The solution of the model was further converted into a computer code using Matlab.

The model developed can be used to simulate contamination of rivers using two different approaches: considering the change of volumetric flow of acidic discharge assuming constant pH or considering the change of pH of acidic discharge assuming constant volumetric flow (fig. 2 and 3), respectively. The (fig. 2 and 3) show results from hypothetic simulation in order to demonstrate the kind of results that can be generated by the model. The values of pH of the main stream and acidic discharge for hypothetic simulation were selected to allow visualization of the quality of the results for a broad range of pH. The alkalinity was selected relatively high to allow the visualization of buffer effect of carbonic acid in water.

Using the two different simulation approaches it is possible to generate graphs showing the resulting pH as function of Q_2/Q_1 for the volume change simulation and as function of pH_2, for the pH change simulation, (fig. 2a and 3a). These kind of results makes it possible to identify the volumetric flow and the pH of the acidic discharge that lowers the pH in the main stream to a predefined threshold. Further analysis can be done by generating the (fig. 2b and 3b). The last two figures show the concentration of carbonate ions, total inorganic carbon and total alkalinity in the resulting stream.

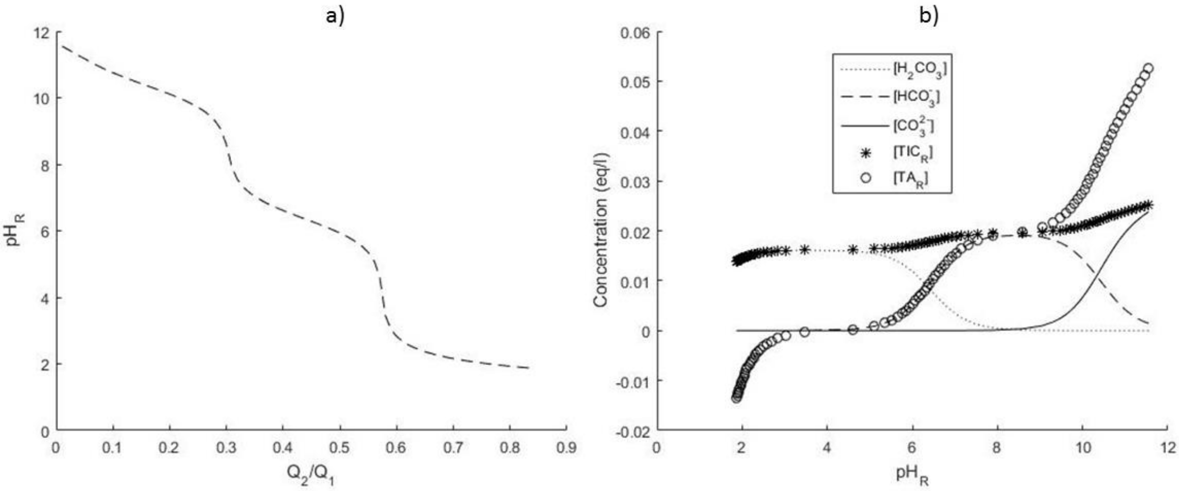

Figure 2 *Hypothetic simulation varying the volumetric flow of the acidic discharge (Q_2). All other parameters are kept constant.($pH_1 = 11.6, alk_1 = 0.05$ eq/l, $pH_2 = 1.1$ and $alk_2 = -0.09$). a) pH in the resulting stream after complete mixing of main stream (1) and acidic discharge (2). b) concentration of carbonate species, hydrogen and hydroxide ions after complete mixing of main stream (1) and acidic discharge (2) in eq/l.*

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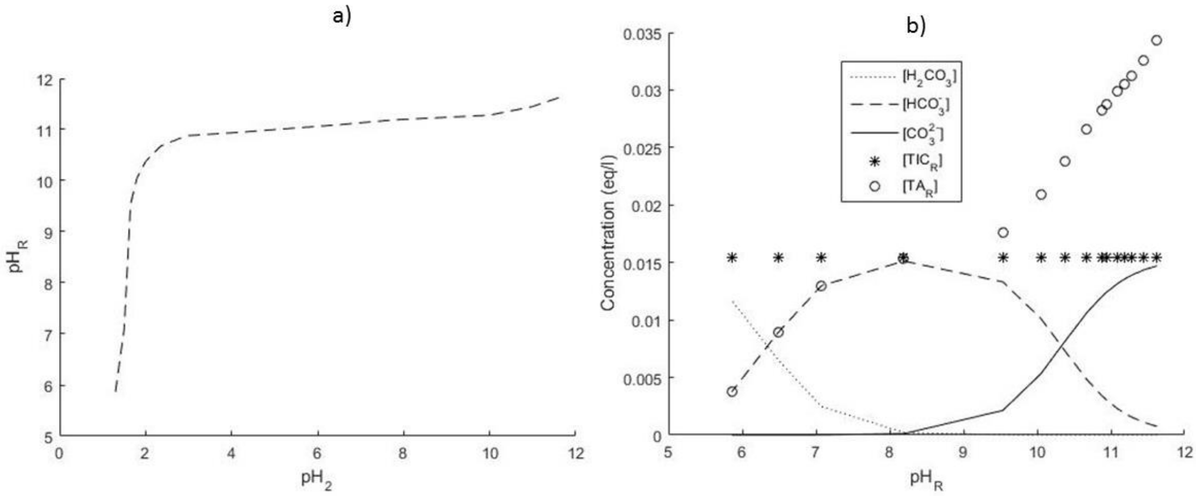

Figure 3 *Hypothetic simulation varying the pH of the acidic discharge (pH_2). The alkalinity of the acidic discharged is computed by the model based on pH_2 and its initial alkalinity. All other parameters are kept constant. ($pH_1 = 11.6$ and $alk_1 = 0.06$ eq/l). a) pH in the resulting stream after complete mixing of main stream (1) and acidic discharge (2). b) Concentration of carbonate species, hydrogen and hydroxide ions after complete mixing of main stream (1) and acidic discharge (2) in eq/l.*

Furthermore data from Zambezi River in Mozambique was used to illustrate a practical application of the model. Zambezi River Basin is the major river basin in Southern Africa with an area of 1.370.000 km^2 and the average discharge at the outlet of 4100 m^3/s. The river is essential for the economy of its riparian countries, which include Angola, Botswana, Malawi, Mozambique, Namibia, Tanzania, Zambia, and Zimbabwe and its outlet is located in Mozambique (Nhantumbo 2013), (fig. 4).

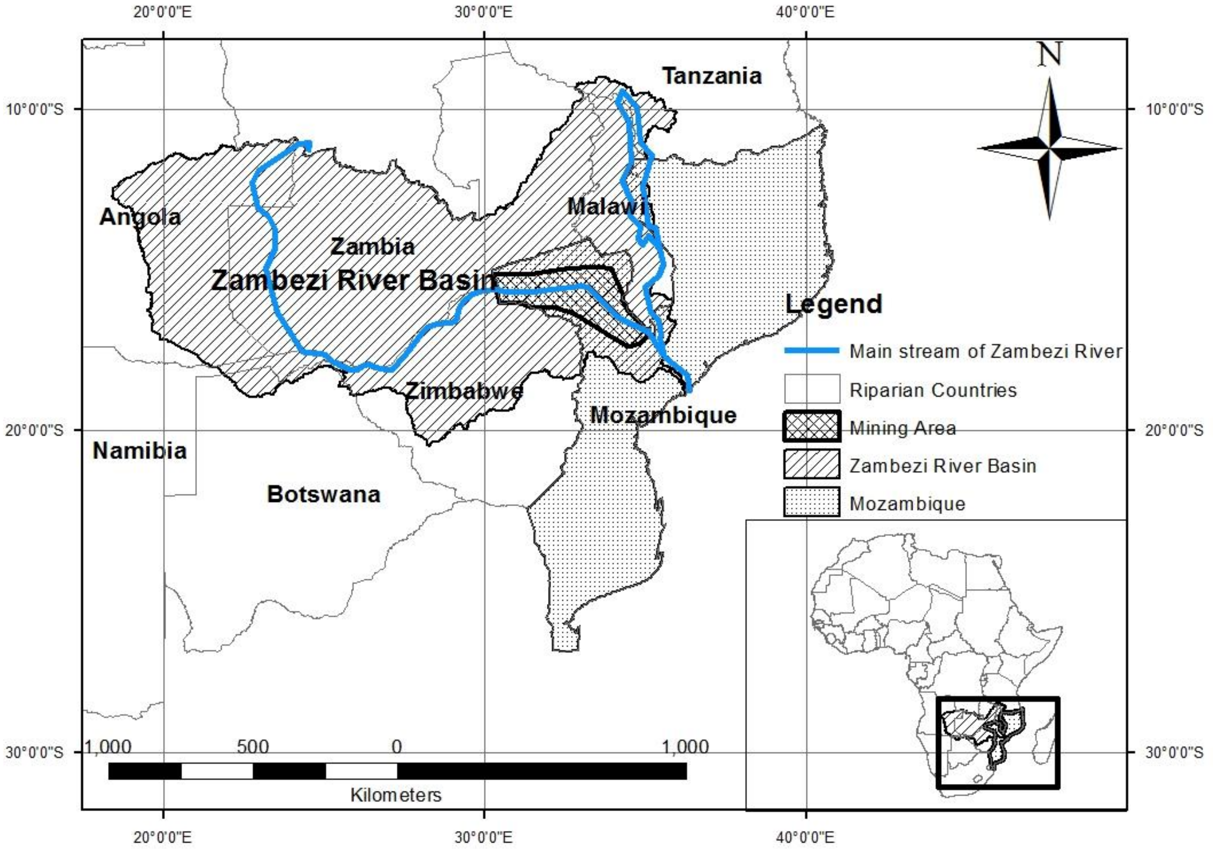

Figure 4 *Zambezi River Basin*

Three major coal reserves of Mozambique are located in the Zambezi River Basin area. Since the last decade, a number of coal mining companies started to exploit coal in the coal reserves and the water quality is at risk of being impacted by acid mine drainage (Nhantumbo 2013). The water quality monitoring agency is not well established to assess the water quality changes and to take actions to protect the water resources. Further on, the lack of resources limits improvement.

It is assumed that the average flow of the main stream and the water coming from the tributaries do not change a lot and that acid mine drainage can lower the pH of the water coming from the mining area with time. If the major interest is to protect the main stream because it sustains life of the people living in the riparian area of the river basin, it is important to guarantee that the water coming from the mining area does not lower its pH to values that may seriously harm the environment. Fish populations, for example, start to reduce when the pH is below 6 (Jennings, et al. 2008). Thus, it is important to guarantee that the pH in the main stream does not go below that limit.

Table 1*. Input data from Zambezi River used for simulation (Nhantumbo 2013)*

	Main Stream of Zambezi River (1)	Tributaries coming from the mining area (2)
Flow Q ,m^3/s	2330	1120
pH	7.6	7.85 (considering varying to 2)
Alkalinity mg/l. $CaCO_3$, (eq/l)	62 (0.00124)	129 (0.00384)

The input data used for simulation, both of the main stream of Zambezi River and tributaries coming from the mining area is given in (tab. 1). The flows and the pH used for simulation are the average values and the simulated results are affected by these averages. However, the simulated results can be used as a clue on what is going to happen in the main stream of the river if the pH of the water of the tributaries coming from the mining area drops. For simulation, the pH of water coming from the tributaries in the mining area was considered to reduce from its original value 7.85 to 2.

By simulation with the presented model in can be shown (see fig. 5a) that the pH of the main stream will drop to values below 6 if the pH of the water coming from the tributaries is below 3. Supplementary information about the carbonate species (H_2CO_3, HCO_3^-, CO_3^{2-}), total inorganic carbon (TIC), total alkalinity in the main stream (TA_R) is given in (fig. 5b).

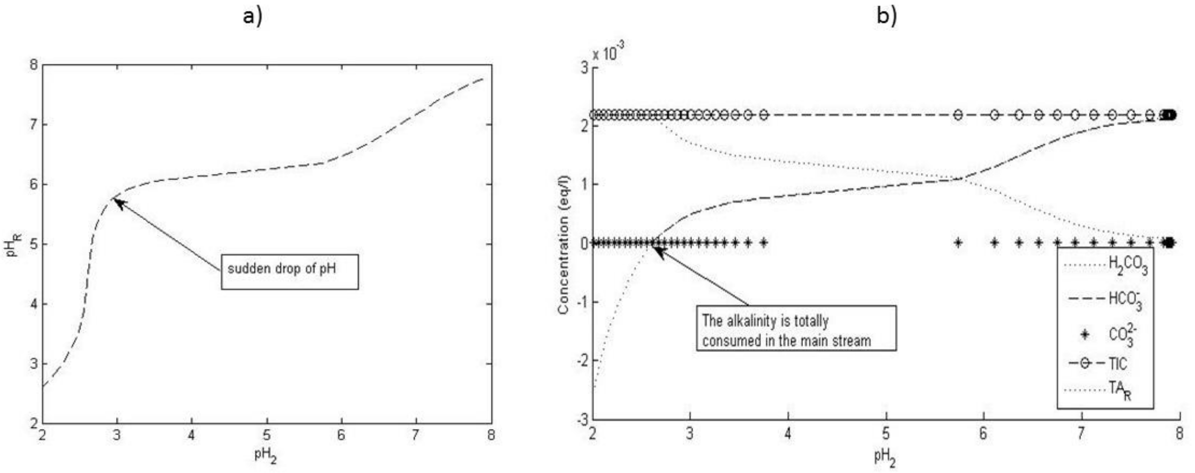

Figure 5 Simulation results for acidification of the main stream of Zambezi River. a) pH in the resulting stream after complete mixing of main stream (1) and potential acidic water coming from the mining area (2). b) Concentration of carbonate species, hydrogen and hydroxide ions after complete mixing of main stream (1) and potential acidic water coming from the mining area (2) in eq/l. Input data is given in (tab. 1).

Conclusions

A model that simulates pH and alkalinity when acid mine drainage or other acidic water is discharged into a river was developed based on the theories of alkalinity and pH in natural waters. The model is based on input of flow, pH, alkalinity and average temperature of both, the main stream and acidic discharge. The model was developed assuming complete mixing immediately after the river and the acidic water merge. The model can do simulations considering two different approaches: the change of volumetric flow of acidic discharge assuming constant pH and the change of pH of acidic discharge assuming constant volumetric flow. The modelled results capture clearly the buffer effect of carbonic acid in water.

Furthermore, the model was applied to simulate possible acidification of the main stream of Zambezi River in Mozambique due to acid mine drainage from coal mining. Using the simulated results it was concluded that the pH of the main stream of Zambezi River will drop to values below 6 only if the pH of the water coming from the tributaries in the mining area is below 3.

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Integrating Surface Water Load Modelling into Mine Closure Performance Evaluation

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Abstract

Predictive water quality models are often used to support mine permitting but too often are not used later in mine life to re-evaluate mine performance. Models have equal or greater value during mine operation and closure as a means of comparing actual mine performance to expected performance. Integrated use of models and water quality monitoring throughout the mining life cycle may provide important early warning signs of potential compliance issues and can serve to pinpoint facilities that may be contributing off-site loading. Mass load models also provide a means of predicting the response in a receiving water from chemical loading from the mine. This paper describes the development and use of a surface water mass loading model for assessing closure success at El Sauzal Mine in Chihuahua State in southwest Mexico. In December 2015, El Sauzal (Goldcorp) became the first mine in the world to be decommissioned in accordance with the International Cyanide Management.

Key words: Mine water, water quality compliance, surface water hydrology, mass load model, Goldsim, modeling

Introduction

El Sauzal Mine (Figure 1) is located in the southern Sierra Madre Occidental Mountains in southwestern Chihuahua, Mexico. Ore was mined from four open pits from late 2004 to late 2014. Mining waste was placed in several waste rock storage facilities and a dry-stack Tailings facility. Large surface water diversions were constructed during mine closure to manage water from steep headwater basins upgradient of the mine. Additionally, waste rock and tailings facilities were re-shaped and covered to reduce seepage contributions from mine facilities. The purpose of this presentation is to describe the framework developed to measure closure performance.

Background

Geology

El Sauzal (Charest et al. 2005, Weiss and Espinoa 2007) is a volcanic hosted high sulfidation epithermal gold deposit (Arribas 1995). Mineralization was caused by circulation of strongly oxidized and acidic water that caused pervasive weathering of feldspars, creating concentric zones of vuggy quartz, quartz-alunite enrichment, argillic alteration, and sulfide enrichment. The entire deposit may be surrounded by zones of propyllitic alteration (enrichment in chlorite with or without carbonates). Numerous surficial red-stained areas are located on strike with the deposit, and are evidence of district scale intensive hydrothermal alteration.

At El Sauzal, gold is hosted in a series of volcanic units with highest gold grades found in vuggy quartz and in quartz-alunite alteration zones. Intensive silica enrichment is found in the center of the deposit, which is dominantly within a “megabreccia” unit. The megabreccia and associated volcanic units consists of a suite of depositional events that includes lithic tuffs (often pyritic), andesite flows, and dacitic to rhyolitic pyroclastic units (breccias). In places, the pit highwalls expose zones with sulfide enrichment. Volcanic rocks are likely of Oligocene age (30 million years before present), typical of the Sierra Madre province (Weiss and Espinosa 2007). The volcanic host rocks are underlain and overlain by andesitic rocks that are generally devoid of sulfides and contain low levels of carbonates.

Climate

The climate in the Sierra Madre Occidental region is dominated by a summer monsoon season that occurs from July through September. Annual rainfall averages 809 mm and nearly 80 % of the annual rainfall at El Sauzal occurrs in July through September. The climate for the remainder of the year is typical of an arid subtropical regime with monthly rainfall averaging only 15 mm per month for October through June (Figure 2).

Hydrology

El Sauzal is located in steep dissected terrain adjacent to Rio Urique, which is a major tributary to the Rio Fuertes an important source of irrigation water for Sinaloa State. Streamflow in Rio Urique exhibits wide seasonal swings in discharge rate with the majority of surface water discharging in July through September. Gochis et al. (2006) found that an average of 13 % of annual precipitation contributes to streamflow in the Urique basin.

Most stream courses are ephemeral at El Sauzal with streamflow occurring for a few hours after larger monsoonal storm events. Perennial flows occur in three drainages that transect the site. Flow and water quality are monitored at these locations (PS-02, PS-04 and PS-05, Figure 3) that are located below the Tailings facility, mine pits and waste rock piles. Flow rates in these small drainages average 50 to 260 L/min, with peak flows from 400 to 1,200 L/min and minimum flows near zero. No regional groundwater has been detected at Sauzal (Jones 2014) so water that exits the mine is believed to travel as surface runoff or via localized subsurface pathways within perched systems in the layered volcanic rocks.

Water Quality

Rio Urique was has low TDS, neutral pH and slightly alkaline water quality that varies little through the year (Table 1). Water quality monitoring stations located upgradient of the mine or at off-site locations show a wide range of background water quality conditions. While many local ephemeral drainages had water that was similar to Rio Urique (low TDS background stations, Table 1), many local background monitoring sites stations had much higher TDS and elevated sulfate. Some higher TDS sites had neutrall pH (moderate DS background stations, Table 1) and many had low pH and high TDS (acidic background stations, Table 1). Acidic water quality stations were located in mineralized areas that exhibited sparse vegetation and prominent iron-staining, which is representative of El Sauzal prior to mine development. The naturally occurring acidic areas were similar to natural hydrothermal scars that occur near the Questa Mine in New Mexico (Meyer and Leonardson 1990 and Logsdon 2011), which can have pH levels of 3 or less. Average water quality downgradient of El Sauzal is similar to the Moderate TDS background water in Table 1.

While water quality in Rio Urique is relatively constant through the year, historic water quality in small basins near El Sauzal showed strong seasonal variations. For most of the year water in small arroyos is neutral in pH and is alkaline with low metal levels. For short durations (e.g., generally days to weeks) after larger rain events, flow rates increase sharply and water tends to become more acidic and higher in dissolved aluminum, copper and zinc. As streamflow decreases, water quality returns to neutral pH-alkaline conditions (Figure 2).

This seasonal pattern in water quality is attributed to interaction of water with localized mineralized rock exposed in mine pits and in natural outcrops near the mine. The seasonal variations in both flow and quality were attributed at least in part to natural background conditions. The hydrological conceptual model developed to explain the short duration pulses of poorer quality water presumes that there are two differing subsurface flow paths that water may follow at El Sauzal. During low flow periods, water is thought to follow a deep subsurface pathway, which encounters carbonates in deeper volcanic rocks. After intense storms, the abundant water tends to follow a shallow flow path where water interacts with quartz-alunite altered rocks that are acidic and devoid of carbonate. Water in springs downgradient of the mine has a very different signature than standing water in the mine pits. Mine contact water has low pH and elevated iron. Water in springs, though still low in pH is high in aluminum and low in iron. The high aluminum water is attributed to interaction with abundant alunite within the mineralized zones where aluminum may swap for iron through solid solution of iron for aluminum in alunite ($KAl_3(SO_4)_2(OH)_6$). A dynamic mixture of slower moving alkaline water and short duration pulses of more acidic water best explains the flow and water quality variation observed at El Sauzal. Water quality in Rio Urique downstream of the mine meets all applicable water quality standards even during the monsoon season when loading from the site is highest.

Mine Reclamation

The goal of site closure completed during 2015 and 2016 is to maintain or reduce loading from the mine site so that water quality in the Rio Urique continues to be protected. An extensive system of surface water diversions was constructed to maintain stability of waste rock facilities and to minimize surface run-on into acidic areas in the mine pits. Facilities were regraded and covered with suitable material to promote vegetation establishment.

Basin Hydrology and Mass Load Model

A GOLDSIM surface water basin model was developed to predict the response of mine facilities to annual and seasonal variations in rainfall. The surface water mass load model has been integrated into post-closure water quality monitoring program at Sauzal to insure that chemical loading is consistent with the expected performance of the closure actions.

The model computes a hydrograph for each hydrologic basin upgradient of key monitoring stations (PS-02, PS-04 and PS-05, Figure 3) by determining the abundance of water from shallow and deep pathways. Water in the shallow pathway has a median travel time of 7 days (e.g. 50 % of cumulative hydrograph discharges within 7 days) versus 70 days for the deeper flow path. The hydrograph recession curve was modeled assuming a fixed proportion of water in storage (B) would discharge (Q) to the stream each day ($Q_n = \alpha\ B_{(n-1)}$). Shallow water is assumed to contain high metals while deeper water is low in metals. Measured and predicted zinc at monitoring point PS-04 (Figure 4) illustrates how the mass load model replicates the seasonal changes in streamflow and dissolved zinc in response to seasonal precipitation events. The model replicates the erratic shifts in dissolved zinc at high streamflow and the low zinc during low streamflow periods.

Integrating Performance Model with Post-Closure Monitoring

The calibrated Goldsim model was used to predict how reclamation would affect future loading from the mine site. Reclamation will change surface runoff routing and will reduce net infiltration into waste rock and mine pits. Reductions in net infiltration are assumed to phase in over ten years as the vegetation slowly establishes in the desert environment.

One problem with modeling a monsoon-driven system is that annual loading is highly dependent on annual rainfall and the number of large storms (over about 30 mm) that occur during a year. To illustrate this variability, future mass loading was simulated in Goldsim using a stochastic precipitation data set after January 1, 2016. A series of five random model realizations with varying climate (Figure 5) show that year-to-year variations in rainfall cause such large variations in predicted loading that long-term trends are completely masked. However, when 100 model realizations are conducted, the median and quartile results (Figure 6) show that median zinc loading at PS-04 is expected to decline from about 0.3 kg/d to 0.15 kg/d in the 10 years following mine reclamation. For the same simulation, predicted zinc in Rio Urique downstream of the mine (P3) remains close to background levels (P1) and zinc levels would not be measurably different below the mine than above the mine.

The El Sauzal basin hydrograph mass load model will be used in conjunction with water quality monitoring to determine the success of reclamation. The primary success criterion for the site will be water quality compliance with NOM-001 criteria at downstream station P3 at Rio Urique (Figure 3). A secondary success criterion would be for water quality at P3 to be the same as at P1 (upstream). A final success criterion is for internal monitoring locations on arroyos (PS-02, PS-04 and PS-05) to remain within a reasonable margin of error of the flows and chemical loads predicted by the mass load model. Inclusion of modeled basin behavior into the monitoring plan provides a tool for identifying whether mine reclamation is performing as expected and supports the objective of protecting water quality in Rio Urique.

Figures

__Figure 1:__ Location of El Sauzal mine site in Chihuahua, Mexico.

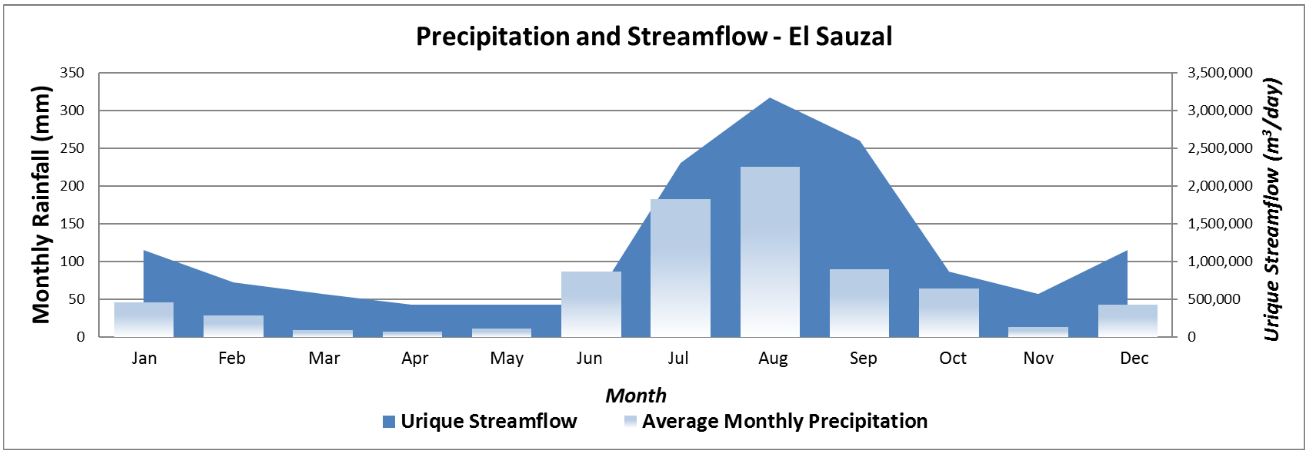

Figure 2. *Monthly rainfall and Urique streamflow at El Sauzal.*

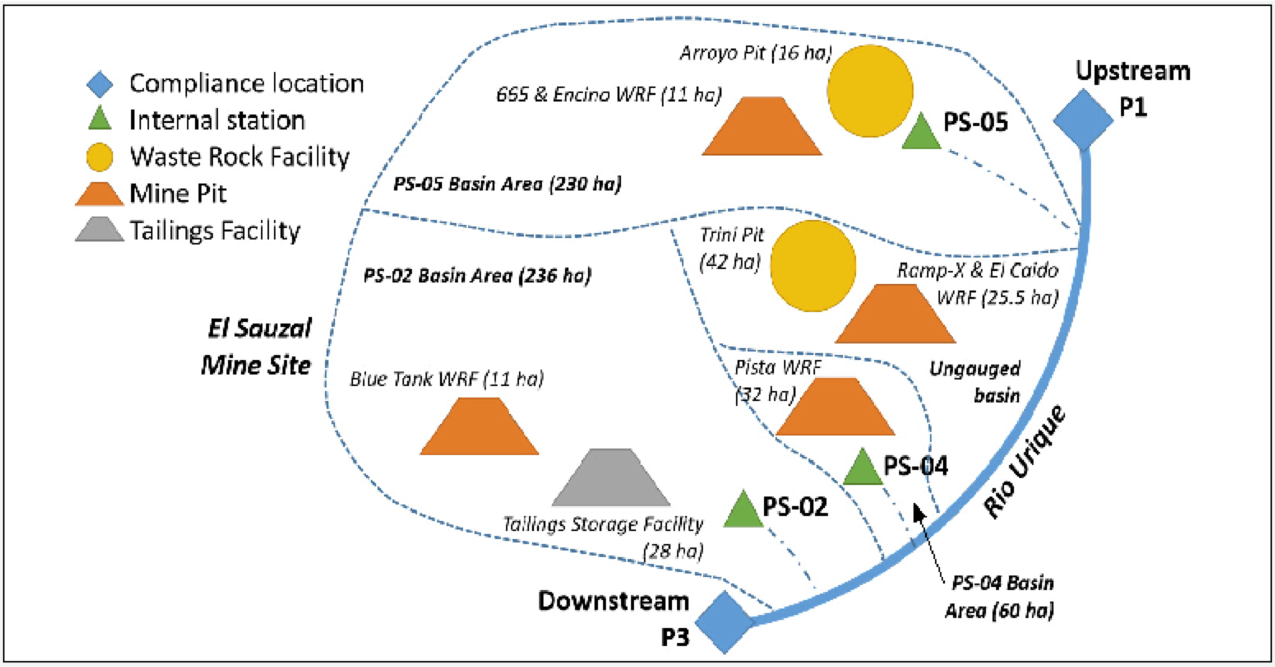

Figure 3: *Schematic of El Sauzal mine site.*

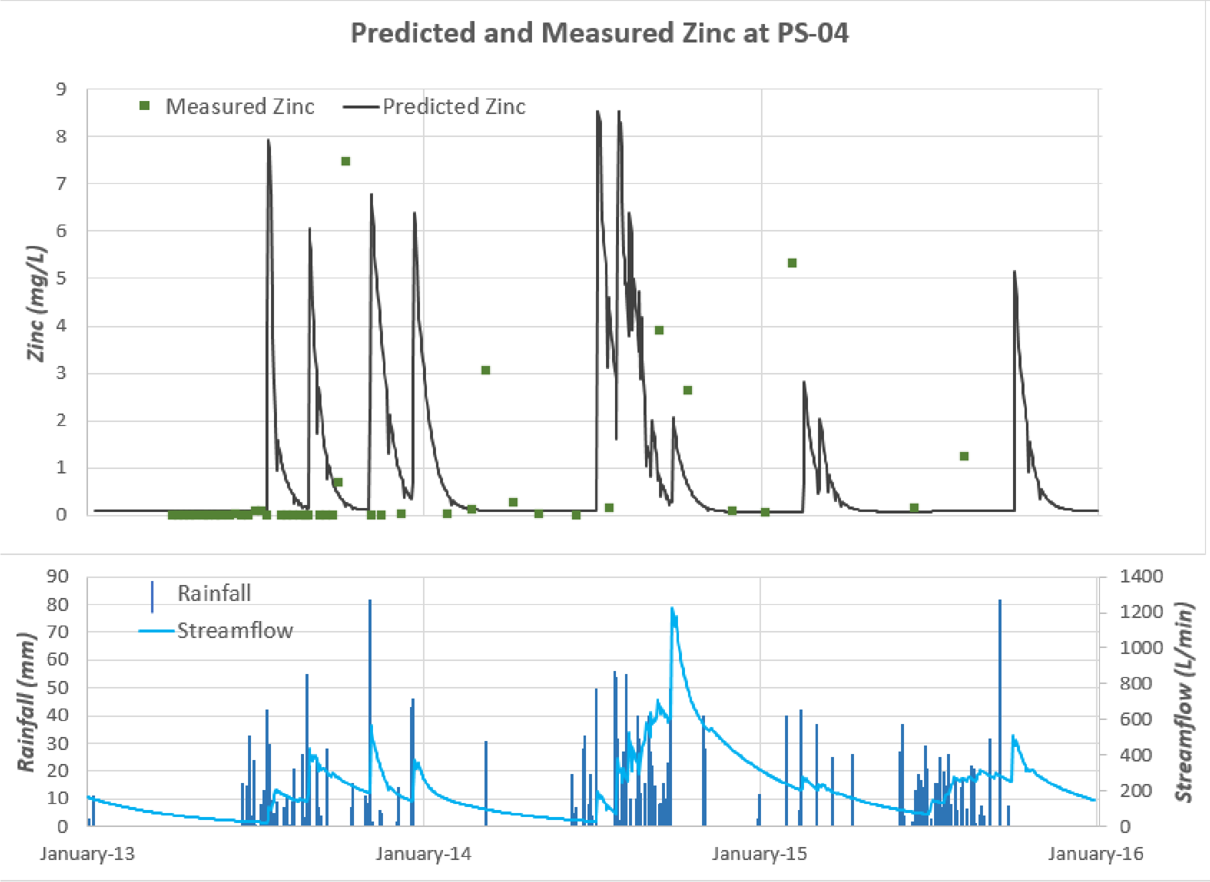

Figure 4: *Seasonal variations in zinc at a downstream monitoring location at Sauzal.*

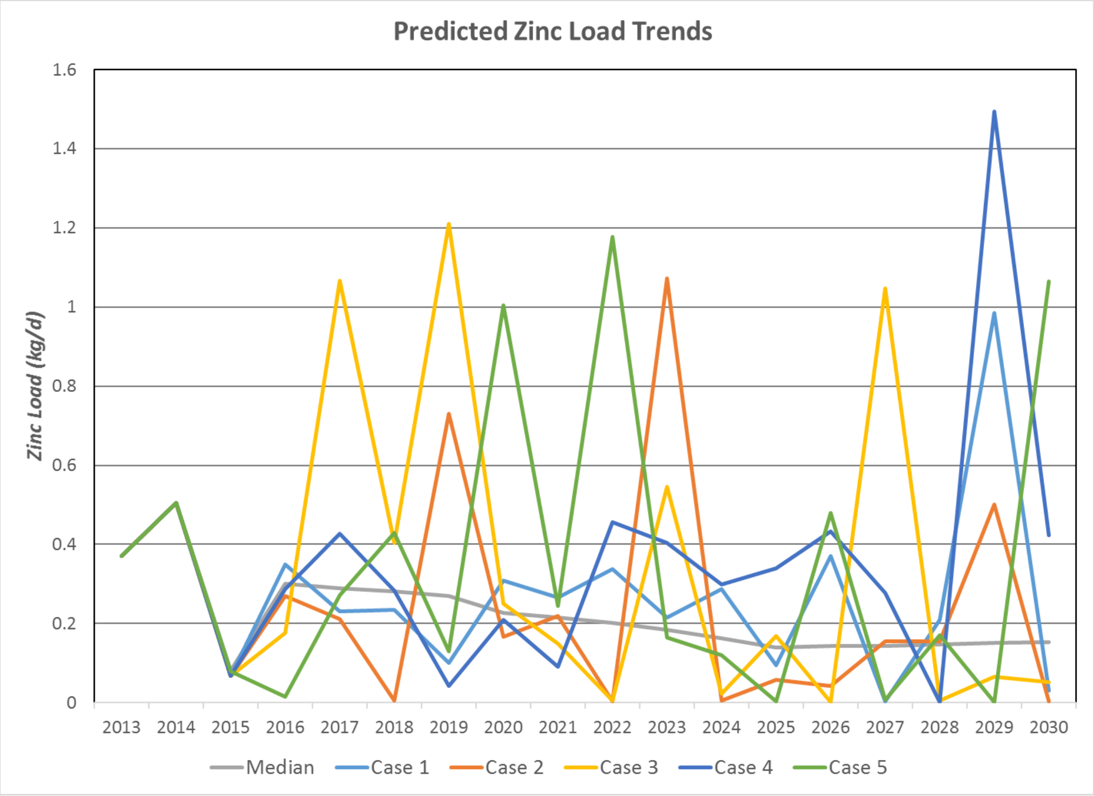

***Figure 5:** Predicted trends in zinc loading for five model realizations.*

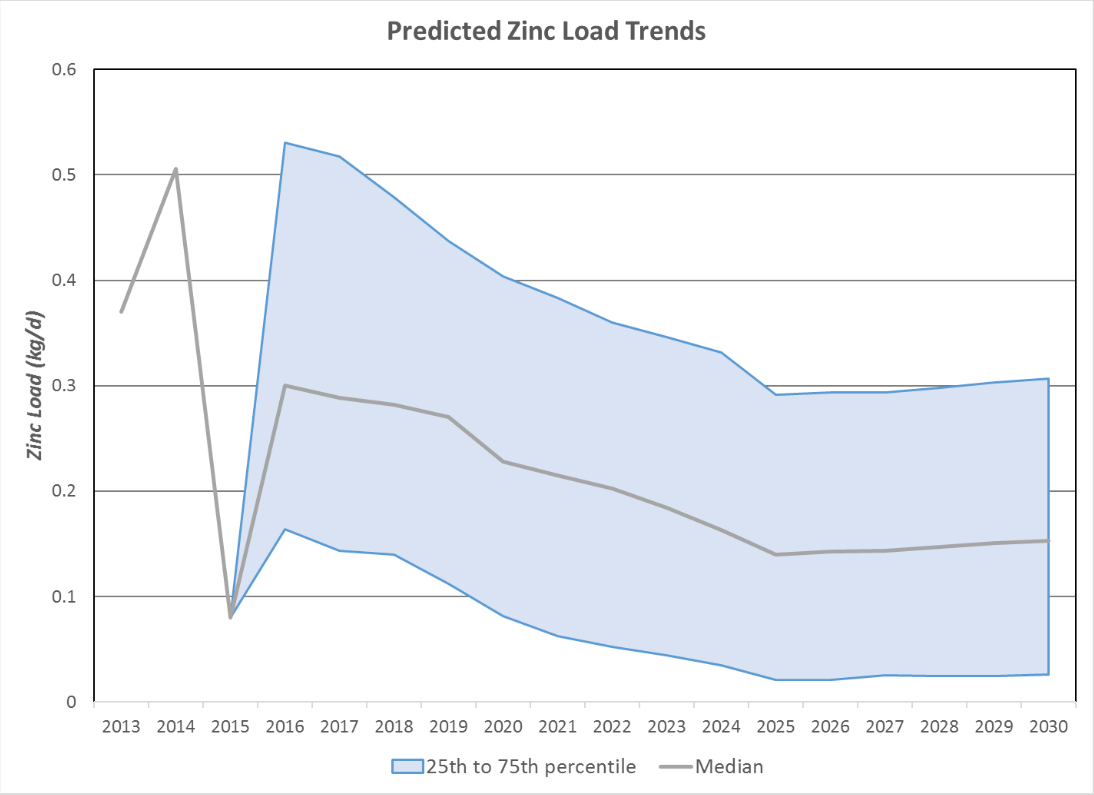

***Figure 6:** Probabilistic forecast for trends in zinc load at PS-04 based on 100 realizations.*

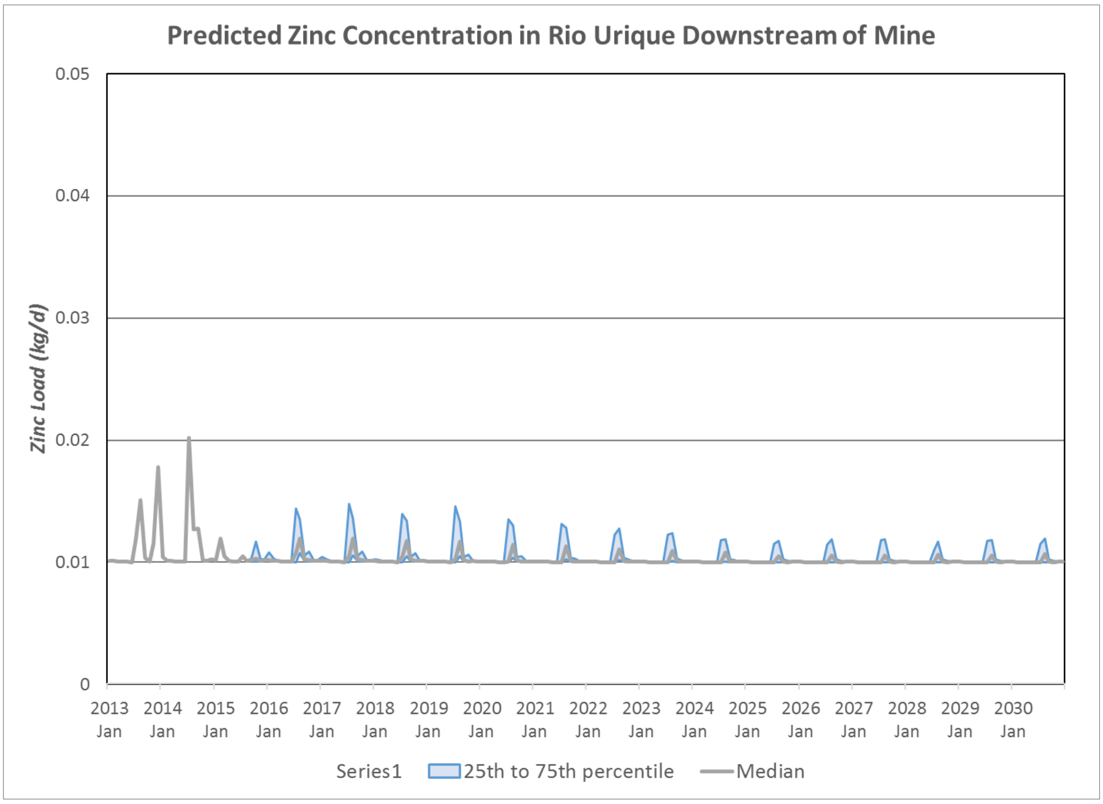

Figure 7: *Probabilistic forecast for trends in zinc concentration in Rio Urique downstream of mine based on 100 realizations.*

Tables

Table 1. *Average water quality conditions for background waters, Rio Urique and monitoring stations downgradient of El Sauzal. Mexican water quality criteria applicable to Rio Urique are also shown.*

Constituent	Rio Urique (P1)	Background Water Quality			Average of Site Monitoring Stations [1]	NOM-001 [2]
		Low TDS Stations	Moderate TDS Stations	Acidic Stations		
pH	7.7	7.9	7.4	3.1	6.9	<5
Specific Conductance (uS/cm)	127	494	2022	3070		
Acidity as ($CaCO_3$) (mg/L)	4.8	<1	<1	1171	51.0	
Alkalinity as ($CaCO_3$)	39	237	141	<1	128	
Sulfate	15	37	1184	2653	1671	
NO3 as N	0.2	0.4	0.1	<0.1	14.4	>15
Total Aluminum	9.4	0.9	1.0	131.6	7.6	
Total Iron	4.4	0.9	0.8	121.5	3.0	
Total Zinc	0.07	0.02	0.02	6.13	0.8	>10

1 – average acidity estimated from average iron and aluminum at PS-02, PS-04 and PS-05

2- Mexican water quality criteria for Rio Urique, Nitrogen standard is for total N. Semarnat 1996

Acknowledgements

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Iron removal from the Spree River in the Bühlow pre-impoundment basin of the Spremberg reservoir

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Abstract

Due to its huge water body, the Spremberg reservoir plays an essential role in retaining the Spree's visible iron load upstream of Cottbus and the Spreewald, caused by rising groundwater levels. During the period from August through December 2014 repair work on the dam at the reservoir had to be done. These repairs became necessary because the damage to the eastern wing wall of the dam ascertained in 2013 had the potential to significantly impair the reservoir's flood control capability. In order to allow the work to proceed, the water level had to be lowered by some meters which involved a notable shortening of the residence time. That increased the risk that iron retention in the reservoir may no longer be ensured.

The preferred option was geared towards achieving iron retention in the pre-impoundment basin by means of sequential conditioning of the river Spree. Building on the results of flocculation tests a corresponding technical unit for a two-stage conditioning of the river Spree upstream of the pre-impoundment basin was designed and constructed. In order to allow for large-scale prefabrication and for ease of assembly, the project was implemented in the form of a mobile container plant. The plant went from design to completion in a couple of months.

The plant as a whole consists of two series-connected units. Located in Spremberg Cantdorf (ca. 1.5 km upstream of the pre-impoundment basin), plant unit 1 ensures production and tailor-made dosage of milk of lime. Production of the flocculating agent suspension and its tailor-made dosage are performed by plant unit 2 at the pre-impoundment basin inlet. A design capacity of 15 m^3/s was established for both plant units, which is equal to the average discharge of the Spree River at the Spremberg gauging station.

Except for a short interruption due to winter conditions in February, the conditioning plant has been in continuous operation since it came on stream in August 2014. Thanks to the efficiency of the conditioning plant, no significant exceedance of the visible iron plume limit of 2 mg/L total iron at the Bräsinchen reference gauge was recorded while damage to the dam was being repaired. Monitoring of the Spree River indicates load-based proportional daily mean iron retention at the Bühlow pre-impoundment basin varying between 30 % and 86 % as a function of concentrations in feed water and an average of ca. 50 %.

The final process step following iron separation from the aqueous phase consists in desludging the pre-impoundment basin and in doing so removing the generated iron deposition from the water body. GIP and project partner TWB are currently carrying out an initial operation intended to remove ca. 30,000 m^3 of sludge from the pre-impoundment basin using two specially equipped suction dredges. The sludge is dewatered on site by two high-performance mobile decantation plants prior to disposal. Following consultation with the proper regulatory authorities, LMBV envisages the continued tailor-made operation of the conditioning plant over the next five years until measures which are currently designed and implemented with a view to decreasing iron-bearing groundwater discharges into the Spree and Kleine Spree rivers will have the required impact. The objective is to achieve safe iron retention in the main dam even at low water storage level and a load-proportional elevated degree of iron retention in the pre-impoundment basin.

Key words: Iron removal, mine water, water treatment, river treatment plant

Background

Progressive groundwater resurgence in mine reclamation areas has resulted in a partial increase of iron concentrations in the Spree River. Current measurements performed at the Spremberg Wilhelmsthal gauging station show total iron levels (Fe_{total}) ranging on average from 5 to 6 mg/L with peaks of 15 mg/L. Concentrations at such a high level do not only cause damages to the watercourse as an ecosystem but also lead to a distinctly visible browning of the water.

Owing to its huge body of water, the Spremberg reservoir plays a crucial role in retaining the Spree's visible iron load upstream of Cottbus and the Spreewald. Iron precipitation measures implemented within the Bühlow preimpoundment and within the main dam reduce the iron load downstream of the Spremberg reservoir by some 75 % [IWB 2013]. Thereby the reservoir performs a crucial protective function for the benefit of the downstream riparian's (Spreewald, Cottbus) against ochre pollution.

From August through December 2014, the State Office of Environment, Health, and Consumer Protection (LUGV) had repair work carried out on the dam of the reservoir. These repairs became necessary because the damage to the eastern wing wall of the dam which had been ascertained in 2013 had the potential to significantly impair the reservoir's flood control capacity. In order to allow the works to proceed, the water level had to be lowered to 89 m a. s. l, which meant a drawdown of ca. 3 meters. According to [IWB 2013], the associated significantly shorter retention time gave reason to expect an essentially lower retention of iron. As early as 2013, a water level drawdown of 2 meters made for reasons of maintenance then led to cutting the retention time in half and significantly diminishing the retention of iron [IWB]. In the process of iron precipitation the area of the Spremberg reservoir was used to its maximum. In case of a significant further water table drawdown like the one that became necessary in the summer of 2014, detection threshold exceedances in the main dam outlet and, by implication, potential restrictions on the use of water had to be expected.

Thereupon, relevant water management competencies (LMBV, Vattenfall Europe Mining AG) were pooled in an ad hoc task force on the initiative of the Brandenburg State Office for Mining, Geology and Natural Resources (LBGR) and in co-ordination with the LUGV Brandenburg with a view to planning and implementing a viable concept which would ensure iron retention within the reservoir under the boundary conditions of dam wall rehabilitation.

Measures to remove iron from the Spree River

Process technological concept

The members of the above-mentioned ad hoc task force studied various measures aimed at enhancing the efficiency of iron retention within the preimpoundment basin. Their preferred option was geared towards a sequential conditioning of the Spree River in order to achieve iron retention within the preimpoundment basin involving the following process stages:

1. pH increase to accelerate iron (II) oxidation;
2. Mixing and contact time within a predetermined flow channel;
3. Flocculation aid addition to enhance flocculation;
4. Preferred settlement of the iron hydroxide sludge (IHS) in the Bühlow preimpoundment.

Based on experience gained from mine water treatment by Vattenfall Europe Mining AG, the Brandenburg University of Technology BTU Cottbus conducted flocculation tests for process optimisation [IWSÖ / BTU COTTBUS 2014]. The efficiency of pH increase and the adjustment of an optimum pH value were considered as a start.

Further tests served to select a flocculation aid suitable for the Spree River water. During these tests, 3 different anionic flocculation aids as well as a dual flocculation process combining cationic PolyDADMAC with anionic flocculation aid were studied.

Additional studies with regard to treatment sequence included:

- Combination of pH increase by way of lime slurry addition and subsequent addition of flocculation aid,
- Impact of contact time between pH increase and addition of flocculation aid, and
- Impact of mixing turbulence at pH increase of addition of flocculation aid, respectively.

Subsequently, the process stages of sequential conditioning were refined as follows:

1. pH adjustment to pH > 8.0 by addition of lime slurry;
2. Mixing channel with minimum contact time of 30 minutes, and
3. Addition of the Koaret PA 3230 T flocculation aid.

In the framework of a technological concept, GIP GmbH Dresden investigated ways to implement the process at short notice.

Planning and technological implementation

Building on the above results, GIP GmbH Dresden designed and constructed a corresponding technological unit for a two-stage conditioning of the Spree River upstream of the preimpoundment basin [GIP 2013].

One standout feature of the project was the very short period of time available for its implementation. Planning work started in April 2014 on the understanding that the unit would come on stream not later than in August 2014. This tight deadline was met thanks to excellent co-operation among all parties involved in the project and partial integration of individual planning stages.

In the light of these circumstances, the following key principles had to be observed in terms of engineering design:

- Complete adaptation of the unit to site conditions;
- use of existing infrastructure;
- to the greatest extent possible, use of available structural conditions in order to pare time and effort at the construction site.

Nonetheless the plant‘s subsystems had to be designed in a way to make sure they would not be affected by flood nor constitute flow channel obstacles in the case of a flood event.

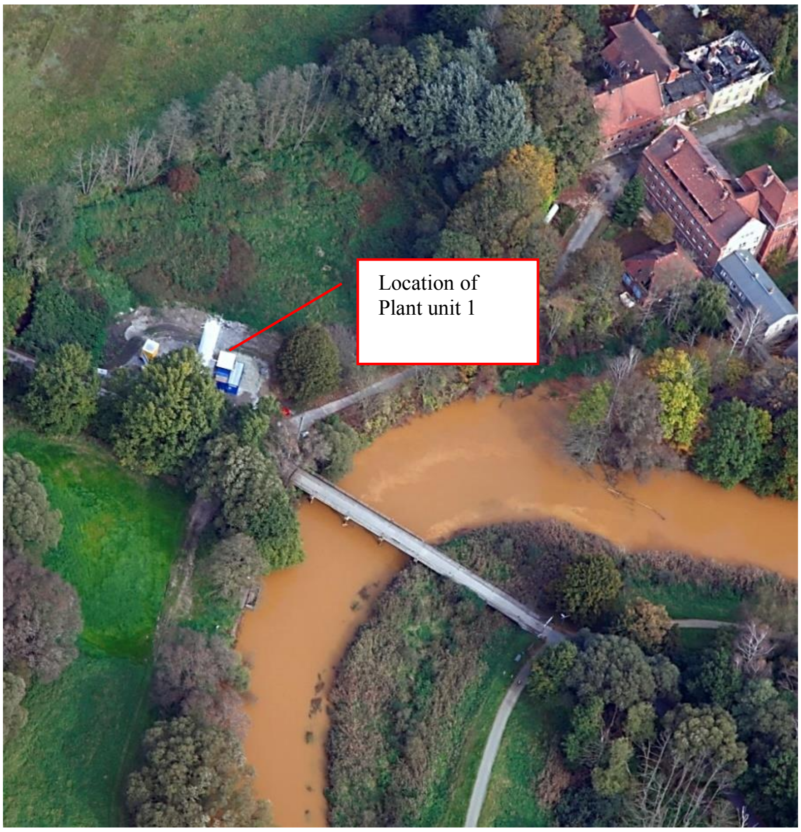

Figure 1 *View of plant unit 1 in Spremberg Cantdorf and in-stream lime dosing*

Two plant units were designed and erected for the two process stages, namely addition of lime slurry (1st process stage) and addition of flocculation aids (2nd process stage) to ensure preparation and tailored dosing. The engineering design was that of a container-based mobile plant with a view to enabling extensive preconstruction and rapid assembly. It was only a matter of months from design to completion.

Plant unit 1 is located in Spremberg Cantdorf, approximately 1.5 km upstream of the preimpoundment basin. At this site, an existing bridge across the Spree River was available for lime slurry supply and blending into the river water. Lime slurry blending is preceded by dilution in a motive water stream and is performed by means of three pairs of nozzles. In doing so, uniform pH distribution can be achieved in the Spree water only a short distance away downstream.

Figure 2 *Container-based mobile plant providing tailored lime slurry dosing (Plant Unit 1)*

Weighing of the batching tank ensures accurate lime slurry preparation. Tailored dosing depending on the flow in the Spree River is performed by a frequency controlled hose pump. In coordination with all parties involved in the project, the plant was designed for a flow rate of 15 m^3/s which corresponds to the Spree River's average discharge flow. Making full use of the facility's design capacity, the maximum dosing is limited to a flow rate of 17 m^3/s.

Preparation and tailored dosage of flocculation aid suspension are ensured by plant unit 2 at the preimpoundment basin inflow. Existing training wall structures (triple intake fan) upstream of the preimpoundment basin were used to provide access to the Spree River (see Figure 3). The flocculation aid suspension was also mixed into a motive water stream, and dosing into the Spree water was channelled by means of three pairs of nozzles. Following completion of horizontal directional drilling, the dosing pipe runs directly from plant unit 2 to the training wall structure within the Spree riverbed. Such taking advantage of site conditions allowed to keep impact on the waterbody‘s channel geometry to a minimum.

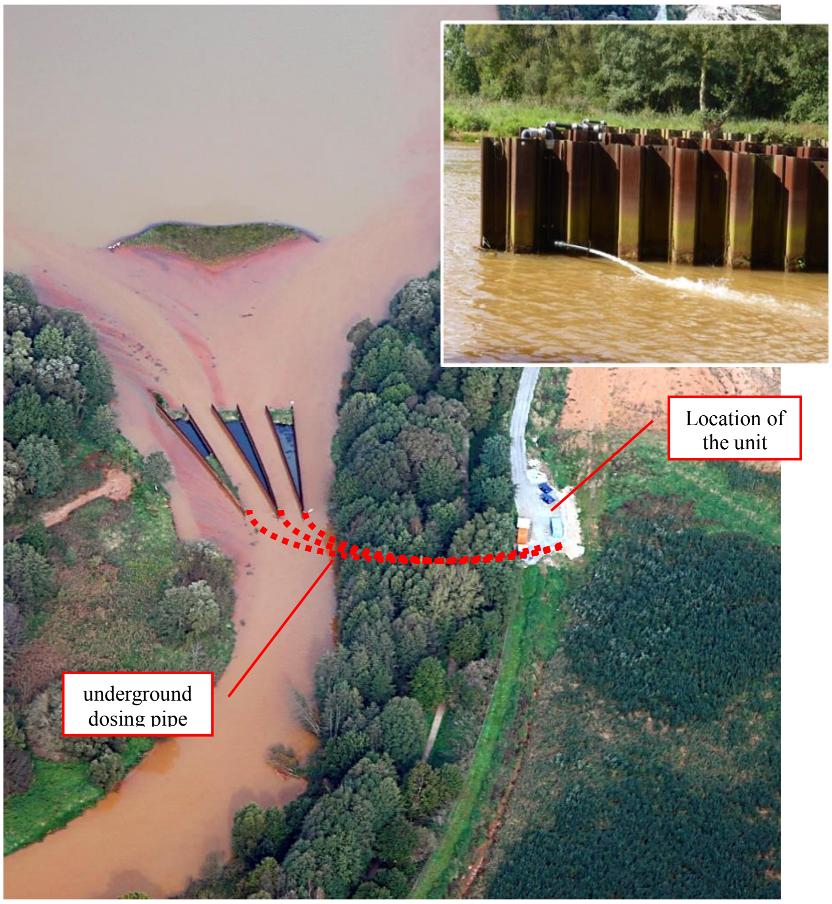

Figure 3 *Plant unit 2 located in preimpoundment basin inflow and nozzle-controlled dosing of flocculation aid*

Results achieved so far by the operation of the conditioning plant

Except for a short downtime due to winter conditions in February 2015 (February 03 to March 04, 2015), the conditioning plant has been in continuous operation since it came on stream in August 2014.

During the period of operation, the Spree River discharge varied from 6 to 31 m^3/s. Lime slurry dosing rate was in the order of 0.25 mol/m^3, with an average lime consumption of 9 t/d. The consumption rose to 19 t/d at maximum capacity utilisation. Average daily consumption of flocculation aids was 200 kg/d with dosing in the 0.1 to 0.2 g/m^3 range.

In connection with this measure, intense monitoring of the Spree River performed since 2012 at three sampling stations was enhanced by an additional measuring point located right in the inflow to the Bühlow preimpoundment basin in order to comply with a regulatory requirement to perform environmental monitoring [IWB].

Long-term monitoring data establish an average iron load (with regard to Fe_{total}) of approx. 7,100 kg/d with mean concentrations in the order of 5 to 6 mg/L in the inflow to the preimpoundment basin. In this connection, the iron levels are essentially a function of discharge rates. Increased discharges induce dilution. However, the increase in stream velocity, which is inevitably connected with an increase in discharge rates, in the first instance, brings about a mobilisation of iron hydroxide sludge deposited along the watercourse. This implicates concentration peaks of up to 15 mg/L.

As a result of the conditioning, the average natural iron retention within the preimpoundment basin was raised from approximately 2,000 kg/d by up to 50 percent to 3,000 kg/d; under optimum conditions, it rose even by 100 percent to 4,000 kg/d (see Figure 4).

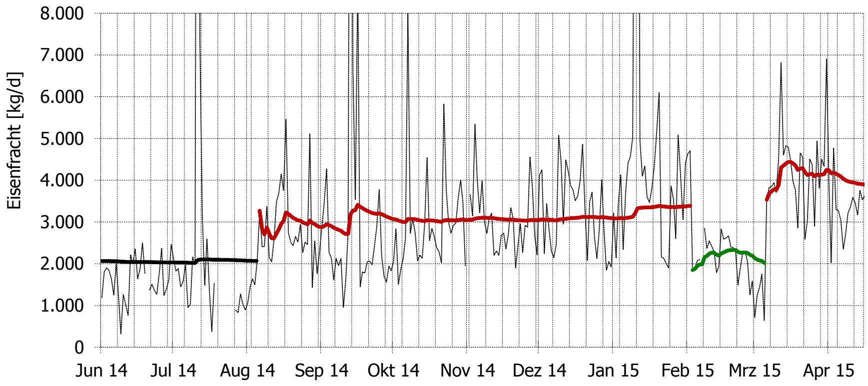

Figure 4 *Daily values (thin black line) and moving average of iron retention in the Bühlow preimpoundment basin from June 2014 to April 2015 (Source: [IWB])*

In particular during the winter months, a significant drop in Fe (II) concentration due to lime addition was observed downstream of the preimpoundment basin (see Figure 5). The nearly complete oxidation of Fe (II) achieved in this way provided the required preconditions for more efficient iron retention within the preimpoundment basin. Hence, total iron concentrations downstream of the preimpoundment basin decreased on average to approximately 2.5 mg/L.

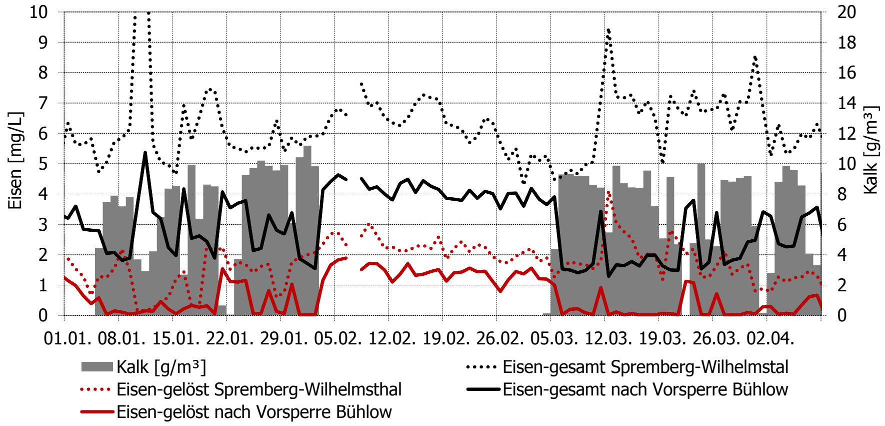

Figure 5 *Time course of concentrations of dissolved iron Fe(II) and total iron - Fe(II) and Fe(III) – upstream and downstream of the Bühlow preimpoundment from January to April 2015 (Source: [IWB])*

Efficiency of lime addition during the first process stage (Plant unit 1) is illustrated by the time course of the individual iron concentrations within the preimpoundment as depicted in Figure 5. During plant downtime in February 2015 Fe (II)-concentrations jumped up to levels of 1.5 to 2.0 mg/L with total iron concentrations rising to approximately 4 mg/L. During that period, iron retention within the preimpoundment basin was notably down.

Thanks to the efficiency of the conditioning plant according to [IWB], no significant exceedance of the visibility threshold of 2 mg/L total iron at the Bräsinchen reference gauge was recorded while damage to the dam was being repaired.

Measures to remove iron hydroxide sludge from the preimpoundment basin

Measures aimed at the sequential conditioning of the Spree River are intended to enhance the settling capacities of iron hydroxide flocs and in doing so to remove iron from the aqueous phase. Iron hydroxide sludge (IHS) generated in this way settles and forms a sludge layer within the preimpoundment basin.

Since there is strongly uneven flow through the preimpoundment basin, as a consequence sludge settlement is also uneven. Measurements accompanying the measure as well as a two-dimensional flow calculation revealed that under current conditions approximately 75 percent of total flow through the preimpoundment basin follows a short circuit pattern through the eastern sector. At the time of sounding on March 13, 2015, the sludge layer in that sector had a thickness of up to 1.9 meter while sounding results ranged from 0.5 to 1 m in the other sectors. Total sludge volume within the preimpoundment basin amounted to 86,510 m³. The settled IHS undergoes a number of aging processes which contribute among others to a progressive thickening of the deposited IHS. While the uppermost sludge layer typically shows dry matter contents in the range from 2 to 5 percent by mass, the dry matter content of low-lying sludge layers rises up to 40 percent by mass.

Sludge removal from the preimpoundment basin and hence the elimination of iron depositions from the waterbody is the final process stage required. During the period from April to August 2015, GIP and their project partner TWB will proceed to perform an initial desludging of the preimpoundment basin. This partial sludge removal is aimed at producing appropriate new volume for the settlement of IHS along the preferred flow path in the eastern sector of the preimpoundment basin. According to a 3D-volume balance based on sounding data, the volume of this partial sludge removal was put at approximately 30.000 m³. Sludge removal from the preimpoundment basin is performed by two specifically equipped suction dredges. Prior to disposal, the dredged sludge undergoes dewatering on site in two mobile decanter units, each with a capacity of 100 m³/h.

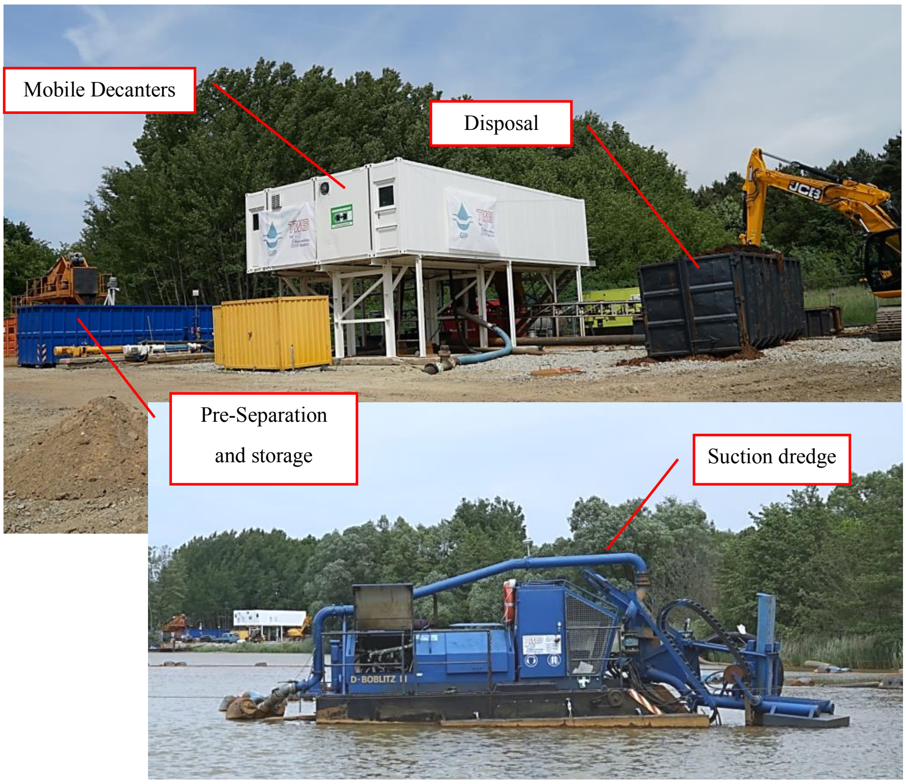

***Figure 6** Desludging the Bühlow preimpoundment basin*

Continuation of iron removal measures

After consultation with the competent regulatory authorities, LMBV envisages to continue the tailored operation of the conditioning plant in the coming five years until a point is reached when the currently planned and implemented measures which are targeted at diminishing the impact of iron-bearing groundwater onto the Spree and Kleine Spree Rivers are beginning to take effect.

Protection of the town of Cottbus and of the Spreewald against visible iron pollution is the primary goal of this measure. A visible browning of the water begins at a total iron concentration of approximately 2 mg/L (visibility threshold). At a total iron concentration of less than 1 mg/L, water presents a slightly appearance.

Analysis of monitoring data from 2012 through 2014 reveals average iron retention in the preimpoundment basis of approximately 2,000 kg/d or ca. 30 percent. A vast special area of protection (SAC) extends along the inflow to the main dam. Therefore, a further objective of the conditioning plant's continued operation is the best possible iron load in the preimpoundment basin. The planning target aims at a load proportional iron retention rate of ≥ 50 percent.

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CHAPTER 4

Investigations on Pit Lakes

New insights into the microbiology of meromictic acidic pit lakes in the Iberian Pyrite Belt (Spain)

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Abstract

Over twenty opencast voids in abandoned mines of the Iberian Pyrite Belt (IPB, Southwest Iberian Peninsula) are now filled with low pH water containing elevated concentrations of soluble metals and other solutes such as sulfate. Few studies have examined the microbiology of acidic metal-mine pit lakes, even though they are a potential source of new species of acidophiles that could be harnessed for mineral bio-processing (biomining) or bioremediation of acidic mine waters. Pit lakes in the IPB are very diverse in size, depth, age and water composition, but they share a common geological framework. The majority are meromictic and display a permanent stratification pattern. Two of these meromictic pit lakes, Cueva de la Mora and Guadiana, were chemically and microbiologically characterized. Acidophilic heterotrophic bacteria and algae populated the mixolimnion in both lakes, the transition layers in both lakes were found to be the most microbially diverse, and where iron and sulfur transformations were more important. In contrast, no bacteria were isolated from the monimolimnion (the lowest anoxic layer). DNA was extracted from two water samples from the monimolimnion (at depths of 55 and 60 m) in Guadiana pit lake, 16S rRNA bacterial and archaeal genes amplified and microbial diversity assessed using terminal restriction enzyme fragment length polymorphism (T-RFLP). Clone libraries of 16S rRNA genes of *Archaea* and *Bacteria* from samples were constructed in order to identify unknown T-RFs. Results obtained in this work indicate that the monimolimnion of Guadiana is populated by different bacterial community to that of the upper layers of the lake. Archaeal communities appeared to be very similar in waters from different depths within Guadiana, and were also similar to that found in the Cueva de la Mora monimolimnion.

Key words: pit lake, acid mine drainage, acidophiles, archaea, bacteria

Introduction

The Iberian Pyrite Belt (IPB) is located in the south-west of the Iberian Peninsula, and extends from the south of Lisbon to the west of Seville. This famous mining district contains many massive sulfide deposits of Palaeozoic (Carboniferous) age classified as giant and supergiant (Sáez et al. 1999), being one of the largest massive sulfide provinces on Earth (Leistel et al. 1998). The IPB has been mined for centuries, since the metal ages up to the present day, with several mines still in operation (e.g. Aguas Teñidas). The most intense mining activity took place in the Modern age, especially between 1880 and 1980 leaving a legacy of mine wastes, old mine structures, and flooded opencast pits. In the Spanish part of the IPB alone, more than 30 pit lakes have formed as a result of the abandonment and subsequent flooding of the former opencast excavations (Sánchez-España et al. 2008, López-Pamo et al. 2009). Pit lakes in the IPB are very diverse in size, depth, age and water composition, but they share a common geological framework. The majority are meromictic and display a permanent stratification pattern, with the water column divided into an upper oxic layer (the mixolimnion), a bottom anoxic layer (the monimolimnon) and a transitional chemocline separating them (Sánchez-España et al. 2009) where redox transformations of iron and sulfur are most dynamic.

Two meromictic pit lakes, Cueva de la Mora and Guadiana, have been chemically and microbiologically characterized (Falagán et al. 2014, 2015). The mixolimnion is characterized by low pH (2.2 – 2.9) and high redox potential (~ +800 mV), whilst the monimolimnion is characterized by high pH (4 – 4.5) and low redox potential (~ +300 mV). The chemocline is characterized by pronounced gradients of physico-chemical parameters where oxidized and reduced forms (as for example iron and sulfur) co-exist. These metal-mine pit lakes are rich in dissolved metals (e.g. Fe, Zn, Mn) and sulfate, which usually increase in concentration with depth.

Acidophilic heterotrophic bacteria and algae populated the mixolimnion in both lakes, though maximum numbers of phototrophs were found at depths in the water column where the incident solar radiation was only ~ 2% of that at the lake surface. This has been ascribed to large variations in phosphorus bioavailability in the water column. The transition layers in both lakes were found to be the most microbially diverse, and included iron- and sulfur-oxidizing autotrophs, iron-reducing heterotrophs and also, in the case of Cueva de la Mora, sulfate-reducing bacteria. Shallow sediments (recovered at 8 m depth) contained similar microbial populations in both lakes, though those located deep within Cueva de la Mora were notably different (Falagán et al. 2014, 2015).

The monimolimnetic microbial community was not studied in depth in previous work. Only archaea were detected in the lower layer of the Cueva de la Mora pit lake, while no DNA was amplified in the Guadiana pit lake monimolimnion. This paper reports new insights into the microbial composition of the anoxic layer of the Guadiana pit lake.

Methods

Site of study and sampling

The study was carried out in the Guadiana pit lake (Herrerías mine, Spain; 37°46’66”N, 6°49’31”W) located in the IPB. The Guadiana pit lake has a mixolimnion that can be subdivided into two layers: an epilimnion (0 – 8 m depth), which is aerobic and influenced by seasonal temperature changes, overlying an anoxic hypolimnion (8 – 20 m depth), within which all measured physico-chemical parameters showed no depth-related changes. The monimolimnion, which extends from 20 to 65 m, is characterized by relatively high pH 4.0 – 4.5 and low redox potential (+330 – +400 mV). The monimolimnion is divided in two sub-layers, all the physico-chemical parameters follow an increasing (e.g. temperature) or decreasing (e.g. redox potential) pattern up to a depth of 50 m, after which all of these parameters are constant down to the lake bottom. The vertical pattern is deeply influenced by the existence of mine galleries intersecting the former mine pit, as reported by Sánchez-España et al. (2014). The Guadiana pit lake monimolimnetic waters are rich in sulfate (~ 7.4 g/L, SO_4^{2-}-S) and dissolved metals (e.g. Mn, ~ 400 mg/L; Zn, ~ 300 mg/L), but the most dominant metal is iron (~ 7.6 g/L) which due to the anoxic conditions of the monimolimnion is mainly as ferrous iron (Falagán et al. 2014). This lake presents very high CO_2 concentration in the monimolimnion (caused by the dissolution of carbonate present in spilites and by mineralization) so that a controlled degasification process is undergoing (Boehrer et al. 2016).

The Guadiana pit lake was visited in October 2014, water samples were collected from 55 and 60 m depth with a horizontal sampling bottle. Water samples were filtered through sterile membrane filters (0.2 µm pore size) and stored at < 20°C until processed.

Biomolecular analyses

DNA was extracted from the filters using MoBio “ultraclean soil DNA isolation kits”, following the manufacturer’s instructions. Ribosomal RNA genes (bacterial and archaeal 16S rRNA genes) were amplified using the polymerase chain reaction (PCR): the primers used were for 16S rRNA bacterial DNA the 27F (Lane 1991) and the 1387R (Marchesi et al. 1998), for 16S rRNA archaeal DNA the 20F and the 915R (Kay et al. 2013).

T-RFLP analyses of amplified genes were carried out to assess the microbial diversity of samples. Amplified DNA was separately digested with three restriction enzymes (HaeIII, CfoI, and AluI), the lengths of the gene fragments were determined using capillary electrophoresis, and the T-RFs (terminal restriction fragments) identified by comparing them with those in the databank maintained at Bangor University.

Two clone libraries were constructed, one with the 55 m sample for *Bacteria* and the other with the 60 m sample for *Archaea*. PCR products were ligated using the pGEM® -T-Easy cloning vector system (Promega, Madison, WI), and the resulting plasmids were transformed into *Escherichia coli* strain

DH5α, in accordance with the manufacturer's instructions. Plasmid inserts that generated different distinct restriction enzyme fragment length polymorphism (RFLP) were purified (StrataPrep Plasmid Miniprep kit, Agilent technologies) and sequenced (Macrogen, Inc., South Korea), (Kay et al. 2013).

Resulting bacterial and archaeal clone sequences were aligned using BLASTN online software (National Centre of Biotechnology Information, NCBI) and compared with those contained in the GenBank database. Sequences were deposited in the GenBank database under different accession numbers (KX083694 – KX083698).

Results

Results indicated that the monimolimnion of Guadiana was populated by different bacterial community to that of the upper layers of the lake. Both water samples, taken at 55 m and 60 m depths, presented similar T-RFLP (fig. 1) profiles for bacterial 16S rRNA digests with the restriction enzyme CfoI. T-RFLP profiles were dominated by two main peaks at 63 ± 2 nt and at 578 ± 2 nt (CfoI digests).

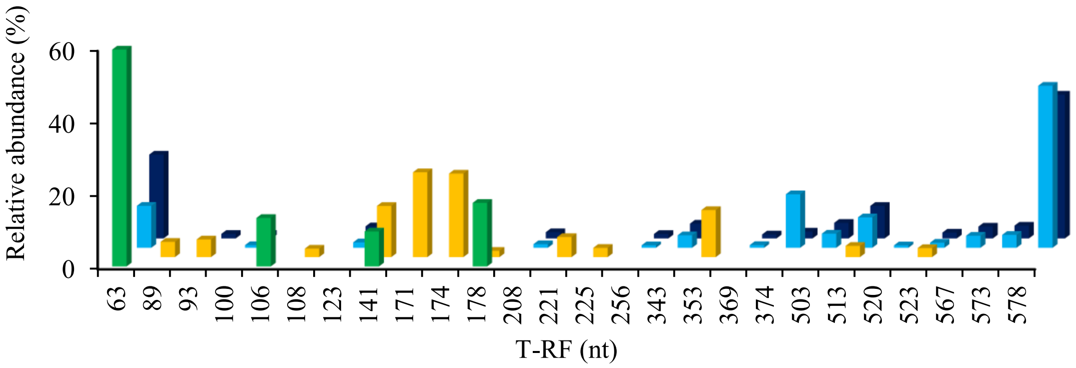

Figure 1 *T-RFLP profiles of amplified bacterial 16S rRNA gene (digested with CfoI) of filtrates from the monimolimnion water samples taken at 55 m (🟦) and 60 m (■), of the Guadiana pit lake sampled in October 2014, and the hypolimnion (15 m deep; 🟩) and the epilimnion (7 m deep; 🟨) sampled on September 2012. The major peaks identified corresponded to Metallibacterium scheffleri (63 ± 2 nt), Acidisphaera rubrifaciens (177 ± 2 nt), MCF86 (144 ± 2 nt), and clones H55B-11, H55B-27, H55B-2-1 and H55B-2-7 (580 ± 2 nt).*

Archaeal communities appeared to be very similar in waters from different depths within Guadiana, and were also similar to that found in the moinimolimnion of the Cueva de la Mora pit lake (fig. 2). The archaeal 16S rRNA T-RFLP profile was dominated by two peaks at 62 ± 2 nt (60 m sample) and at 213 ± 2 nt (55 m sample). The 60 m sample appeared more diverse than the 55 m sample.

Analysis of the clone libraries has given insights into the indigenous microflora of the enigmatic anoxic layer of the Guadiana pit lake. Few distinct clones (four for bacteria and one for archaea) were identified by RFLP analysis of complete libraries. Two bacterial clones (H55B-2-1 and H55B-2-7) were 98% similar to *Thiomicrospira* (*T.*) *crunogena*^{T}, a sulfur-oxidizing bacterium that was first isolated from a hydrothermal vent in the Pacific Ocean, which was reported not to grow at pH < 5.0 (Jannasch et al. 1985). Clone H55B-11 was related 95% to *Gallionella ferruginea*^{T}. *G. ferruginea* is a neutrophilic iron-oxidizing chemolithotrophic betaproteobacteria found in micro-aerobic environments such as well waters (Hallbeck and Pedersen 1990), though related strains (which probably represent at least one distinct species) have also been found in acidic environments, such as acid mine drainage waters (Hallberg et al. 2006). Clone H55B-27 was very distantly related to any described species, being 92% and 91% related to *Hydrogenovibrio* (*H.*) *marinus* ^{T} and *T. crunogena*^{T}, respectively.

The CfoI restriction enzyme cut the amplified 16S rRNA gene in positions 578 ± 2 nt for H55B-27, H55B-2-1 and H55B-2-7 clones and 582 ± 2 nt for the clone H55B-11, which corresponds the main peak (580 ± 2 nt) of the T-RFLP profile of bacterial 16S rRNA for samples of water from 55 and 60 m depths (fig. 1). Other peaks were not identified.

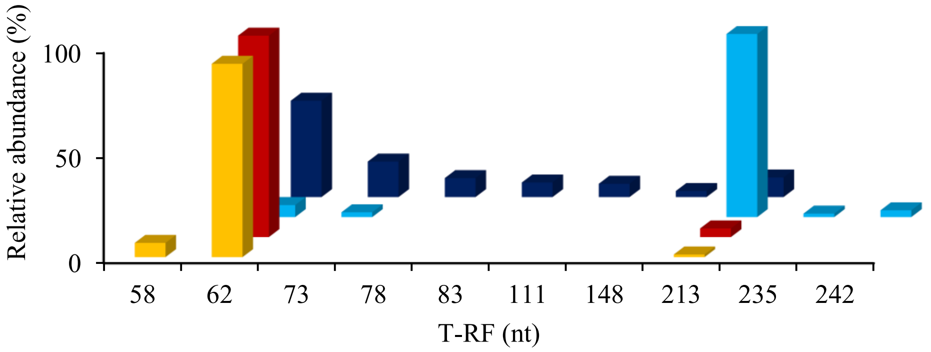

Figure 2 *T-RFLP profiles of amplified archaeal 16S rRNA gene (digested with HaeIII) of filtrates from the monimolimnion water samples taken at 55 m (🟦) and 60 m (■), of the Guadiana pit lake sampled in October 2014, and the monimolimnion water samples taken at 15.2 m deep (🟨) and 35 m deep (🟥) sampled on March 2012.*

Unlike the obtained bacterial clones, just one archaeal clone (H60A-9) was successfully obtained from the archaeal 16S rRNA clone library. This was 97% related to another clone (clone 38F-8) obtained from the monimolimnetic sediments of the pit lake Cueva de la Mora (Falagán et al. 2014). These clones are confined to the *Crenarchaeota* phylum, members of which are thought to be ubiquitous in aquatic and terrestrial environments (e.g. Abreu et al. 2001, Kemnitz et al. 2007)

Discussion

Prior to this study no indigenous bacteria or archaea had been identified in the monimolimnetic waters of the Guadiana pit lake, and archaea could only be detected in a similar pit lake of the IPB, the Cueva de la Mora pit lake (Falagán et al. 2014). The monimolimnetic waters of these lakes account 40 – 50% the lake volume. These waters are very rich in dissolved metals (e.g. Fe(II), Zn, Mn, As) and sulfate. Moreover, the monimolimnion of the Guadiana pit lake has extremely high CO_2 concentration, explained by water/rock interaction (carbonate dissolution) and by an inflow of ground water at 50 – 55 m deep (Sánchez-España et al. 2014, Boehrer et al. 2016).

In a recent study of these metal-mine pit lakes by Falagán et al. (2014), no DNA was obtained from a monimolimnetic water sample from the Guadiana pit lake. In the present work, although no isolates were obtained, archaeal and bacterial DNA was amplified from water samples taken from this anoxic layer. The T-RLFP profiles show that the bacterial communities were very similar in both water samples of the monimolimnion of the Guadiana pit lake, but they were different to that found in the upper layers of this lake (fig. 1; tab. 1). The archaeal community appeared to be very similar in waters from different depths within Guadiana, and were also similar to that found in the Cueva de la Mora monimolimnion (fig. 2).

Only a few bacteria were detected in the construction of the clone library; however, it is possible to have a good insight into the microbial composition of the monimolimnion. Clone HB55-11 was very closely related (identity of 95%) to *G. ferruginea*^{T} suggesting that it may not be the same species though it is likely to belong to the same genus. *Gallionella* is a group of iron-oxidizing bacteria firstly isolated from ferrous iron-containing fresh waters (Hallbeck and Pedersen 1990). *Gallionella* spp. form twisted stalks that are easily observed in water samples where inhabits, and use ferrous iron as energy source and carbon dioxide as carbon source (Hallbeck and Pedersen 1991), which both are found in high concentrations in the anoxic bottom layer of the Guadiana pit lake (Sánchez-España et al. 2014).

Clones H55B-2-1 and H55B-2-7 were found to be 99% related to uncultured clones obtained from deep-sea waters, and 98% related to *T. crunogena*^{T}. These clones (H55B-2-1 and H55B-2-7) were also 98% similar to an uncultured clone obtained from a marine shore sulfidic mine tailings dump (Chañaral Bay, Atacama Desert, northern Chile; Korehi et al. 2012). *T.crunogena* was firstly isolated from a hydrothermal vent at 2,600 m deep (Jannasch et al. 1985). This species can grow between pH 5.0 to 8.5 (Jannasch et al. 1985), whilst the monimolimnion of the Guadiana pit lake pH is 4.0 – 4.5. Given that the low pH at which *T. crunogena* can grow is higher than the pH of the monimolimnion, H55B-2-1 and H55B-2-7 could possibly be different species, but at least are distinct strains of the same species.

Thiomicrospira spp. are chemolithotrophic sulfur-oxidizing bacteria typically found in marine environments, *T. crunogena* uses reduced-sulfur compounds (i.e. sulfide, thiosulfate, and elemental sulfur) to obtain energy and carbon dioxide as carbon source (Jannasch et al. 1985).

Table 1. *Identities of cloned genes obtained from the monimolimnion of the Guadiana pit lake and physiological characteristics of the closest described species. Genbank accession numbers are given in parenthesis.*

Clone designation	Closest relative	% Identity (16S rRNA)	Fe/S transformations	pH range	Reference
H55B-11 (KX083694)	*Gallionella ferruginea*^{T}	95	Fe^{2+}-ox	5.0-6.5	Hallbeck and Pedersen 1990
H55B-27 (KX083695)	*Hydrogenovibrio marinus*^{T}	92	S_{red}-ox	5.0-8.5	Nishihara et al. 1991
	Thiomicrospira crunogena^{T}	91	S_{red}-ox	7.5-8.0	Jannasch et al. 1985
H55B-2-1 (KX083696) H55B-2-7 (KX083697)	*Thiomicrospira crunogena*^{T}	98	S_{red}-ox	7.5-8.0	Jannasch et al. 1985
H60A-9 (KX083698)	Clone 38F-8	97			Falagán et al. 2014
	Nitrososphaera viennensis^{T}	83		6-8.5	Stieglmeier et al. 2014

The other bacterial clone H55B-27 is distantly related to any described bacterial species (92% to *H. marinus*, and 91% to *T.crunogena*), and given this it is impossible to ascertain the metabolic function of this unknown bacterium.

Falagán et al. (2014) described the microbial composition of the upper layers of the Guadiana pit lake. The epilimnion of the Guadiana pit lake was dominated by heterotrophic bacteria belonging to the genera *Acidobacteriaceae*, *Acidocella* and *Acidisphaera*. The hypolimnion was the most microbially-diverse layer in the Guadiana pit lake. The dominant bacteria identified in this layer were very closely related to the iron-reducing moderate acidophile *Metallibacterium scheffleri*, and betaproteobacteria of the genus *Thiomonas* sp., which are sulfur-oxidizing bacteria typically found in acid mine drainage of pH 3 and above. Other bacteria able to catalyze biogeochemical transformations of iron and sulfur were also isolated from the hypolimnion of Guadiana. In contrast the majority of the bacterial clones from the monimolimnion are related to bacteria typically found in seawater. The salinity of the deep anoxic waters of this lake, mainly caused by SO_4^{2-}, Fe^{2+} and Mg^{2+} (36 – 37 ‰) is very similar to the salinity of seawater, which is mainly caused Na^+ and Cl^- (~ 35 ‰). Total dissolved solids in the monimolimnion of this metal-mine pit lakes increases with depth. The osmotic pressure under which the microorganisms might cope in this layer is therefore comparable to that found in seawater. Thus, the presence of microorganisms highly tolerant to the presence of salts is highly feasible in the monimolimnion of the Guadiana pit lake.

Three other meromictic mine pit lakes in the IPB have also been microbiologically characterized, Cueva de la Mora, the Concepción and the Nuestra Señora del Carmen pit lakes, the latter two of which experience periodic mixing. No bacteria were detected in the monimolimnion of the Cueva de la Mora pit lake Falagán et al. (2014), which is physico-chemically very similar to the Guadiana pit lake. *Nitrospira*, *Actinobacteria* and *Chloroflexi* were detected in the monimolimnion of the Nuestra Señora del Carmen while only *Betaproteobacteria* and *Actinobacteria* were detected in the monimolimnion of the Concepción pit lake (Santofimia et al. 2013).

Only one archaeal clone (H60A-9) was obtained from the 60 m sample, which was distantly related to all other classified archaeal species, though it is closely related to a clone obtained from a sediment sample collected from the Cueva de la Mora pit lake. Even though both clones are affiliated with the *Crenarchaeot*a phylum, no affiliation to a genus or species level could be inferred. The major peaks present in the T-RFLP profiles of the archaeal 16S rRNA genes from this water layer have not been identified. However, in a similar study carried out in the Cueva de la Mora pit lake, several clones obtained from water and sediment samples shared the same T-RF length (HaeIII digests) of 63 ± 2 nt. Those clones were grouped within the *Euryarchaeota* phylum, including clone 5A-1 which was obtained from a water sample from the monimolimnion in this lake (Falagán et al. 2014). Whether euryarchaeotes inhabit the monimolimnion of the Guadiana pit lake is uncertain as no clones with sequences related to any euryarchaeotal species were found. The similarity between Guadiana and Cueva de la Mora pit lakes could infer that this archaeal group may be also present in the Guadiana pit lake monimolimnion.

The presence of iron-oxidizing and reduced-sulfur compound oxidizing bacteria in the monimolimnion of the Guadiana pit lake suggests that transformations of both sulfur and iron are taking place within this zone, though electron acceptors other than oxygen (which is absent) would have to be used by these microorganisms. For example, *Sulfurihydrogenibium* (*S.*) *subterraneum* and *S. azorensens* use selenite or arsenate as electron acceptor (Takai et al. 2003, Aguiar et al. 2004, respectively), both of which are present in the monimolimnion of the Guadiana pit lake (Sánchez-España, personal communication). However, it is possible that enough oxygen could still be present in the monimolimnion at very low concentration difficult to detect, and acts as electron acceptor. The physico-chemical characteristics of pit lakes influence and are influenced by the microbial composition of their waters. The specific features of the metabolism of these bacteria and their role in the cycling of these two important elements clearly deserves further research.

This study highlights the scarce information existing of the bacterial and archaeal species inhabiting anoxic waters in metal-mine pit lakes in the IPB and the potential of these environments for discovering novel species of microorganisms, some of which could be potentially used in biotechnology.

Conclusions

The monimolimnion of the Guadiana pit lake is inhabited by bacteria that catalyze the oxidation of both ferrous iron and reduced-sulfur compounds, and therefore transformations of these elements are likely to be occurring in this anoxic zone of the pit lake.

The bacterial community of the Guadiana pit lake water column is divided in three different communities, corresponding to the physico-chemical stratification of the water column itself. The epilimnion is inhabited by phytoplankton and acidophilic heterotrophic iron-reducers, the hypolimnion by acidophilic iron- and sulfur-oxidizers, and the monimolimnion by neutrophilic iron-oxidizers and other bacteria related to that found in seawater. This is the first time that *Gallionella* has been reported in pit lakes of the IPB, as well as other species that are not typically found in acid mine waters, such as *Thiomicrospira* sp. The presence of salt-tolerant microorganisms in metal-mine pit lakes is probable and more effort needs to be done to isolate bacterial (and archaeal) species from the metal-mine lake waters as these are complex environments shown to be highly bacterially diverse.

While these findings shed new light on the complex microbial communities of metal-mine pit lakes, they also show that more research is required to understand fully how these both influence and are impacted by geochemistry of these environments.

Acknowledgements

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Persistance of Meromictic Stratification in Post Mining Lakes

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Extended Abstract

Water quality in future mining lakes strongly depends on their thermal and chemical stratification. High salinity groundwater inflow accumulating in the deepest parts of the lake can generate a permanent stratification, a monimolimnion [1, 2]. However, turbulence generated by wind action and convective mixing during cooling periods in autumn and winter will deepen and on the long run can dissolve the chemocline, thus leading to an overturn of the water column. In general the persistence of meromixis in pit lakes is dependent on the interplay of external factors (climatic conditions, groundwater inflow), as well as internal processes like turbulent mixing and possibly double diffusive convection [3, 4]. The build-up of a monimolimnion might or might not be a desired feature of mine pit rehabilitation. The question then arises, under which conditions and on what time scale such a permanent stratification is persistent. The knowledge of these hydrodynamic processes and their time scales will allow for better management of mine lakes.

Here we use a one-dimensional, vertical lake mixing model (LAKEoneD) capable of including other biogeochemical processes and successfully used in mine pit simulations [5, 6, 7]. It is driven by hourly meteorological data and parameterized by chemocline depth and salinity of the monimolimnion to simulate thermal and salinity stratification in a lake over periods of up to fifty years. The lake model is based on a one-dimensional formulation of k-epsilon closure and the vertical description of heat and momentum exchange solved on a vertical grid with 0.5 m resolution using time steps in the range of 300 seconds. Meteorological drivers like air temperature, irradiance, wind speed, relative humidity and cloudiness or longwave radiation are given as hourly time series available from a nearby meteorological station. The model simulates thermal and salinity stratification over several decades. Results are then analysed for the development of the chemocline depth over this time period. Driving the model with different types of climate input – chosen here as individual meteorological years representing different climate conditions – repeated over half a century results in empirical relations of meromictic persistence in relation to chemocline depth and salinity gradient.

Simulations using a set of 15 salinities in the range of 0 - 10 g/L, a set of 21 chemocline depths between 1 - 50 m and 30 years of meteorological data were run for a future post mining lake as they are created, e.g., in the Lausitz lignite mining district, Germany. The analysis of the ~10000 lake simulation runs shows a consistent pattern of overturn in such possibly meromictic post mining lakes after several years or decades whenever there is no additional saline inflow maintaining the permanent stratification. The generated catalogue of timings of lake overturn in relation to salinity structure and chemocline depth can serve as lower bound for the time scale of meromictic persistence in post mining lakes.

Key words: Pit lake, meromixis, turbulent mixing, hydrodynamics, lake model

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Findings from flooding residual pits remaining after coal mining in the Czech Republic

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Abstract

The work summarizes more than twenty years of experience in designing reservoirs in residual pits remaining after mining of brown coal in the Czech Republic, monitoring their flooding and development of lakes after filling. There are currently 3 artificial lakes in residual pits with a water surface of 225 to 496 hectares. In the future there will be another 5 lakes covering area in the range from 390 to 1,300 hectares. The beginning of their flooding is expected mostly after year 2035. Due to complete lack of natural lakes in the Czech Republic, the main expected use of these artificial lakes is recreation, including sport fishing.

Rehabilitation projects of mined areas are processed for many decades prior to the termination of mining. This planning gives the possibility to optimize the morphology of the residual pit with minimal cost. Subsequently, studies have repeatedly supplemented and corrected. However coal mining is currently associated with the risk of early termination of mining, when the residual pit does not have the optimal morphology. This also concerns all residual pits with regulated flooding in the Czech Republic.

The stabilization of residual pit slopes is associated with the greatest cost and problems, which are mainly the consequences of water saturation of soils that had been drained for decades. Especially expensive is the fortification of shoreline at the final water level. Abrasion during lake filling is confined to a strip not exceeding 2 m around the perimeter surface and does not affect the overall stability of the slopes.

For flooding the preferred option is water with the least contamination. There are enough data on the quantity and quality of water selected to flood the residual pits. On the contrary little data are available about the quantity and quality of water flowing from the slopes of the quarry. It is crucial for the development of the water quality of lakes in the period after of their filling.

Water quality is not a problem in the Czech conditions. The resulting pH of lake water in all cases is slightly alkaline. This, together with good oxygenation of the water leads to a drop in metal concentrations below the limits for surface water even during filling. Nowhere was found significant contamination by chemicals or bacterial contamination. Trophic state is adapted to the amount of inflowing nutrients and depth of reservoirs within a few months. Residues of mine water on the bottom of the pit cause short-term or long-term meromictic state. In one lake is formed near the bottom anaerobic state, which on the end of November, affects about one third of the lake area.

The concentration and species composition of plankton, benthos and fish is strongly influenced by very low water trophy. Problems with cyanobacteria water blooms were not observed and this situation is sustainable. Submerged vegetation develops rapidly and large reservoirs are attractive for water birds.

There is no clear definitive future owner of the lakes due to fears of the high costs associated with the maintenance of the lakes.

Key words: residual pit, lake, Czech findings

Introduction

Pits remaining after the surface mining of minerals are often spontaneously flooded by rain and by surface and underground water. Flooding sometimes occurs already during extraction, particularly in sand and gravel mining. In the Czech Republic there are tens of thousands of such flooded pits from the past. They usually cover a small area and the process of flooding was not regulated. Closing of large open pit lignite mines created the need for the controlled flooding because the spontaneous flooding would take many decades or even century. Controlled flooding is in accordance with Czech legislation regulating the extraction process and following recultivation of the territory after stopping of mining. It also ensures relatively rapid achievement of the target state and thus accelerates considerably the use of the resulting lakes. Controlled flooding also allows modifying some features of lakes according to their expected future use.

Currently there are in Czech Republic three lakes built in the brown coal residual pits with a water surface of 252 to 496 hectares. In the future there will be another 5 lakes with a surface ranging from 263 to 1,312 hectares. The beginning of their flooding is expected however mostly after the year 2035th. In the meantime it is convenient to sum up past experience and adjust projects of the flooding of other quarries accordingly.

History

In the Czech Republic there are many dozens of larger reservoirs formed by flooding pits after the open pit coal mining, which originated mainly after year 1945. Spontaneous flooding lead to creation of lake up to 60 hectares in size and over 50 m deep - Barbora near Teplice. This lake is extensively studied for 30 years and is the source of much valuable knowledge about the behavior of mining lakes. As a rule, however, spontaneously flooded lakes are significantly smaller and shallower, eg. water areas in the residual pits of former small surface mines Otakar, CSM, Liebig, Dukla near Teplice or Elizabeth near Most. The water quality of these lakes is much better than in ponds and dam reservoirs. Some lakes are meromictic with elevated concentrations of salts and some metals under chemocline. In general they are used for sport fishing and swimming.

Several smaller pits were flooded artificially. In the early 70s of the 20th century residual pit quarry Benedict in the vicinity of Most was filled and used as a natural swimming pool. But the bottom of the reservoir was not sufficiently sealed and it lost water. The reservoir had to be rebuilt and reduced, which was implemented in 1999. It now has a water area of 4.7 ha. In early 90s the site of a former quarry Vrbenský on the edge of the town Most was built and Matylda reservoir was artificially filled up and used for water sports. It has an area of 39 ha, but the maximum depth of only 4 m. If necessary, it can be drained. In 2002 additional reservoir in the residual pit mine Michal near Sokolov was artificially flooded. It has 30 ha and maximum depth of 5 m and can be drained if necessary, which has already been done twice. It serves as a natural swimming pool. The reservoir is currently inhabited with purposeful fish stock.

These shallow reservoirs have naturally higher trophic conditions than deep lakes. Water quality is monitored systematically only in the Michal reservoir. Although it succeeded in maintaining pure water with perennial transparency 3-5 meters without cyanobacteria, it is clear that eutrophication of the reservoir is uncomfortably fast. Without the fish stock, its biocenosis develops highly unpredictable and there are various problems that must be solved operatively: mass reproduction of toads, macrovegetation overgrowing, Swimmer's Itch, etc. Specialized fish stock must be chosen very carefully in order not to cause excessive release of nutrients from the bottom to the water column.

Some residual pits were or still are used to store fly ash. This is not their final state and falls outside the focus of this work.

Since the last decade of the last century there were closures of big mining quarries with pits large enough to enable creation of lakes up to 1,300 ha in size with a maximum depth of 200 m. For these potential reservoirs, controlled flooding is part of the reclamation of the entire mining area. In early 90s of the last century there was a broad initiative addressing the selection of optimal recultivation method for the post-mining territory. The possibility of filling these pits with waste material stored in dumps was dismissed as economically and ecologically unfavorable. Instead, the initial recommendation was to build shallow and flow reservoirs. Based on limnologic theory the contrary was justified - that to achieve good water quality the lakes should be as deep as possible and with little flow. The need for a thorough isolation of coal seams from the water column has proved unnecessary. To achieve stability of the bottom rapid filling with water in 4-8 years was advised even for the biggest pits. This approach has been used for the controlled flooding of three residual pits: Chabarovice (Milada), Most and Medard. Findings presented in this work are based on lessons learned from their flooding. Table 1 gives an overview of lakes in large residual pits after mining with the currently considered parameters.

Table 1 *Overview of lakes in large residual pits in Czech Republic.*

quarry name	water area (ha)	altitude (m)	volume (10^6 m^3)	mean depth (m)	maximum depth (m)	start of flooding year	end of flooding year
existing lakes							
Chabarovice	252,2	145,7	35,6	14	25	2001	2010
Most	309,4	199	70,5	23	75	2008	2014
Medard	495,8	400	119	24	50	2008	2016
planned lakes							
CSA	666,1	180	270,3	41	130	2026	
Bilina	930,6	200	706,1	76	200	2038	
Libous	939,8	275,2	235,7	29	76	2038	
Jiri	1 312,3	394	514,9	39	93	2038	
Vrsany-Sverma	263,5	206	44,8	17	40	2050	

Projects of controlled flooding

Flooding of residual pits is solved individually for each quarry within the Reclamation Plan, which is an integral part of the so-called Plan of opening, preparation and extraction. On this basis the license for mining activities in accordance with the Mining Act is issued. Water management solution of residual pit flooding is usually progressively refined by updates of so called General plan of remediation and reclamation, which solves the overall concept of rehabilitation and reclamation of areas affected by mining. Implementation of the project of the final site remediation precedes the EIA process.

Viable project should contemplate and if possible incorporate various alternative uses: recreation, quality water source, pump storage plants, fishing, retention of flood waves, bird reserve etc. Because of the complete lack of natural lakes in Czech Republic, the use of mine lakes primarily for recreation, including sports fishing prevails. No project is currently aimed at using these lakes for protection against flood.

The first study of reclamation is prepared decades before the termination of mining. This theoretically allows even during mining itself to cheaply optimize the final shape of the residual pits mainly in the areas of future shoreline. Reclamation projects are associated with considerable uncertainties especially in extent of mining. Gradually they are updated and refined. The greatest risk is currently a sudden early termination of mining, resulting in suboptimal morphology of residual pit. This has occurred in all still controlled flooded residual pits. The reclamation projects solve the slope stability, bottom sealing, fortifications of coastal line, colliding with underground mining, the amount of water needed for flooded pits, spreading capacity of water resources and their quality. Prediction is made of the water quality immediately after filling of lakes and its further development. An effort to reduce the cost of reclamation leads to the assessment of variants with reduced water levels, which is inconsistent with the optimal solution to the future lakes with long term benefits.

Experiences with controlled flooding of pits

The water quality is monitored in detail by mining organizations during filling and the monitoring continues even after filling. Independent monitoring was conducted in the framework of various research projects. These lakes will become independent artificial water bodies of stagnant water under the Framework Directive of the EU water policy. At present there are filled lakes also monitored according to the requirements of this Directive. Development of water quality and biota of artificial lakes, especially during relatively long flooding, differs from new dams and natural lakes with steady conditions. From this perspective, this monitoring and its findings stimulate the development of hydrobiological theory. The topic of residual pits flooding in the Czech Republic has been repeatedly presented at IMWA conferences (e.g. Svoboda et al. 2008; Vrzal et al. 2011; Prikryl, Spacek, Koza 2011; Peterka et al. 2011; Peterka, Kubecka 2011). Results of a broad-based project investigating the flooding of Most lakes are published eg. in the works Rehor , Frastia , Schmidt 2013 and Vagnerova, Svoboda, Brejcha 2013. Much of the data is in non-public reports to the mining companies.

The monitoring of all three still flooded large residual pits shows that the predictions of their water quality were generally successful. We were unable to predict only the emergence of chemoclines in two lakes and high concentrations of some substances in the oxygen-free water layer under chemocline. Water under chemocline at greater depths, however, is well insulated from higher layers and does not significantly affect its chemistry. Water under chemocline represent only a few percent of the lake volume and is usually located in depressions on the bottom. If necessary, the chemocline can be inexpensively eliminated. Formation of long-term stable chemoclines can prevent the inclusion of local depressions in the bottom of quarry before flooding.

The quality of water in the upper stirred layer corresponds well to expectations. This is confirmed by extensive monitoring of all three lakes. In comparison with the quality of the inlet water the concentration of nutrients quickly decreases, so lakes are oligotrophic usually already during filling. Small production of live biomass allows for maintaining high concentration of oxygen in the water column with the partial exception (Lake Chabarovice) described below. The catchment area of the lake itself, i.e. slopes adjacent quarries and dumps, consists of impermeable clay soils with weak erosion. Some of the springs on the slopes of quarries may be enriched with metals, and thus contribute to their concentration in the lakes in the long term. However, the share of acid water is small and the resulting mixture of water from its own catchments area has an alkaline pH. The combination of high oxygen concentrations and sufficiently high pH leads to a rapid decrease in the concentration of metals. Selected organic toxic substances (in the lake Chabarovice approximately one hundred substances) in water and sediment were also monitored. No measurement of these substances exceeded applicable limits. For all currently flooded residual pits the high water transparency is adequate - in the summer from 5 to 10 m, in winter even higher.

During the flooding there were some unforeseen problems that have raised fears of mining organizations regarding meeting the conditions of required water quality: increased turbidity of water in the initial period of pits flooding, oxygen deficit in the metalimnion during heavy inflow of river water, high concentrations of nitrates originating from reclaimed areas, high concentrations of chlorophyll in metalimnion, the stratification of dissolved substances and complicated vertical structure of their concentration. These problems have been explained and during flooding mostly disappeared.

Most of the pits in the Czech Republic are in an area with a lack of rainwater and without major rivers. Great attention is therefore paid to the water sources for the flooding. Preferred are waters with the least pollution, which is a certain problem of mining areas. Nevertheless, there are sufficient data on the quantity and quality of water selected for the flooding of residual pits. On the contrary, there are little data on the quantity and quality of water flowing from the slopes of quarries. That over several decades will replace the water from an artificial source. It will then be crucial for the development of water quality in lakes in the period after the flooding. These waters sometimes have a high salt concentration and enormous concentrations of metals. Their quality after termination of mining is changing quite rapidly, which complicates forecasting the development of water quality in lakes. A separate problem is discharging sewage from the expected intense recreation outside the lakes.

Even with an overall excellent quality of water-filled mine lakes, some indicators will exceed the current limits for surface water. This concerns in particular dissolved substances and sulfates, sometimes calcium or magnesium. Exceeding the limits in this case is not a sign of water pollution because it is in these conditions a natural state. It would be desirable that these properties of lake water also take into account the Government Decree on the values of permissible pollution of surface waters.

Protection of buildings constructed during the existence of the quarries below the original level of ground water forced the reduced levels of water compared to natural levels in lakes Chabarovice and Most. It has certain negative implications for the water quality. Chabarovice Lake has an average depth of only 14 m. The result is a very small volume of the layer called the hypolimnion, in which oxygen enters only in the circulation water in the cold season. Although the lake is oligotrophic, there is not enough store of oxygen to the mineralization of organic matter falling from the upper layers of water. Oxygen deficit is increasing gradually during the year from greatest depth. In November, before re-mixing the entire water column anoxia will hit bottom about one third of the lake. The concentration of iron, manganese, ammonia nitrogen and total phosphorus increases in oxygen-free water. The lake is under permanent threat of inner eutrophication, which would greatly deteriorate water quality for recreation. Lake Most was built as endorheic due to reduced water levels. The level is chosen so as to compensate for the inflow and evaporation and minimal enough water filling from external sources or occasional pumping to maintain the level of the selected range. The lake has a sufficient depth so there is no risk of internal eutrophication. However, water with increased concentration of dissolved substances flows into the lake from its own watershed and these substances are concentrated in the lake due to evaporation. Unlimited growth of solute concentration in the longer term could degrade the water for recreation. It will therefore be necessary to ensure greater exchange of water than is sufficient to maintain normal water level.

The concentration and species composition of plankton, benthos and fish in large residual pits are strongly influenced by very low water trophy. The amount of planktonic organisms is very small and their species communities are rather poor in comparison to the dam reservoirs and ponds. No problems with cyanobacteria water blooms have been reported to this date and this situation is sustainable. Monitoring has demonstrated surprisingly high species richness of benthic organisms, for instance 17 species of aquatic mollusks in the lake Chabarovice. Submerged vegetation develops spontaneously relatively quickly, mainly due to the high transparency of the water. Rare and protected species, especially those with high demands for clean water are also present already in the first years of flooding. Large reservoirs are attractive for water birds, although they do not have sufficient food supply. Waterfowl are potentially a significant source of eutrophication of these reservoirs. Incidence of non-native species of plants and animals was also reported, but it poses no significant risk for the lakes. Mining lakes do not meet the needs of anglers. Due to the low trophic conditions of lakes fish stock reaches approximately 10 kg / ha, at most several tens kg / ha. This can be partially compensated by the occurrence of a record size fish, which is the common in many small spontaneously flooded residual pits. Anyway sport fishing in these lakes will have to be very carefully regulated.

Water quality in terms of various indicators can be evaluated as very good and no action to improve it was required yet. The same cannot be said about the technical reclamation. Experience shows that the greatest costs and challenges are associated with residual pit slope stabilization. These are mainly the consequences of water saturation of soils, which were drained for decades. Planned recreational operation of filled lakes can be delayed for years due to the need for slopes stabilization. Sealing the bottom of pits is costly, especially if it threatens to flood the underground space with still active mines. Especially expensive is the fortification of shoreline at the final water level. Fortification is done for the minimum water level fluctuations (usually plus or minus 0.5 m). Greater fluctuations in the water level or even a small change of level compared to the project necessitate larger fortifications. The impact of coast abrasion during flooding of the lakes is noticeable already after several centimeter change of water level. Abrasion is confined to a strip not exceeding 2 m along the perimeter surface and does not affect the overall stability of the slopes. Therefore the limited extent of damage caused by abrasion is not the reason for fast flooding of lakes. It is thus possible to save considerable costs associated with building the capacity of supply channels and pipes or buying water pumped to remote locations.

There are high expectations associated with the lakes originated by coal mining, because there are no large natural lakes in the Czech Republic, where it would be possible to do water sports. Several small mountain lakes are part of a protected area with restricted access. Another favorable aspect is the predicted and documented excellent water quality in mining lakes in comparison with dams and ponds. Grandiose ideas arose about the extent of recreation on lakes and their surroundings. The adjacent large cities as well as smaller municipalities showed initially great interest in operation of these reservoirs. The problems with the stability of the pit slopes and costs associated with troubleshooting cooled this enthusiasm considerably. Municipalities are now reluctant to take ownership of the ready-made lakes, because they fear the costs spent on their maintenance and payments for water required for their recharge. They are unsure of their ability to meet the conditions of handling regulations. Strict legislation on the quality of surface water and lack of professionals in the municipalities with understanding of this issue undoubtedly contribute to these concerns. State-owned enterprises which take care of the streams and dams, are not interested in the management of these lakes either, because they are not their usual source of revenue that are the water sale and electricity production. These companies do not have the promise of state funding necessary for the lake maintenance, as they are used to receive for watercourses. Maybe this situation will extend the existence of the residual state enterprise, which ensures the completion of reclamation of old mining areas and currently employees group of experts knowledgeable in the mining lakes subject. This applies to lakes Chabarovice and Most. Lake Medard remains owned by a private mining company Sokolovská uhelná, which plans the use of land in its post-mined territory in the future. This company already operates Michal reclaimed pit lake used as a natural swimming pool. Therefore there should be no issues with the operation of this lake. Currently we are awaiting the first major investment in sports and leisure facilities in filled lakes which would be inspiration to other investors. Lakes definitely have the potential to generate enough money for their maintenance from these activities.

Conclusions

For practical reasons, the residual pit should be flooded soon after extraction to accelerate the start of their expected usage.

The water should preferably be at the level of the surrounding streams so that excess water can be drained by gravity. Alternatives with reduced levels lead to the need for costly long term water pumping, which also causes water quality deterioration. Lakes with a strongly recessed surface are poorly usable for recreation.

It is advisable to design either relatively shallow lakes with an average depth of 6 m (a maximum depth of about 15 m) or vice versa deep lakes with an average depth of over 20 m (maximum depth over 50 meters). In lakes with an average depth of about 6-20 m, hypolimnion with a small volume and inadequate supply of oxygen is formed. The result is the emergence of annual anaerobic layers at the bottom and a strong tendency to internal eutrophication.

It is not necessary to rapidly flood the lakes, originally justified by the fear of abrasion shores. Conversely, it is possible to save considerable costs associated with building a capacitive supply channels and pipes and pay for the water that must be drawn from streams. Use of less abundant streams from which water flows to residual pits by gravity is more cost efficient.

For good properties of the lakes, unscheduled early termination of mining activities that does not allow for proper shaping of the residual pit is a particular risk. Subsequent landscaping is much more expensive. Big problems associated with improper morphology of residual pit will probably arise in quarry CSA unless the so-called territorial environmental limits are exceeded.

If formation of chemocline and meromixis would be assessed as undesirable in the future, it is possible to significantly reduce their occurrence by filling depressions at the bottom of the quarry.

Phosphorus as a main limiting nutrient gets to water reservoirs through different ways. Only a very small proportion of phosphorus flows away from the reservoirs or escapes. Water reservoirs are therefore gradually eutrophicated; in contemporary eutrophic cultural landscape uncomfortably rapidly. Supply of phosphorus during flooding can be quite precisely assessed depending on the quality of water from different sources. In contrast, the sources of phosphorus after flooding can only be estimated on the basis of current knowledge and their balance is very inaccurate. Data to support measures to slow eutrophication are unfortunately not abundant. Research on this issue in the conditions of Czech coalfields is therefore very necessary.

During the flooding of other residual pits greater attention should be dedicated in time to the balance and quality of water flowing from its own catchment. Its influence has been underestimated so far. However, in a long term perspective, it will determine the quality of the lake water virtually in all quarries.

In the ongoing evaluation of data acquired by monitoring it is necessary to take into account the changing characteristics of lakes during the climb levels and already identified patterns of the various stages of flooding. It is to be expected that despite the overall excellent quality of water, several indicators may not meet the normal limits for surface water in the whole volume of the lakes or more frequently in a specific water layer. In whole volume it is mainly a solute, sulfates and sometimes calcium or magnesium. Under eventual chemocline the limits for surface water may be greatly exceeded and for more substances then in the whole volume, as well as concentrations of some metals and ammonia nitrogen and moreover deficiency of dissolved oxygen. Oxygen deficit can occur temporarily during flooding and persists for some time after flooding even in the upper water layers. The pH limit may be breached in some lakes in the summer due to photosynthetic activity of macrovegetation. In all these cases exceeding the limits does not adversely affect the anticipated use of lakes, i.e. recreation and recreational fishing. The high pH value is not the indicator of pollution in this case, but the natural property of waters in the catchment area of lakes in the residual pits.

Irrespective of the previous comments, good quality of water suitable for the needs of recreation and fish life, exceptional for the usual conditions in the Czech Republic, can be realistically expected in these new lakes. Most of the lakes will be very resistant to the effects of eutrophication. The mass development of cyanobacteria algal bloom, which is in recent decades a major problem in today's recreational vessels, is not a threat in these lakes. Flooded residual pits will hold large strategic reserves of high quality water, which at the appropriate management can be pumped from new lakes also for other uses. These lakes will be undoubtedly beneficial to the biodiversity as well. The new artificial lakes can certainly serve these and other functions with minimal maintenance costs for hundreds or thousands of years.

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Advanced treatment of pit lakes using limestone and carbon dioxide

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Abstract

In Lusatia (Germany) a lot of pit lakes were flooded due to rising groundwater over the last few years. Many of the newly developed lakes are affected by an inflow of potentially acidic groundwater from the adjacent overburden dumps. Therefore, technical treatments are necessary for a sufficient water quality. Liming is the most widely used treatment. At present various liming procedures are used. However, the most of them have a relatively low buffering capacity i.e. less than 0.3 mol/m³. This leads to, repeated treatments at short intervals being necessary.

A significantly higher buffering capacity can be achieved by the use of limestone and carbon dioxide. In 2015 a pilot treatment was conducted within the pit lake "Scheibe", one of the largest pit lakes in Lusatia with a volume of 110 Mm³. The input of limestone and carbon dioxide was carried out with two underwater nozzle pipelines. This technology has already been used for the primary neutralization of Lake Scheibe (Strzodka et al. 2013). In this paper we will present this new treatment concept in detail and the results of the pilot test.

Key words: Mine water, pit lakes, buffer capacity, treatment

Introduction

Usually, after open pit mining ceases, the residual hole is filled and a pit lake is created. In the Eastern German Lusatian lignite mining area, this will result in Europe's largest artificial lake district. Many of these lakes comprise large water volumes and surface areas and are therefore amongst the largest lakes in Germany (Nixdorf et al. 2001). The inflow of potentially acid groundwater from the adjacent overburden dumps results in sulphate dominated acidic conditions.

Usually, lime products are used to neutralize acidified lakes. After pure lime treatment the waters show pH-neutral, weakly buffered waters. These environmental factors can only be maintained for a relatively short time. A continuous inward flow of acidic ground water leads to successive re-acidification and sometimes costly follow-up treatments.

A stronger pH buffering can also be reached with developing a hydrogen carbonate buffer (Alkalization) in the lake water body with the application of lime products and CO_2 (Koch 2009) thus reducing the periodic treatment cycles. The aim is to produce a reaction of the components incorporated into the lake water to produce hydrogen carbonate. The restriction of producing hydrogen carbonate solution in a technical reactor can be avoided by transferring the reaction to the water body itself (LfULG 2012). A considerable advantage is the utilizable reaction volume and the longer reaction times.

This paper presents our work with the aim to develop and test an inexpensive and efficient procedure of feed-in the alkalization media lime and CO_2.

Methods

To produce a hydrogen carbonate buffer a lime product and CO_2 are usually fed into the lake water body. The chemical reaction between the reactant and the lake water produces hydrogen carbonate which is the aim of the Alkalization process. The advantages of transferring the reaction to the water body itself lies in the utilizable reaction volume and much longer reaction periods for the hydrogen carbonate solution to reach a target concentration for the desired lake water quality.

The feed-in technology uses the underwater nozzle pipeline (UNP) with jets which had already been proven suitable to mix and produce a lime suspension (Strzodka et al. 2013). From the start of the pilot project of developing the procedure and concept of the system to neutralize the Lake Scheibe the existing UNP from the past treatment (as of now liming plant) was fully integrated in the planning phase.

To have an efficient method with a minimum of energy and thus inexpensive incorporation of CO_2 there are similar requirements as in introducing lime. An evenly mixed alkalization medium in the lake water body (hypolimnion) is vital for the procedure. Bearing this in mind and using the free jet principle, another plant was erected on the existing site to feed in CO_2 (as of now CO_2-plant).

The technological approach was to apply the lime in suspension using the existing liming plant from the past liming treatment. The suspension will be fed over the UNP close to the lake surface (epilimnion) using the free jet principle. Within the same time frame and in the same area, conditioning of the deep waters (hypolimnion) with CO_2 will be carried out using the newly erected CO_2-plant. The CO_2 will be dissolved in water drawn from the lake into the plant on land and then fed via the UNP pipelines using the free jet principle once again towards the bottom of the lake.

By using the procedure in the natural thermal stratification period of summer the suspension spreads horizontally along this boundary layer (metalimnion) due to the density differences. In addition the boundary layer metalimnion has a function of reducing the premature CO_2 loss to the atmosphere. The lime particles dissolve successively on the way through the hypolimnion reacting with CO_2 and thereby have a buffering effect on the hypolimnion from the hydrogen carbonate. In the course of the water body´s full circulation there will be an even distribution throughout the entire lake.

Area under Investigation

The test of the UNP procedure for Alkalization was carried out in the Lake Scheibe near the town of Hoyerswerda. It has a volume of 110 Mm^3 and is rated as one of the largest pit lakes in the Lusatian lignite mining area. It has a length of 5.2 km and a maximum width of 1.7 km. As a result of the lignite mining technology used, the lake's morphology is characterized by two distinct features: the eastern part of the lake consists of the former pit's inner dump with a shallow water area with a depth of 2-6 m and the western part with a water depth of 35 m (fig. 1). Lake Scheibe is characterized by dimictic conditions with full circulation phases in spring and fall.

Determining aspects of the water composition of Lake Scheibe are the ground water inflows into the lake: from the south, from the mother rock a slightly acidic ground water with acidity of approximately 1.0 mmol/L and from the inner dump water an acidity of 6.7 mmol/L.

The initial determined state for Alkalization of the Lake Scheibe to be treated was 0.07 mmol/L buffering, and a pH around 5.0.

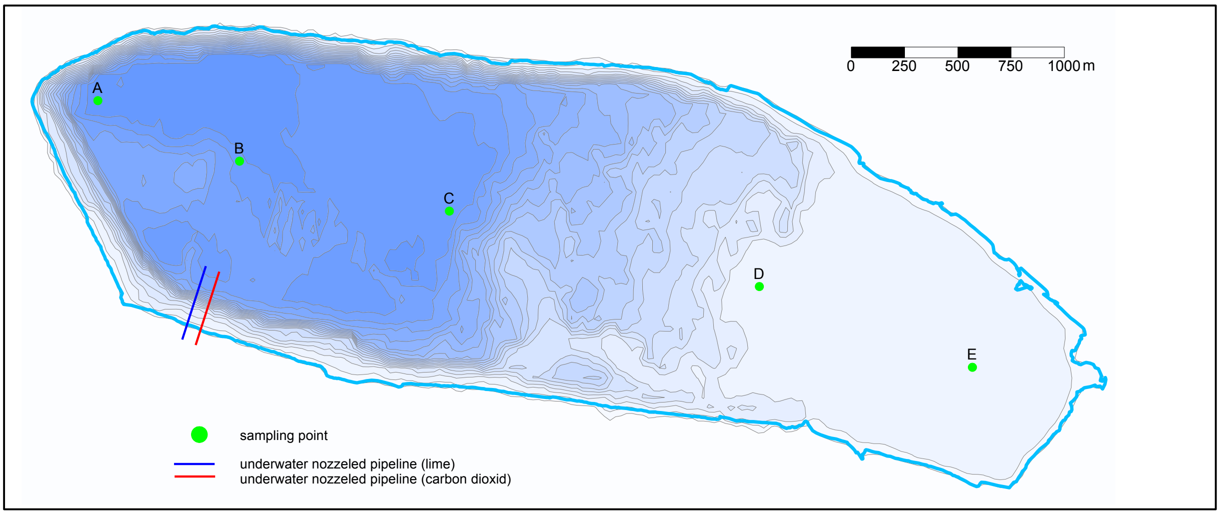

***Figure 1** Morphometric of Lake Scheibe and sampling points.*

Pilot Project Implementation

To neutralize the water body a constant layering of pulverized limestone (KSM 60/3) in the epilimnion and CO_2 in the hypolimnion was planned. The change from using the quicklime (used in the primary neutralization) to KSM was necessary as for procedural purposes this lime product lies on the metalimnion with a more concentrated effect and so the time it is transported into the hypolimnion is retarded. During liming the feed quality requirement of the epilimnion must still be maintained. This is only possible with a carbonated lime product (may not exceed the pH-value of calcite saturation). Simultaneously the acceptable pH level in the epilimnion necessary for flora and fauna is retained.

After the full circulation in fall, a buffering of 1.0 mmol/L throughout the lake water should be attained. For KSM lime 83 g/m³ is the required dosage to reach a 65 % chemical efficiency. 9.075 t KSM is fed into the entire lake.

Firstly in buffering the hypolimnion the stoichiometric required amount of CO_2 to dissolve the pulverized limestone has to be present in the water. Secondly there must be enough driving force to be able to reach an adequate chemical efficiency of the reaction. As a result of pretesting it was established that a temporary lowering of the pH in the hypolimnion is necessary by feeding CO_2 to reach $pH \leq 5.5$. It was planned to feed in a total of 5,000 t CO_2 in within 10 weeks. The aim was to feed in 3.3 t CO_2/h with 1,000 m³ pumped lake water per hour.

The process related components of the UNP procedure to alkalize the Lake Scheibe were kept very simple (fig. 2).

To produce and introduce the CO_2 solution, submersible pumps are used to draw lake water from below the metalimnion and feed it into the gaseous dissolving reactors on land. In this mixing installation, gaseous CO_2 from a tank and intermediate vaporizers is dissolved in untreated water. Pumps on land with an additional capacity ensure the required feed pressure. The CO_2-rich water is then pumped through the pipes in the hypolimnion. As in the lime suspension feed process there are jets in pairs installed at the end of these pipes (positioned close the bottom of the lake - deep water area), for injecting the CO_2-rich water according to the free jet principle. For the system at Lake Scheibe 10 pair nozzle configuration at intervals of 10 m was planned. To ensure a gaseous free exit from the jets the pipeline is kept under positive pressure.

With the proportion of the size of the water body to the entire configuration of the Alkalization – facility one point of feed only is needed (fig. 3).

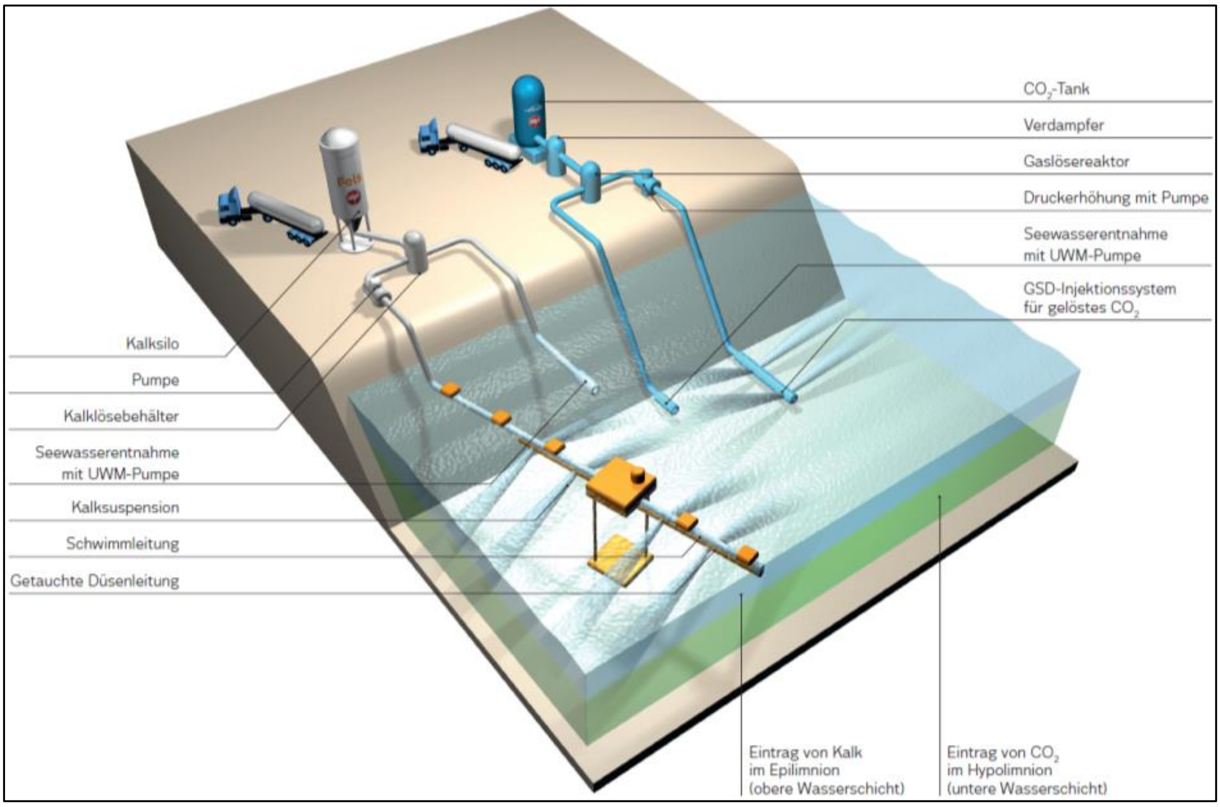

Figure 2 *UNP-equipment to neutralize the Scheibe lake (left: components of existing liming equipment right: components of the newly erected CO$_2$-plant).*

Figure 3 *Lake Scheibe with the Alkalization facility in operations (foreground, centre of picture.*

The pilot project to alkalize the Lake Scheibe started 10.06.2015 (lime- and CO$_2$-conditioning) After 14 weeks in operation the CO$_2$-feed ended 28.09.2015. There was an interval with reduced CO$_2$-feed as well as a break in operations (fig. 4).

The liming treatment ended 30.10.2015 after 17 weeks of operations. As a result of the reduced CO$_2$-dosis and the break in operations in the CO$_2$-plant the liming was temporarily stopped.

In monitoring the lime and CO_2-conditioning 14 water samples were taken and analyzed, at weekly intervals at 5 sampling points (fig. 1). Based on the changes of the water quality, the specifications for the further operation of the Alkalization plant were determined.

The monitoring of the hydraulic conditions of the lake provided the basis for validating a 3D lake model (MOHID-Water Modelling System). Both data were used to verify the design calculation algorithms previously used.

Results

The thermal stratification of the lake was fully developed when the treatment began at the beginning of June. The lake´s metalimnion was 10 m below the water surface. At the end of September 2015 the thermal stratification began to gradually breakup. The phase of full circulation only started in December.

The change of the average lake water´s condition over the time period is demonstrated in fig. 4. The measure for alkalinity is derived from the parameter neutralization potential NP (Evangelou 1995) as modified by Schöpke 2008.

During the course of feed-in of the materials carried out to October 2015, the buffering effect of the lake water increased to 0.87 mol/m³. The periods of both interruptions of the liming plant and that of the CO_2-dosing can be seen in fig. 4. With the interruption of the feed-in of pulverized limestone the NP of the lake water remained constant.

Samplings of the after-run period showed that after the end of treatment the re-acidification due to a net-acidified groundwater was not immediately detectable. A secondary reaction progressed into December 2015, which was able to overcompensate for the acidity in the ground water inflow. Measurements in December indicate a lake water NP of 0.9 mol/m³. In March 2016 there was an NP of 0.79 mol/m³ (fig. 4). If the re-acidification trend of the values measured in December and March are followed to the end point of Alkalization (30.10.2015) it corresponds that the treatment had an effect of producing a final NP value = 0,95 mol/m³. The buffering of the lake water was increased by 0.88 mol/m³. The target value if 1.0 mol/m³ was thus not quite reached.

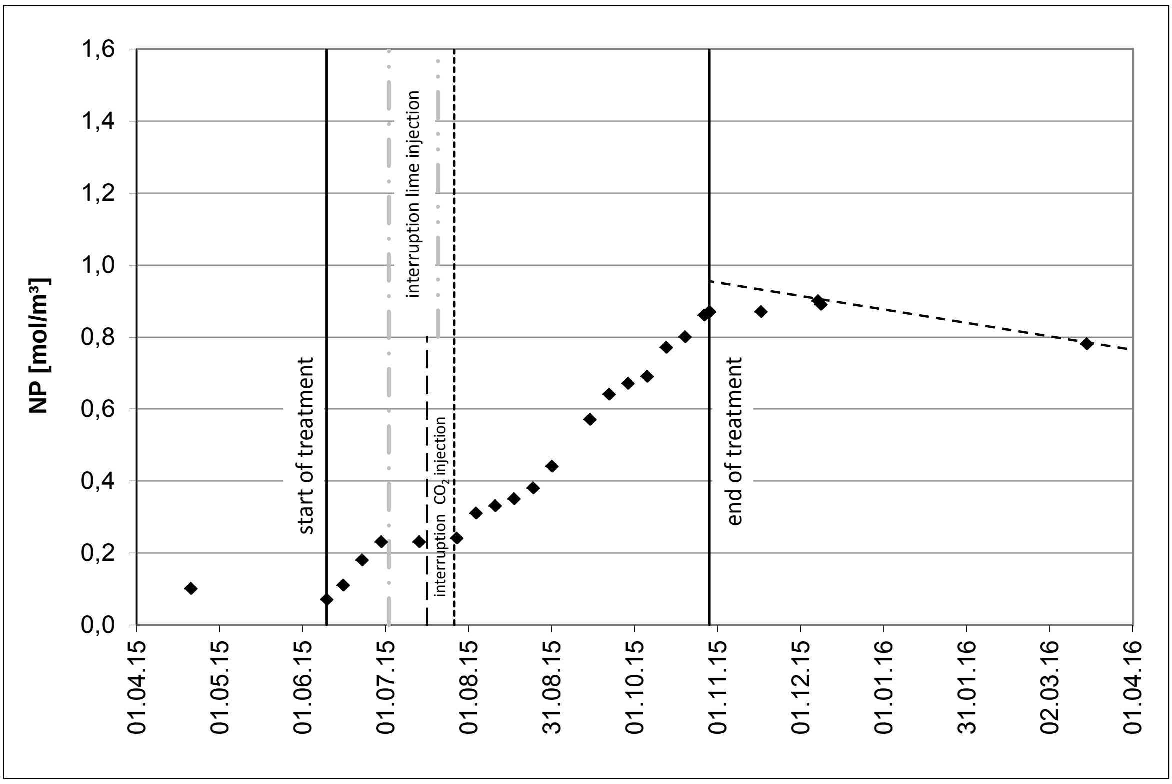

Figure 4 *Temporal progress of the lake Scheibe treatment.*

As a result of the surface treatment with the pulverized limestone and the introduction of CO_2 close to the bottom of the lake a characteristic pH-profile developed which remained throughout the duration of the entire treatment. The Epilimnion remained pH-neutral. Towards the bottom of the lake the pH value was lowered to approx 5.5 due to the in-feed of CO_2.This had an effect of providing a driving-force or at least maintaining it, to dissolve the pulverized limestone. With the interruption in the CO_2-feed on 29.09.2015 there was a hypolimnion with a successively higher pH-value.

With the UNP equipment, CO_2 is fed into the lake with virtually no losses during the summer stagnation. At this stage there was no abnormal increase in CO_2 loss into the atmosphere. The CO_2-pipeline with mass dosage of up to 3.6 t/h is unique in the context of lake quality restoring.

In September 2015 a side reaction was detected with demanganesation within a period of three weeks only. However this reaction was restricted to the epilimnion. The reduction of the manganese content from 0.9 mg/l to 0.1 mg/l was presumably from a catalytic reaction of microbial origin. With the precipitation of the manganese oxide hydrate, the bottom of the lake turned temporarily black giving the water a black appearance.

A further microbiological metabolic process was detected, the decrease in ammoniacal nitrogen, from the end of September into November. In contrast to the demanganesation the metabolic materials did not remain exclusively in the epilimnion. Due to the pH and temperature gradients the reaction started up in the epilimnion, due to the favourable conditions. Although for nitrification the pH-environment in the hypolimnion was suboptimal (Rusten et al. 1995), comparable concentration differences to the epilimnion were reached. In total the lake´s average only changed from 1.1 to 0.7 mg NH_4-N/l. A key limitation of the metabolic conversion rate and the biomass growth is caused by the low concentrations of phosporus in the iron-rich water or previously iron-rich water. (De Vet et al. 2012, Nordeidet et al.1994).

Since 2010 the development of the water quality of the lake has been simulated based on a balance model. This balance model continues to serve for forecasting future developments. Over the last few years there has been a steady increase of acidic water introduced via the groundwater. The annual inflow of acidic was previously 20 mio. mol and has now reached 30 mio. mol. The forecast is made on the assumption that the hydrogen carbonate buffering capacity is exhausted after 3 years. In comparison to simple liming the treatment intervals could be more than tripled.

After conditioning the lake water with lime and CO_2 buffering with hydrogen carbonate is 5.5 times more effective than plain lime, costs of alkalization 4.6 times. With this the economic viability of the pilot project was confirmed.

Conclusions

The UNP-procedure for introducing limestone and CO_2 was technically and economically proven as effective in the Alkalization of Lake Scheibe.

An Alkalization medium of pulverized limestone and CO_2 was evenly applied and mixed into the lake water in a targeted manner over a period of 100 days. The required mass flow rates achieved within a lake water restoration context are unique. With the introduction of CO_2 the driving force was produced to dissolve the KSM (pH-ratio in the hypolimnion of 5.5) was created and maintained during the entire treatment time. The CO_2 -feed followed under stratification conditions during the summer stagnation with virtually no losses. With the completion of Alkalization the buffering was increased to an average of 0.9 mol/m³. The target value of 1.0 mol/m³ was partially reached. The forecast for re-acidification is based on the hydrogen carbonate buffering effect being exhausted after 3 years. This is equivalent to more than three times of a plain liming treatment. The field of application of the UNP procedure was successfully extended.

Acknowledgements

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Efficiency of in-lake liming of acidic pit mine lakes

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Extended Abstract

In-lake liming is the most effective strategy for the neutralization of acid pit mine lakes. However, each lake has its own characteristics. Important factors are size, depth, exposure to impact of wind on the lake, water chemistry, hydraulic contact to acid groundwater, and last but not least the chemical composition and grain size distribution of the liming product in combination with the application technology used.

The efficiency of the in-lake liming of acidic pit mine lakes strongly depends on the quality of the used neutralization agents as well as on the reaction conditions within the lake body, which may strongly vary with respect to time and space. According to the state of the art, the lime suspension is inputted into the lake as uniformly as possible using pipelines or boats. However, this approach does not consider wind-induced flow in the lake.

Optimal conditions for the reaction in the lake to be as complete as possible can be guaranteed by an online monitoring network, which measures and records pH over time, and the lake's surface area and depth. This data is radio-transmitted and provides the information needed for optimizing the lake liming in particular for repeat liming, which might be needed due to acidic groundwater inflow into the lake. Online data of wind speed and direction is used to simulate in 3d the wind-induced flow in the lake. This makes it possible by means of inverse modeling to optimize the location and amount of the lime input by boat.

Simulating the lake treatment with a calibrated lake circulation model (e.g. ELCOM) is one of the prerequisites. For the calibration of this kind of models data about meteorology, circulation velocity by means of drift bodies, water parameters (e.g. pH and temperature at different depths and locations) and the behavior of the lime products are needed.

Fig. 1 exemplifies the arrangement of a pH monitoring network in the pit mine lake Partwitz in the Lusatia region, Germany. Within the R&D project OILL [1], based on measurements using drift bodies in a pit mine lake, it was shown that the flow regime in such lakes can be predicted using the model ELCOM. **Fig. 2** depicts the flow regime in the pit mine lake Burghammer under westerly wind conditions that are typical for that region.

Figure 1: *proposed pH network for the pit mine lake Partwitz*

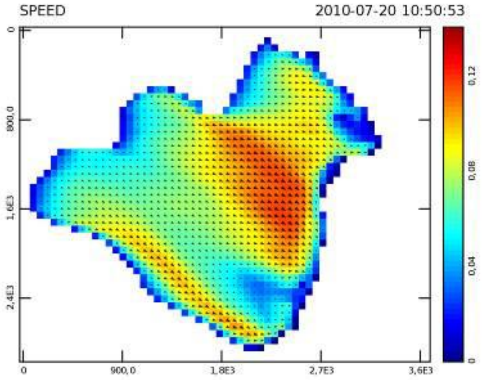

***Figure 2:** Flow regime in the upper layer of the lake body (water depth: 0 – 0.5 m) in the pit mine lake Burghammer under westerly wind conditions (3 m/s)*

For the in-lake liming to be successful, the selection of a suitable lime product is of central rele-vance [2]. Chalk products with a proper grain size have been shown to be a very good choice.

By means of several laboratory experiments different lime products have to be tested with respect to efficiency and reactivity. Such experiments have to be performed with original water from the pit like because even trace elements may have a significant impact on the solubility and reactivity of the different products. Only based on these experiments and including the different application techniques (ship or pipe) a cost-benefit study can be performed providing the best result for a certain pit lake.

Series of batch experiments at TU Bergakademie Freiberg proved that chalk can also create a stronger buffer against the re-acidification of a treated pit mine lake. Within the column experiments (**Fig 3**), chalk from the island of "Rügen" provided the best results. **Tab. 1** shows the corresponding $K_{a\,4.3}$ values for all neutralizing agents used during the experiments.

***Table 1:** pH and net alkalinity K_{al} and net acidity K_{ac} (buffer capacity) in mmol/L for 5 products*

pH of lake water: 2.9	Before liming	Column 1	Column 2	Column 3	Column 4	Column 5
Neutralization agent		Filter cake 63 µm	Semi-calcined dolomite	Calcined dolomite	**Chalk from "Rügen"**	Fine lime RK
pH after liming		6.8	6.1	4.1	7.0	9.4
Kac 4.3 [mmol/L]	3.35			0.09		
Kac 8.2 [mmol/L]	4.41	0.40	0.42	0.66	0.43	
Kal 4.3 [mmol/L]		1.16	0.24		1.66	0.66
Kal 8.2 [mmol/L]						0.28
Efficiency	%	ca. 80 %	ca. 55 %	< 50 %	ca. 90 %	ca. 80 %

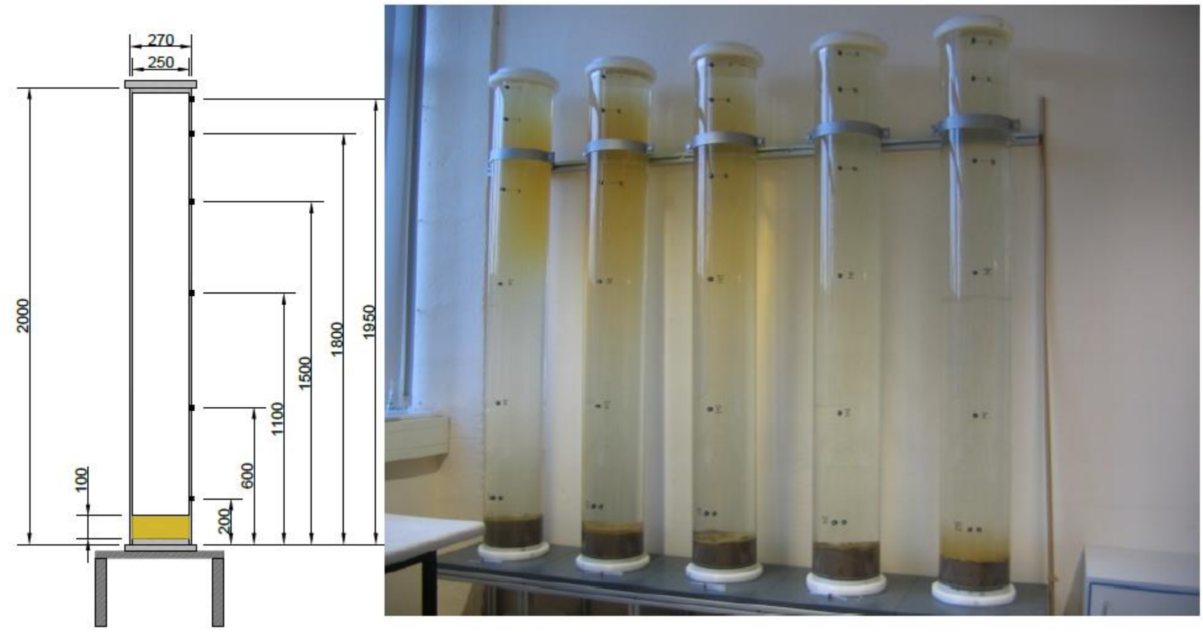

***Figure 3**: Lab tests (column experiments)*

Key words: Optimizing, lime application, lake circulation model, ELCOM, lime products

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Estimation of the qualitative characteristics of post mining lakes in different lignite fields in Greece

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Abstract

This paper summarises available information on water quality associated with post mining lakes of the lignite fields in Greece. In Greece there are three distinctive districts of lignite mining: Ptolemais-Amynteon basin in Northern Greece, Aliveri district in central Greece and Megalopolis in South Greece, Peloponnese. Small lakes have been already formed in some of the remnant voids, while in others the creation of lakes is the main option, after the end of exploitation. Results of various research projects carried out or financed by PPC, concerning the water quality, of the existing and future remnant lakes were used. All remnant lake water is alkaline, due to the alkalinity of geological formations, natural soil and fly ash. The co-dumping of fly ash with mine waste material in the dumping sites improves the absorption of heavy metals and is an unfavourable condition for the dissolution and mobility of heavy metals. Most of them indicate low concentrations or are below detection limits. High values of Mo and Sr are noticed in water of the sumps in Megalopolis and B and Ba in Amynteon, due to their high leaching potential. S content of the lignite is low, usually <1% and even <01%, resulting in relatively low SO_4^{-2} in remnant lakes. Occurrence of carbonate rocks and calcareous sediments in the basement and in the sediments of the fill of the basins plays also an important role. Surface waters from rivers and streams and unaffected ground waters are of good quality, contributing to the acceptable quality of mine water, according to the environmental limits in South field. In Aliveri, mine water is enriched in sodium. The main conclusion of this study is the significant role of the water – rock interaction on the final lake water quality.

Key words: Pit Lake water, geochemical environment, quality, post mining, lignite

1. Introduction

Open lignite mining has become increasingly common over the last few decades due to the improvement in excavation technology techniques where considerable volumes of ore and waste rock are excavated from one or more surface excavations (Castendyk and Eary 2012). After the closure of surface mines, large and deep enough voids are left behind. The creation of remnant lakes is usually an aesthetically acceptable solution for these voids, but with a high possibility of environmental risk. Qualitative characteristics are of great importance both for environmental as well as for industrial purposes.

Pit lakes have unique characteristics such as very small catchment areas, usually great depth, erosion activity on the slopes and unstable geomorphological environment. Water of the remnant lakes is in many cases contaminated with metals, metalloids and trace elements. Its physical and chemical characteristics vary significantly and they rarely approach natural water body chemistry. Geochemical conditions of the remnant lakes is influenced by the evaporation, oxidation and leaching; the variable kinetics of water-rock interactions, the changing influxes and the composition of surface and ground waters.

In Greece there are three distinctive districts of lignite mining: Ptolemais-Amynteon basin in Northern Greece, Aliveri district in central Greece and Megalopolis in South Greece, Peloponnese. Small lakes have already been formed in some of the remnant voids, while in others the creation of lakes is the main option after the end of the exploitation. This paper describes the results of various research projects carried out or financed by PPC, concerning the water quality of existing and future remnant lakes. It also provides a comparative view of the mine water quality of the different lignite fields.

1.1. Geological setting

Amynteon and South lignite field are located in Northern Greece. They belong to Florina – Vegoritis – Ptolemais graben, a large basin filled with Neogene – Quaternary sediments. They consist of rhythmic alternations of lignite beds with lacustrine and fluvial sediments, which overlay both Paleozoic metamorphic rocks and Mesozoic crystalline limestones. Metamorphic rocks, mainly gneiss – schists form the NW boundary of the basin (Dimitrakopoulos 2001).

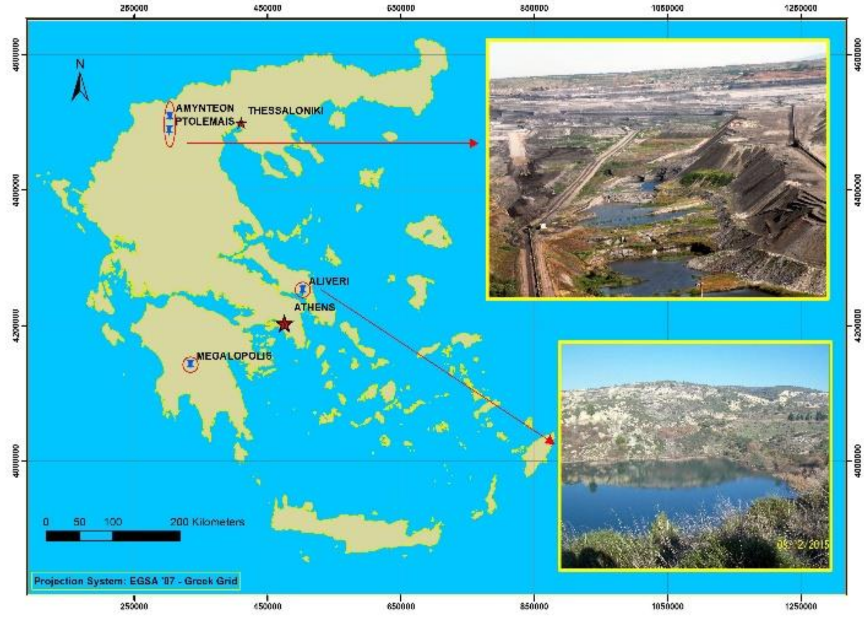

Figure 1 *Map of study mine sites in Greece*

The Neogene-Quaternary sediments of the basin are divided into three lithostratigraphic formations. The lower formation (Upper Miocene to Lower Pliocene) consists mainly of conglomerates, marls, sands and clays. The middle formation (Pliocene) contains the lignite beds. The upper formation (Quaternary) consists of terrestrial and fluvio terrestrial conglomerates, lateral fans and alluvial deposits. The lignite beds alternate with marls, clays and sands (Sachanidis 2001).

In Aliveri area lignite deposits overlie the mio-pliocenic sediments, which consist of marls, conglomerates and breccia (Fig. 2). Above the aforementioned Neogene sediments there are alluvial deposits. In the basement and the surrounding rocks, Jurassic-Cretaceous karstified limestones occur. Surface mining ended in 1990. A wider part of the final void is covered with mine waste dump while a small lake has been created at the lower part. Its dimensions are ~250x250 m, its depth 50 m and its volume 1.000.000 m^3 (Dimitrakopoulos et al, 2009).

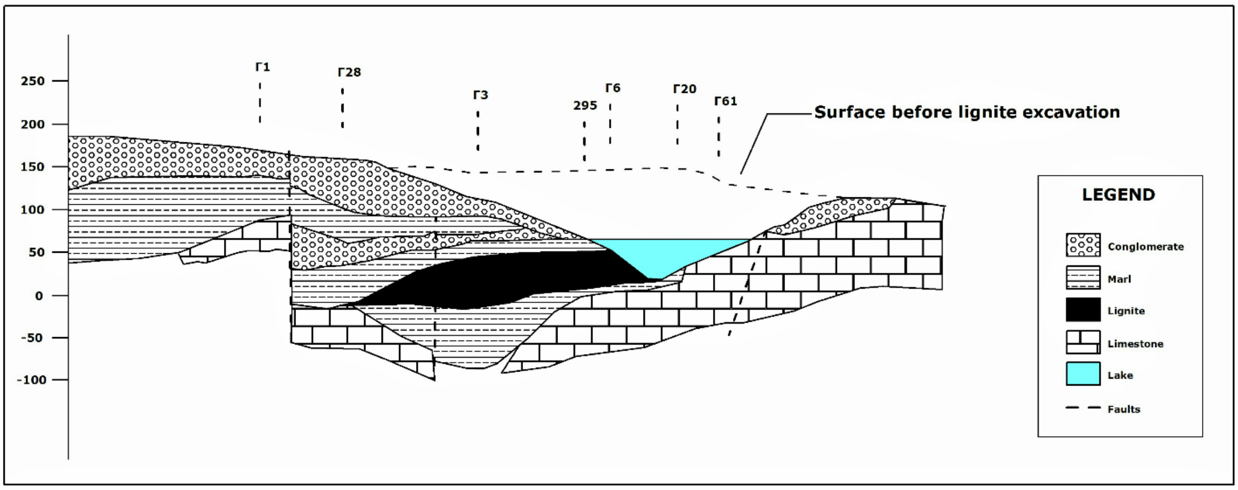

Figure 2 *Geological section of Aliveri area (Minwater 2003)*

In Megalopolis area the overburden consists mainly of marly and clayey material. Basement and surrounding rocks are mainly karstified limestones. Floor of the mine in Kyparissia mine is in contact with the karstic aquifer (sampling from BR), which exists in the limestone, so the pit lake (PK1), which has been created, is hydraulically connected with this aquifer. Dimensions of the lake are (300-500) x1500 m, maximum depth 45 m and its volume is estimated 10.000.000 m^3. Altitude of the lake surface, and consequently its depth and volume, is fluctuating, following roughly the fluctuation of the karstic aquifer. Ponds have been created in the remnant Thoknia mine (Pond I-II), and Choremi mine (P23-P27), which are hydraulically isolated between mine waste dump and impermeable marly formations of the bottom of the mine (fig. 3).

As a conclusion an important aspect of the geology of the Greek lignite mining districts is the occurrence of Mesozoic karstified carbonate rocks in the basement and the surrounding mountains of the mines, and the prevailing of calcareous sediments (marls, marly clays etc) in the filling of the lignite basins.

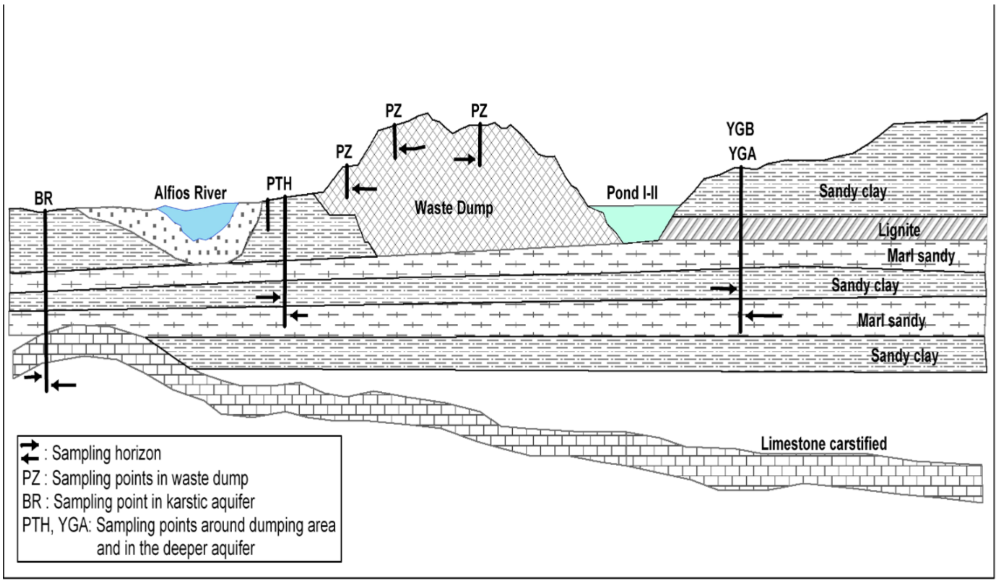

Figure 3 *Pit Lake in Megalopolis lignite site (Pond I-I, Waterchem 2007)*

1.2. Climatic Data

The under investigation areas are situated in a typical Mediterranean climate zone. Time series of more than 30 years of Climatic Data (HNMS[1] and PPC) have been evaluated, since there are meteorological stations around the mines. Rainfall ranges with minimum values in summer and maximum values in winter. Mean annual rainfall is about 900 mm in Megalopolis, 600 mm in Ptolemais-Amynteon basin and 730 mm in Aliveri. Temperatures are mild with relatively high thermal range (~22^0 C). Mean monthly temperature varies between 2,5-24 ^{0}C (average value is 12,9^{0}C) in Ptolemais basin. In Megalopolis the range of temperature is 5-26,5^{0}C (av. 15,6^{0}C) and in Aliveri 9,4-26^{0}C (av. 17,2^{0}C).

2. Materials and methods

2.1. Sampling

Samples of mine water (lakes or sumps of the open pits) were collected and analysed, mainly during dry and wet season in 2015. Also samples from natural soil and soil from the dumping areas, where mine waste and fly ash is co-deposited, were analysed. Finally analyses of unaffected ground and surface water from the areas around the open pits were evaluated. The aim was to define the correlation between the geochemical environment of the areas under investigation and the chemistry of mine water of the lakes and sumps.

In Amynteon mine, 13 boreholes were drilled in internal and external waste dumps. Mine waste and fly ash were co-deposited there during the last 10-18 years. Also 4 boreholes were drilled in the natural soil in the perimeter of the mine. Chemical analyses and leaching tests were performed in 48 solid samples taken from these boreholes. Also 6 samples of surface water from the sumps or springs in the dumps were analyzed. D1es, D214b, D4bp, D10kat, D12 are waters flowing along the inside area of the pit, they interact with some of the geological formations or material of the dump and take some chemical load. D3 is the water of the final sump (table 1). Samples from the final sumps at the bottom of the open pits are considered to be representative of the quality of pit lake water.

In South field 4 leaching tests were performed. Two representative samples of the greenish-gray clay and clayey sand series, the overburden geological formation of lignite series, were studied. Water samples were taken from the sumps (E4 and E7), in different periods. Soulou River which is the main drainage body of the area, outflows into Vegoritis Lake at the northern part of the basin. The water that is pumped out for the protection of the mine (from wells or directly from the mining sumps) outflows into Soulou River, so this could be noticed as mine water The water used in the cooling towers of the Power plants of the area is also rejected into Soulou River. 4 samples were taken from it in two different sites, two periods (wet and dry) during 2015.

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[1] Hellenic National Meteorological Service

In Aliveri area, 6 water samples were collected from pit lakes in different time periods (2000-2015).

In Megalopolis 16 water samples were collected, mainly during wet and dry season in 2015 Pond I-II are sumps at the bottom of the exhausted Thoknia mine and P23-P27 are sumps in the bottom of Choremi mine. PK1 is the pit lake, which has been formed in Kyparissia mine after the end of the exploitation. A1-A6 are samples from Alfios and E1 from Elissonas River. Also results of previous investigations (Dimitrakopoulou 2010, Waterchem 2007) concerning ground water quality were used. Samples were coming from the karstic aquifer (water wells Br) and from the poor aquitard around Thoknia mine (boreholes PTH, YGA, fig.3)

2.2. Analytical methods

Chemical analyses were performed according to the National German Standard Methods (DEV/DIN). PH, Temp, EC, were measured immediately after sampling with professional plus portable temp/pH/ORP meter. Dissolved ions (K, Na) were measured in a no-acidified sample by flame atomic spectrometry; NH^+_4, SO^{2-}_4, Cl^- and NO^-_3 by photo spectroscopy; HCO^-_3 by titrimentry. In the acidified samples Ca, Mg and Fe were measured by atomic absorption, and trace elements (Cu, Zn, Cd, Cr, Pb, Ni, Mn, Co) were determined by inductively coupled plasma mass spectroscopy. The leaching potential of overburden formations in metal elements was determined by performing leaching tests, applying the European Standard Leaching Test EN 12457-2 (CEN, 2002).

3. Results-Discussion

In Amynteon mine, pH values of the solid samples from natural soils and waste dump material (fly ash and waste) range between 6,5-7,4. Concentration of sulphates range 2160-12600 mg/kg. Values of Cd, Hg, Co, Be, Se, Mo are below detection limit. Values of Ni range 18 mg/kg - 295 mg/Kg and 5 samples are over the action values of the new Dutch list (210 mg/kg). According to Petaloti (2003) most of the investigated trace elements in Ptolemais basin have EF (enrichment factor) values less than the unit. This suggests that the origin of these elements is mainly natural (crustal origin). She also mentions that minerals in Western Macedonia consist to a large extent of ophiolites, which are known of their high Cr and Ni content that justifies the relatively high values of Ni.

In the leaching tests of the same solid samples, pH of the leachates ranges 7,8-8,5. Concentrations of Pb, Cd, Cr, Cu, Mo, Ni, Zn, Hg, Se and Sb, are below detection limits. This fact verifies findings of previous investigations (Moutsatsou 2011), that the mixing of fly ash with the waste material in dumping sites improves the absorption of heavy metals. Values of SO_4^{2-} in eluates of natural soil and material of the waste dump range 435-4.000 mg/kg, indicating relatively high leaching potential of the geological formations (Dimitrakopoulos 2016). The fact that the samples of the natural soil show similar behaviors indicates that the low content of SO_4^{2-} is possibly due to the mineralogical composition of the sediments of the basin.

In mine water samples, pH ranges 7,87-8,50 indicating clearly alkaline environment. Content of heavy metals and trace elements are below detection limit with the exception of only Mo (18,65-290 µg/l) and Ba (40-150 µg/l). Sulfate ranges 330-1114 mg/l.

In unaffected groundwater pH ranges 7,23-8,27. At the NW of Amynteon basin, where gneiss-schist bedrock emerges hardness is 337 ppm $CaCO_3$, while in other areas, where carbonate rocks prevail, hardness increases up to 800 ppm $CaCO_3$. Respectively EC ranges from 1043 to the NW -up to 2300 µS/cm to the areas of carbonate influence. Content of heavy metals and trace elements are below detection limit with the exception of Sr (138-938 µg/l), Ba (52-160 µg/l) and B (59-7589 µg/l). Sulfate ranges 20-350 mg/l (Dimitrakopoulos 2016). High Boron content according to Iordanidis (2002) implies a fresh water to middle brackish depositional environment in Amynteon basin.

In Aliveri Pit Lake the mine waters are slightly alkaline, pH values range from 7 - 8. Average values for EC is 1305 µS/cm in the lake and 1780 in the Pond. Dominant water type is Ca-Mg-Na-SO_4. In Pond the chlorides are increased (147-380 mg/l). Sulphates range between 222-1008 mg/lt and higher value is observed in the Pond. There is a tendency of reduction of sulphates in big lake with the time. Trace elements that were measured are below the limits according to Greek legislation. There is no significant change in the water quality of the final lake 17 years after its formation.

In South field the overburden of lignite series consist mainly of illite, vermiculite, chlorite, quartz, feldspars and calcite. Their leachates are alkaline (pH=7,7-8,2). Values of Si, were measured in a range of 4252-10166 ppb. Values for heavy metals are very low in leachates, Cr 0.6-1.5 ppb, Mo 0,7-2 ppb, Rb 0,48-1,29 ppb, Sr 38.4-88.4 ppb and As 2-2,7 ppb (Vasileiou et al. 2015). In Soulou stream, in South field, the average pH value is 8.27, that indicates alkaline waters, the average value of EC was measured at 789 µS/cm. Water type for both samples is Ca-Mg-SO_4-HCO_3. Average concentration of sulphates was 210 mg/lt. All trace elements and heavy metals are below the acceptable limits, considering the environmental legislation.

***Table 1**: Chemical analyses of mine water in different mine sites.*

Site	Mine Water	Water Type	pH	EC	SO_4^{2-}	NO_3^-	HCO_3^-	Mg	Ca	K	Na	Ni	Cr	Ba	Mo	Mn
				µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/l	µg/L
Amynteon	**D1_ ES**	**Mg-Ca-HCO3-SO4**	8,5	1286,0	350,0	2,8	550,0	89,2	109,2	3,9	19,0	n.d.	n.d.	n.d.	290,0	n.d.
	D2_14B	**Mg-Ca-SO4-HCO3**	8,2	1373,0	435,0	0,0	456,0	107,4	110,0	2,8	36,3	n.d.	n.d.	n.d.	270,0	n.d.
	D4_ Bp	**Mg-Ca-SO4-HCO3**	8,5	1043,0	330,0	1,5	391,0	85,8	54,8	3,1	54,7	n.d.	n.d.	150,0	240,0	n.d.
	D10_ KAT	**Mg-SO4-HCO3**	8,1	2300,0	990,0	5,5	760,0	261,4	92,7	3,5	98,5	n.d.	n.d.	110,0	190,0	n.d.
	D12	**Mg-Ca-SO4**	7,9	1597,5	1114,5	27,8	158,0	158,0	136,7	3,7	91,3	20,2	n.d.	131,3	18,7	89,8
	D3_ ANT	**Mg-SO4-HCO3**	8,4	1325,0	445,0	8,3	478,0	128,8	65,7	3,4	62,4	n.d.	n.d.	40,0	210,0	n.d.
	Average mine water		**8,3**	**1487,4**	**610,8**	**7,7**	**465,5**	**138,4**	**94,8**	**3,4**	**60,4**	*****	*****	**107,8**	**203,1**	*****
Megalopolis	**POND1**	**Ca-SO4**	7,9	3180,0	1807,0	13,0	171,0	64,3	402,0	100,0	88,1	<20	<10	81,0	8882,0	435,0
	PONDII	**Ca-SO5**		990,0	402,5	22,5	64,0	15,2	131,0	18,0	26,0	<20	<10	100,0	1015,0	43,5
	EPN4	**Na-SO4**	11,0	630,0	123,0	13,0	0,0	1,5	5,8	3,9	108,0	<20	<10	18,0	547,0	<10
	P23	**Ca-Mg-SO4-NO3**	7,7	2650,0	715,5	525,5	274,0	76,0	314,0	3,5	104,3	11,8	<5	118,5	136,2	261,7
	P24	**Ca-Mg-SO4-NO3**	7,6	2360,0	640,0	449,0	203,0	62,4	281,0	3,0	77,8	11,7	<5,0	155,0	126,0	374,0
	P25	**Ca-Mg-SO4**	7,5	2630,0	1409,0	234,0	137,0	108,0	449,5	2,5	88,1	59,0	<5	75,7	39,2	300,0
	P26	**Ca-Mg-SO4**	7,3	2895,0	1420,5	275,0	218,0	90,5	470,0	2,9	90,7	24,0	<5,0	114,5	89,4	723,0
	P27	**Ca-Mg-SO4-NO3**	7,5	2100,0	693,0	424,0	156,0	65,0	317,0	2,3	52,7	14,3	<5,0	59,8	42,4	255,0
	PK1 (2003)	**Na-Ca**	7,3	3830,0	125,0	30,0	257,1	16,0	360,0	59,0	685,0	12,0	6,0	38,0		150,0
	PK1 (2015)	**Ca-SO4-HCO3**	7,9	1330,0	575,0	11,8	193,0	26,6	258,0	1,6	16,7	11,9	<5,0	61,9	32,3	3,3
	Average mine water		**8,0**	**2259,5**	**791,1**	**199,8**	**167,3**	**52,5**	**298,8**	**19,7**	**133,7**	**20,7**	**6,0**	**82,2**	**1212,2**	**282,8**
	E1	**Ca-Mg-SO4-HCO3**	8,2	575,3	90,7	11,5	223,3	23,1	63,0	2,2	13,2	<20	25,0	32,7	49,0	39,5
	A1-A6	**Ca-SO4-HCO3 (Na)**	7,8	706,2	141,9	10,6	237,8	13,5	100,7	4,2	18,6	<20	<10	57,5	334,0	19,3
Aliveri	**Pond 9/2/00**	**Ca-Na-Mg-SO4-Cl-HCO3**	7,0	1591,0	349,0	0,0	244,0	58,9	181,1	3,1	163,9	<10	94,0	18,0		33,0
	Pond 30/3/01	**Ca-Na-Mg-SO4-Cl**	7,5	1970,0	1008,0	0,0	183,0	77,5	228,0	3,5	210,0	15,0	<10	15,0		<10
	Lake 9/2/00	**Mg-Ca-Na-SO4-HCO3**	7,7	1302,0	222,0	0,0	256,0	90,9	131,4	3,1	95,1	<10	<10	34,0		<10
	Lake 27/11/00	**Mg-Ca-Na-SO4**	8,0	1310,0	665,0	0,0	183,0	86,8	109,0	3,0	105,0	<10	<10	36,0		<10
	Lake 30/3/01	**Mg-Ca-Na-SO4**	7,6	1260,0	530,0	0,0	189,0	97,6	117,0	4,4	101,0	<10	<10	19,0		<10
	Lake 2015	**Mg-Ca-Na-SO4-HCO3**	7,7	1350,0	399,0	0,0	257,0	79,0	102,7	4,1	74,4	11,0	<0,5	33,9	1,0	2,2
	Average mine water		**7,6**	**1463,8**	**528,8**	**0,0**	**218,7**	**81,8**	**144,9**	**3,5**	**124,9**	**13,0**	**94,0**	**26,0**	**1,0**	**17,6**
South Field	**Soulou 1**	**Ca-Mg-Na-SO4-HCO3-Cl**	8,4	774,0	223,0	6,7	137,5	35,0	75,0	2,7	48,4	<10	<5	34,3		30,0
	Soulou2	**Ca-Mg-SO4-HCO3**	8,2	804,0	197,0	12,7	223,0	39,5	96,5	2,9	27,8	<10	<5	41,4		37,0
	E4	**Ca-Mg-SO4-HCO3**	7,6	848,0	166,0	9,9	184,0	30,2	98,0	1,3	10,6	4,6	2,7	48,9	1,4	14,3
	E7	**Ca-Mg-HCO3-SO4**	7,9	792,0	177,0	19,5	243,0	40,1	112,0	1,7	9,3	7,9	5,3	36,2	4,7	8,5
	Average mine water		**8,0**	**804,5**	**190,8**	**12,2**	**196,9**	**36,2**	**95,4**	**2,1**	**24,0**	**6,3**	**4,0**	**40,2**	**3,1**	**22,4**

***Table 2**: Chemical analyses of unaffected groundwater in mine study areas.*

Average	pH	EC µS/cm	TDS mg/l	HCO_3^- mg/l	SO_4^{--} mg/l	NO_3^- mg/l	Ca^{++} mg/l	Mg^{++} mg/l	Na mg/l	K mg/l	Fe µg/l	Mn µg/l	Ni µg/l	Crtot µg/l	Ba µg/l	Sr µg/l	Mo µg/l	B µg/l
Amynteo	7,6	1006,4	647,5	555,6	111,6	1,4	89,5	57,5	73,8	8,3	337,0	203,1	11,0	<5	99,7	427,7	<10	1932,0
South Field	7,8	490,0	306,8	260,0	53,0	16,0	67,1	28,2	12,3	0,9	30,0	281,0	<10	12,9	35,7	199,0	9,5	72,1
Megalopolis-Thoknia	7,7	1533,6	984,3	689,2	276,5	11,6	191,0	30,7	95,5	53,8	271,6	594,2	14,3	21,5	166,5	771,9	109,0	
Megalopolis-Karstic aquifer	7,3	574,0	342,5	134,0	51,5	9,4	92,5	19,5	10,2	1,0	18,0	22,2	11,7	<5	46,1	450,0	100,2	128,4

In the sumps of South field, the water is alkaline and also their water type is Ca-Mg-SO_4-HCO_3. Measured values of pH range 7,5-7,93. Concentrations of sulphates were in a range of 166-200 mg/l. Concerning trace elements and heavy metals, only nickel exceeds the acceptable limits according the Greek legislation (20 ppb).

In Megalopolis area, mine water from sumps and ponds is alkaline (pH=7,70-11,00). Water type of the water of the sumps varies a lot, the main type is Ca-SO_4 with the presence of Na, HCO_3, Mg. Average value of EC is 2260 µS/cm (630-3830 µS/cm). Higher values are observed in smaller ponds or at the beginning of the formation of pit lake in Kyparissia. Increased values of sulphates (640-1420 mg/l) are noticed, the higher of them in smaller sumps PondI, P25, P26, where evaporation is higher and recharge is poor. Higher values of Mo (20-8882 µg/lt), are observed in Pond I-II, where water comes into contact with dumping of fly ash (intervention value of the New Dutch list 300 μg/lt). Mn values vary from <10 to 723 μg/lt. Higher values are recorded in mine waters from the sumps and lower in Kyparissia pit lake. Comparing with the Greek legislation acceptable limit (50 μg/lt), the concentration is considered high.

Alfios River and Elissonas flow between the mines. Their water quality (E1, A1-A6 table 1) is generally good, even though the domestic sewage of Megalopolis town and mine water are rejected in Alfios. Water is alkaline, average pH value is 8. Average values of sulphates is 141,90 mg/l, lower than the acceptable limits (250 mg/l). Average value of Mg in Alfios and in Ellisonas is 18,3 μg/lt, below the acceptable limits (50 μg/lt). Values of Mo are increased in Alfios, (334 μg/lt) comparing to Ellisonas, due to the influence of rejection of mine water and sewage of Megalopolis.

In pit Lake of Kyparissia (PK1), significant changes were recorded during this decade. As it seems from table 1, sodium and EC, were very high in 2003, but in 2015 there are low in normal levels in comparison to natural waters.

Natural waters in Megalopolis, presents similar quality with mine water, the noticeable concentration of them concerning manganese, which is significantly high (Table 2).

Hydrochemical water type of each sample comes from the process of solution kinetics, rock–water interactions, geology and contamination sources. Chemical data of the water samples is also presented by plotting them on a Piper trilinear diagram (Fig. 4). Piper diagram classifies the samples based on the ionic composition of different water samples. This diagram reveals the different types of waters in the four mine sites. In the study sites the type of water that predominates is mainly Ca–Mg–HCO3 type which is mainly due to the geology of the area which comprises limestones. Ca^{+2} is almost the dominant cation for all water samples. According Wilcox diagram, most of samples are classified as C3S1 (High salinity and Low sodium), only one sample from Megalopolis (PK1-2003) is improper even for irrigation uses (C4S3), but the recent one sample, from the same site indicates that this qualitative characteristics were transient.

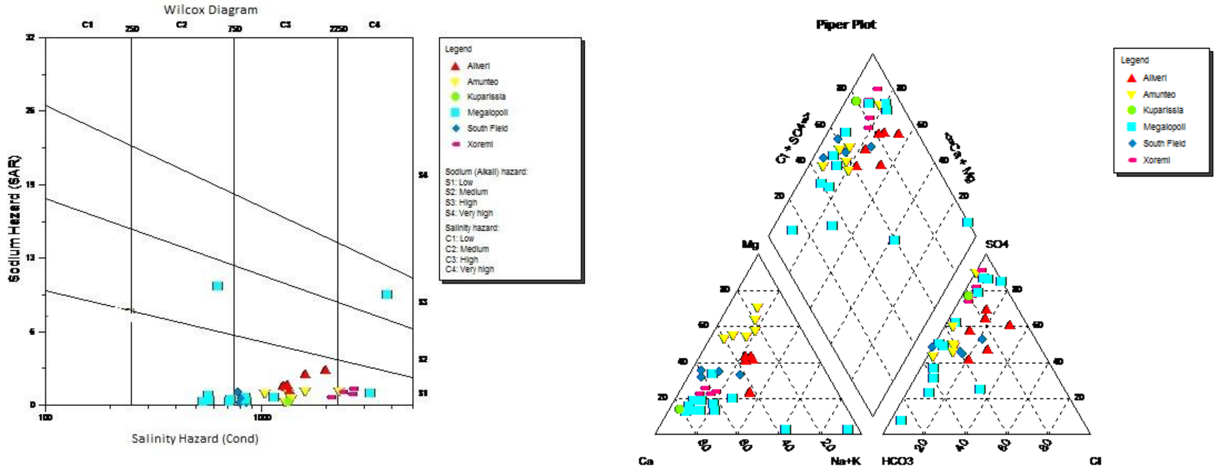

***Figure 4** a) Wilcox diagram and b) Piper diagram in mine waters.*

Ficklin diagram shown in figure 5, illustrates the base metal content of the waters associated to the mine sites in Greece. It is obvious that in Megalopolis, the total dissolved metals/metalloids in water are increased comparing with the other mine sites. Water from pit lakes in Aliveri presents the lower leaching potential. In all mine sites the environments are alkaline, which are not favorable in mobilization of metals (-oids).This is the main reason that most of heavy metals/loids concentrations are undetectable in mine and in natural water. In Megalopolis, molybdenum shows high leaching potential because it is mobile and soluble in alkaline environments. In the other pit mines, it is not observed high leaching of Mo, although there are also alkaline environment, because the geochemical composition of lignite is different from site to site, in Megalopolis the lignite ore is enriched in Mo. All the other heavy metals\oids that are compounded in lignite are immobile in alkaline environment.

The most important parameter that controls pit water quality is pH. This is because the mobility of most metals and metalloids is strongly pH-dependent (Soni 2014). In our study sites, pH values indicate an alkaline environment. Consequently pit lakes water contain low concentrations of heavy metals (e.g., Al, Cd, Cu, Fe, Mn, Ni, Pb, Zn) and/or metalloids (e.g., As, Sb, Se, Te) that can pose a threat to the environment.

Despite the prevalence of acidic pit lakes in central Europe (Schultze et al 2010), pit lakes in Greece are neutral or even slightly to strongly alkaline. If a lake is in contact with a source of carbonate such as limestone or dolomite, a carbonate-cemented sedimentary rock, it may neutralize some or all of the acid produced by oxidation of pyrite and other minerals (Eary 1997). Both alkaline ground water and the very low level of sulphur in and around the lignite seams are probably responsible for the generally good water quality in the lignite pits (Castro 2000). Calcium and magnesium concentrations reflect the ability of buffering any acidity produced by pyrite oxidation (dissolution of carbonates, ion exchange, dissolution of silicates, etc.), the initial composition of overburden and lignite and the source area of the current lake water.

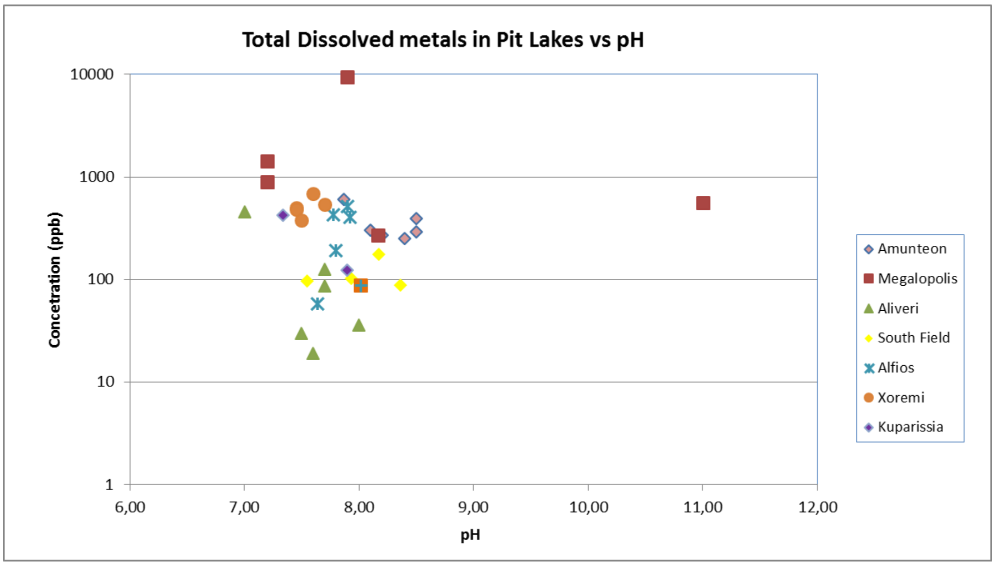

Figure 5 *Ficklin diagram, about the total dissolved metals in mine and natural waters.*

4. Conclusions

Mining pit lakes display a wide diversity in water quality and dependence on the mineral deposits that were extracted. General trends in pit lake chemistry have been reviewed by several researchers (Friese 1998, Eary 1999, Castro 2000, Delgado 2008) and they reflect a wide complexity regarding the chemical analysis.

Post mining lakes in lignite fields in Greece are of good water quality and have acceptable values in most of the elements, as these are described in environmental legislation (EU and Greek law).

Most of Greek lignite pit lakes are surrounded mainly by carbonate formations (limestone, dolomite), ultramafic rocks and neogene-quartenary deposits. This geochemical environment may neutralize some or all of the acid produced by oxidation of pyrite and other minerals. Also the lack of available sulphide minerals and/or large amounts of carbonate in the surrounding rocks of the lignite basins and the sediments of the fill, are probably responsible for the generally good water quality in the lignite pit lakes.

PH values are the most important control factor for the mobilisation of metals/oids and their dissolution in waters. In all mine sites the waters are alkaline. Low values of EC indicate the generally relatively low concentrations of dissolved solids in the pit lake water, which are mainly sulphates, bicarbonate, calcium and magnesium. The highest values of electrical conductivity originate from small lakes or ponds, which are influenced by evaporation, are hydraulically isolated and are not recharged sufficiently by natural ground or surface water.

Low concentrations of heavy metals (i.e. Pb, Cr, Hg, Cd, Cu, Ni, Co, Zn, Mn) were recorded in the mine and in natural waters. The geochemical environment (i.e. high calcite content, high pH values, low Fe, S) also creates favourable conditions for the diminishing of their leaching potential. Mainly the potential contaminants are below mandatory concentrations or exceeding the limits in some sites but as point pollutants. The mixing of fly ash with the waste material in dumping sites improves the absorption of heavy metals (Moutsatsou 2011).

The main conclusion of this study is the significant role of the water – rock interaction that was evaluated in order to assess the water quality of pit lakes at each mine site. All pit lake waters are alkaline, which is an unfavourable condition for the dissolution and mobilisation of heavy metals.

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On the relevance of meromixis in pit lakes – an update

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Abstract

The term “meromixis” means that a lake contains a chemically different, deep water layer due to incomplete mixing over the year. Ten years ago, Boehrer and Schultze (2006) discussed the relevance of meromixis for pit lakes. More than 100 papers have been published on meromixis in pit lakes since 2006, suggesting an update.

Newly published papers have dealt with the interaction of underground workings and ground-water within meromictic pit lakes, double diffusion and erosion of the chemocline, climatic influences on meromixis, biogeochemical processes and microbial ecology in the water column and sediments, and predictive modelling. Results of the monitoring of meromictic pit lakes improved the understanding of processes and allowed in some cases to prove results of earlier modeling. Experiences with the management of meromictic pit lakes were also published.

Meromixis is not the common mixing regime in pit lakes. However, meromixis seems to occur more frequently in pit lakes than in natural lakes due to the shape of the basin of pit lakes and the occurrence of chemically different waters in the catchment of many pit lakes. Therefore, and because of the particular chances and risks related to meromixis, it is of particular relevance in pit lakes. Based on the findings of the last ten years, predictive modeling of future pit lakes and the management of existing meromictic pit lakes can be made much better today.

This contribution gives a brief introduction to the phenomenon of meromixis in pit lakes, summarizes the findings from the last ten years and draws conclusions regarding the management and predictive modeling of meromixis in pit lakes.

Key words: pit lake, meromixis, management, modeling

Introduction

Findenegg (1935) introduced the term ‘meromictic’ into limnology in order to name lakes which do not experience a full overturn, and where the deep part of the waterbody which is excluded from uverturn is chemically different from the regularly mixing upper part of the lake. The lower part of the lake was named the ‘monimolimnion’ by Findenegg (1935) while the upper part was named the ‘mixolimnion’ by Hutchinson (1937). Figure 1 shows a scheme of a meromictic lake and temperature, salinity and pH in Lake Goitsche (Germany), a pit lake in a former open cast lignite mine.

The incomplete mixing is caused by the density difference between mixolimnion and monimolimnion. Other factors like: (1) the shape of the lake basin, (2) sheltering from wind forcing at the lake surface (e.g. by steep side walls of a former mine void or by surrounding forest or montains), or (3) climatic conditions (e.g. formation of an ice cover) may also contribute to the formation and stability of meromixis. However, such factors are not able to cause the formation and stability of meromixis alone as some earlier literature suggested (e.g. Lyons et al. 1994; Doyle and Runnels 1997). Jöhnk (2001) demonstrated that ‘relative depth’, a geometric relationship between the surface area and maximum depth often used to quantify the shape of lake basins, is not a reliable predictor for meromixis.

The above mentioned difference in density between mixolimnion and monimolimnion needs to be sustained. There are several mechanisms that can sustain the density difference and also cause the formation of meromixis. According to Hutchinson (1937, 1957), these include: (1) inflow of saline surface water into a fresh water lake or fresh surface water into a saline lake, forming and stabilizing a fresher layer of water on top of a more saline and denser water layer at the lake bottom, named 'ectogenic meromixis', (2) inflow of saline groundwater into a lake, called 'crenogenic meromixis', and (3) liberation and enrichment of solutes in the deeper part of a lake mainly due to biological activity (e.g. decay of organic matter in the deep part of the water body or in the lake sediment), called 'biogenic meromixis'. Walker and Likens (1975) distinguished two classes of meromixis based onthe mechanisms causing and stabilizing meromixis: ectogenic (i.e. developed from external mechanisms) and endogenic (i.e. developed from internal mechanisms). The first class encompases Huchison's ectogenic and crenogenic meromixis while the second class comprises Hutchison's biogenic meromixis plus meromixis caused by downward settling of precipitated minerals as well as sinking of salts excuded during ice formation.

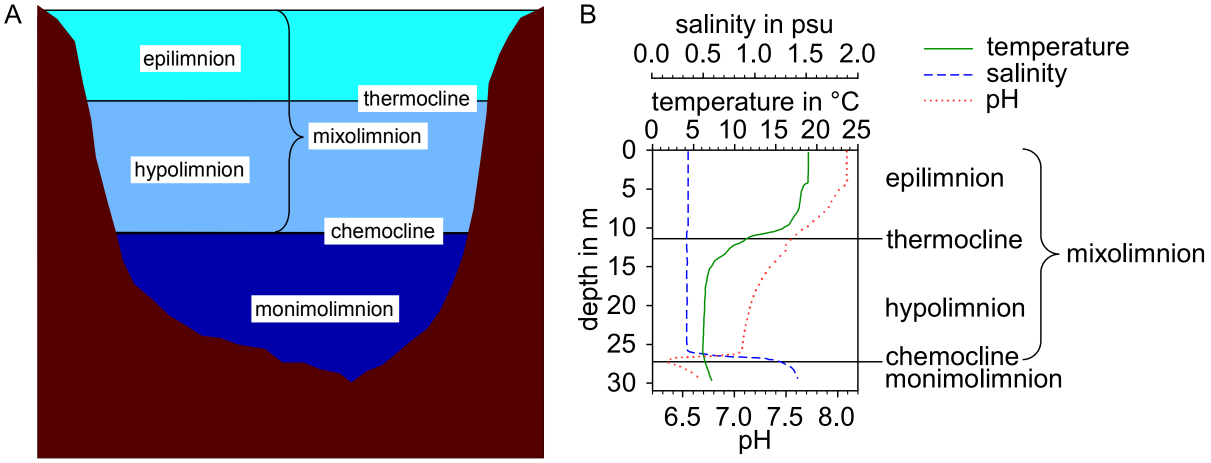

Figure 1 *Terminology of stratification in meromictic lakes (details see text): panel A - generalized cross-section through a meromictic lake (under conditions of temperate climate during summer, i.e. thermal stratification in the mixolimnion); panel B - profiles of temperature, salinity and pH in Lake Goitsche (Germany; sampling site XP4) on August 23rd, 2005 (psu – practical salinity unit, Fofonoff and Millard 1983; for further information on Lake Goitsche see e.g. Boehrer et al. 2003).*

Publications of the last ten years (2006-2015)

Bibliographic analysis

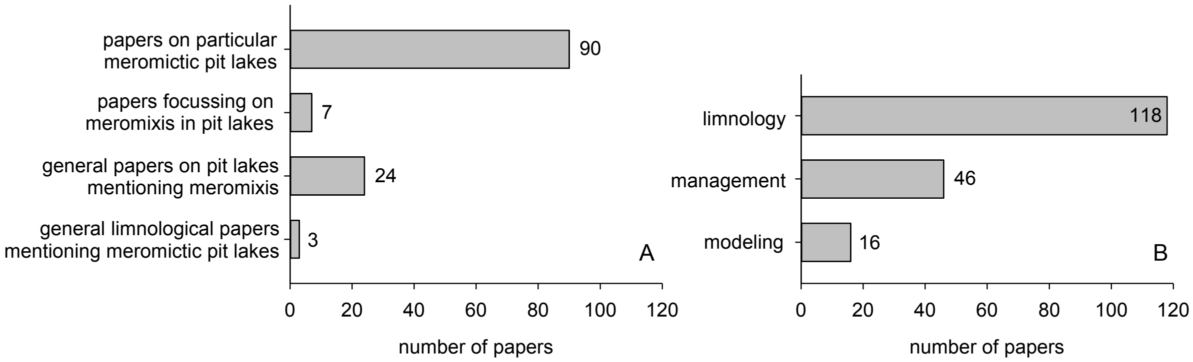

Figure 2 *Analysis of papers published on meromixis in pit lakes since 2006. Panel A: all papers are considered for one category only. Panel B: Papers may be considered for more than one category (limnology comprises physics, chemistry and biology).*

In order to get an overview of what has been published in the last ten years, we had a look into our collections of literature and also did a search using Google Scholar using the combined key words ‘meromixis’, ‘meromictic’, and ‘pit lake’. Figure 2 shows a simple statistical evaluation of the outcome. We found 124 publications to be considered. They comprise conference papers, journal papers, book chapters and PhD theses. The majority (72.6%) reported findings from particular meromictic lakes. Some lakes have frequently been subject of research and publications: Cueva de la Mora (Spain), Waldsee (Germany) and Berkeley Pit Lake (USA). Only few publications (5.6%) have focused on meromixis in pit lakes while 19.4% of the publications generally dealt with pit lakes and mentioned meromixis. In three cases (2.4%), meromixis in pit lakes was mentioned in general limnological publications related to stratification in lakes.

Thematically, the majority of publications covered limnological aspects of meromictic pit lakes, i.e. physical, chemical and biological properties and processes of the pit lakes. However, management and modeling have also been important aspects. Regarding management of meromictic pit lakes, the Island Copper Mine pit lake is doubtless the most prominent example: no other meromictic pit lake has been reported that experiences such strong artificial control of creation, hydrology and biogeochemistry (Fisher and Lawrence 2006; Pelletier et al. 2009; Wen et al. 2015).

Limnology of meromictic pit lakes

In pit lakes, ectogenic and crenogenic origin of meromixis (sensu Hutchinson 1937, 1957) are by far dominant. Flite (2006) reported the rare case of biogenic meromixis in the filling pit lake of the former Kennecott Ridgeway Gold mine in South Carolina. He underlined the role of the basin shape in this case. Sánchez-España et al. (2009) also discussed the role of the basin shape. However, the actual contribution of the basin shape to the stability of meromixis was not quantified in either of these cases.

Mixing between the mixolimnion and the upper part of the chemocline (‘erosion of the chemocline’) is one of the processes which eventually may remove meromixis. Boehrer et al. (2014) quantified this effect based on long term observations in Lake Wallendorf (Germany). The importance of a good understanding of this process appeared in the Island Copper mine pit lake (Canada): The erosion of the chemocline was much smaller than predicted by the modeling before filling the lake (Pelletier et al. 2009). Therefore, the so-called “Middle-layer-lifting-system” had to be developed and implemented in the Island Copper mine pit lake. It transfers water from the monimolimnion to the mixolimnion in order to limit the rise of the chemocline which results from the injection of acid drainage into the monimolimnion for treatment and deposition (Pelletier et al. 2009). This approach is possible only because the renewal rate of the mixolimnion by inflow of fresh and slightly brackish water is fast enough to keep the density difference between mixolimnion and monimolimnion big enough.

A further example underlining the importance of mixolimnion renewal was presented by Santofimia et al. (2012). They observed a full overturn of the formerly meromictic pit lake Nuestra Señora del Carmen (Spain) as a consequence of the exceptionally late onset of rain in autumn. The evaporation during summer caused an increase in density in the mixolimnion eventually making the density difference between mixolimnion and monimolimnion too small. Early onset of rain in the following autumn re-established meromixis (Santofimia et al. 2012).

The importance of (in particular long lasting) ice covers for the stability of meromixis in pit lakes was investigated by Pieters and Lawrence (2009, 2014). Ice covers act in two ways: During freezing, salts are excluded from the ice. Therefore, melting ice forms a fresh water layer on top of the lake. Snow melt in the catchment of the pit lake may also contribute to this. In addition, the highly concentrated water forming immediately below the ice is moving downward due to its high density and contributes to accumulation of dissolved solids in the monimolimnion. The second effect of an ice cover is hindering of mixing at the chemocline by protecting the water body against wind forcing. A similar effect was observed by Boehrer et al. (2014). The filling of Lakes Wallendorf and Rassnitz (Germany) with river water created additional chemoclines on top of already existing meromictic water bodies and hindered erosion of the chemocline. Seasonal establishment of thermoclines in the mixolimnion also contributed to this effect.

Sánchez-España et al. (2009) and Santofimia et al. (2013) demonstrated the relation between abandoned underground workings and the layering in meromictic pit lakes in Spain (Cueva de la Mora, Concepción, respectively). Surprisingly, Sánchez-España et al (2014a) found by studying the isotopic composition of the water that the current exchange between the underground workings and the lake is very small. The underground workings were mainly important for the formation of meromixis during the filling of the lake (Sánchez-España et al. 2014a; Diez-Ercilla, 2015).

Double diffusion had been demonstrated to occur and to be important in meromictic pit lakes (Boehrer et al. 2009; von Rhoden et al. 2010; Sánchez-España et al. 2014a; Diez-Ercilla 2015). It is the formation of staircase-like profiles of temperature and concentrations in density stratified water bodies, which results from largely different diffusivities of dissolved substances and heat. In case of meromictic Lake Waldsee (Germany) double diffusion even caused a complete mixing within the monimolimnion (Boehrer et al. 2009).

Lake Waldsee was also the first meromictic pit lake where the contribution of the single constituents to the density difference between mixolimnion and monimolimnion was quantified (Dietz et al. 2012). In this case, iron and bicarbonate were most important (Dietz et al. 2012). The quantification was based on the calculation of water density using the partial molal volumes of the water constituents (Boehrer et al. 2010). This approach enables the identification of options for selective manipulation of the stability of meromixis by promotion or hindering of biogeochemical processes in the monimolimnion as part of the lake management.

The case of Guadiana pit lake in Herrerıás mine (Spain; Sánchez-España et al. 2014b) confirmed the expectations of Murphy (1997) that limnic eruptions (sudden uncontrolled release of high amounts of gas accumulated in the monimolimnion) are possible in pit lakes. In Guadiana pit lake, the concentration of CO_2 in the monimolimnion (as a result of water/rock interaction leading to carbonate dissolution) became high enough that there is a real risk of a limnic eruption, and measures for a controlled removal of the excess CO_2 were tested in the field (Boehrer et al. 2016).

In Cueva de la Mora (Spain), the mixolimnetic algal growth was found to be the main source for the reductive microbial processes occurring in the chemocline, monimolimnion and sediments (Wendt-Potthoff et al. 2012; Falagán et al. 2014). An interesting finding was that precipitation of copper and arsenic sulphides worked well as a natural attenuation mechanism while precipitation of iron sulphide was found only exceptionally and only at greater depth although ferrous iron was present in concentrations of >400 mg/L (Diez-Ercilla et al. 2014).

Pit lakes in former open cast sulphur mines are rare. There were several publications on a meromictic pit lake in a former sulphur mine within the period 2006-2015: Lake Piaseczno (Poland). Due to origin of the sulphur deposit from microbial transformation of gypsum to sulphur bearing limestone, the lake water is neutral. Most relevant for the density difference between mixolimnion and monimolimnion are sodium and chloride (Frankiewicz and Pucek 2006). For more details of chemistry, biology and sediments see Żurek and De Pauw (2006), Mazurkiewicz-Boroń et al. (2008), Szarek-Gwiazda (2008).

Management of meromictic pit lakes

In the Island Copper Mine pit lake, the basic applicability of the initial planning and modeling approaches was confirmed (Fisher and Lawrence 2006; Pelletier et al. 2009; Wen et al. 2015). However, some adaptations were needed. Application of fertilizer was found to be necessary year-round to ensure sufficient adsorption of trace metals to algae and their removal from the mixolimnion by sedimentation. Also, the above mentioned 'Middle-layer-lifting-system' had to be implemented. The management of the Island Copper Mine pit lake is a good example for adaptive management based on monitoring and additional field experiments (Pelletier et al. 2009, Wen et al. 2015).

The Anchor Hill pit lake (South Dakota, USA) turned meromictic due to a full scale test of a treatment approach for its acidic, metal and nitrate rich water (Park et al. 2009). After initially raising the pH from 3 to 5, a mixture of molasses, methanol and proprietary ingredients was added as nutrient for anaerobic bacteria. Following a re-adjustment of pH to 6, wood chips were added as substrate for bacterial growth. Nitrate and sulphate reduction worked well and the metals were precipitated as sulphides. In order to remove excess hydrogen sulphide and to meet discharge criteria for the treated water, hydrogen peroxide was finally added (Park et al. 2009). Since discharge criteria were met, this is a successful new approach for treating acid mine drainage in a batch process, using the monimolimnion as a biochemical reactor.

The Berkeley pit lake had long been known to be meromictic (Davis and Ashenberg 1989). However, there was a period of holomixis caused by a land slide, which was terminated by diverting more fresh water to the lake (Gammons and Tucci 2013). Later on, the ex-situ recovery of copper from monimolimnetic water and the release of the treated water into the mixolimnion made the lake holomictic again (Gammons and Tucci 2013; Tucci and Gammons 2015). Although terminating meromixis may not have been fully intended, this experience is very instructive and valuable because it is well documented and published. Others can learn and benefit from this development: when increasing the density of the mixolimnion by addition of treated monimolimnetic water, the density difference between mixolimnion and monimolimnion becomes gradually smaller and mixing between both layers increases. Furthermore, permanent extraction of monimolimnetic water eventually removes the monimolimnion.

A clearl case of intended meromixis cessation is the Zone 2 Pit Lake at Colomac mine site (Canada; Pieters et al. 2015). Here, artificial destratification known from the abatement of anoxia in eutrophic lakes (Cooke et al. 2005) was applied to improve lake water quality. The main goal was to enhance microbial conversion of thiocyanate and ammonia resulting from cyanide gold mining. The approach fully succeeded (Pieters et al. 2015).

Long term observations at Lake Vollert Süd (Germany) demonstrated that the storage of contaminants in the monimolimnion has so far been successful (Stottmeister et al. 2010; Wiessner et al. 2014). In this case, mainly phenolic wastes from lignite gasification and coke production were removed from the mixolimnion by flocculation. This allowed for the development of common plankton in the lake and for oxidation of remaining organic compounds and ammonia in the mixolimnion (Stottmeister et al. 2010; Wiessner et al. 2014).

Modeling of meromictic pit lakes

Only few models of meromictic pit lakes could be tested by real data since the models were often used for predictions in the course of planning mine closure. For the Island Copper Mine pit lake (Canada), predictive modeling was basically successful although some of the predictions were not fully met by reality (see above sections). The prediction of Boehrer et al. (1998) for Lakes Wallendorf and Rassnitz (Germany) were also accurate (Schultze and Boehrer 2008; Boehrer et al. 2014). The modeling of Lake Waldsee (Germany) by Moreira et al. (2011) underlined the importance to include biogeochemical processes into the modeling of meromictic pit lakes. While Moreira et al. (2011) coupled a hydrodynamic and a geochemical model, Castendyk and Webster Brown (2007a,b) did the predictive modeling of the future lake in Marta Mine (New Zealand) separately for hydrodynamics and geochemistry. Predictive modeling of the future lake in Aitik Mine (Sweden) by Fraser et al. (2012) demonstrated the importance of the sequence of the use of chemically different water sources for lake filling which was found to be decisive for the formation of meromixis.

Making use of investigations from existing meromictic pit lakes for improving the reliability of predictions for future pit lakes is a very valuable strategy (see Mueller et al., 2012). The very long perspective of the predictive modeling for future pit lakes in De Beers' Gahcho Kué Mine (Canada; Herrell et al. 2015; Vandenberg et al. 2016) is rather exceptional. These studies demonstrate both the need of such long term predictions and also the uncertainties caused by the potential change of the hydrological conditions in a period of about thousand years. The climate has already changed considerably in the last thousand years at times when the anthropogenic influence was much smaller than in recent years, e.g. during medieval climate anomaly and little ice age (e.g. Mann et al. 2009). Further anthropogenic climate change could significantly affect the accuracy of contemporary pit lake predictions which frequently assume consistent climate and water balance conditions in the future.

Conclusions

As shown by the reviewed literature, successful active management of meromictic pit lakes is possible. It requires a comprehensive understanding of all relevant processes in the pit lakes. Models are key instruments for planning meromictic pit lakes and also the management strategy. Adequate monitoring, the critical evaluation of its results, and a regular updating of management strategies are indispensable for the successful management of meromictic pit lakes.

The findings of the last ten years underlined that biogeochemical processes have to be included into modeling of meromictic pit lakes. In order to validate and improve models, more monitoring results have to be published from existing meromictic pit lakes. This is not only a scientific need but also of interest for mining companies and authorities. Improved models well-tested, using published data would minimize the re-creation of past errors, maximize the knowledge gained from past experience, reduce the remaining risks during decision making, and increase public acceptance of decisions. From a more scientific point of view, a systematic and comprehensive model study on the influence of lake basin shape on formation and stability of meromixis is desirable. However, funding such project would also result in benefit for industry and authorities via improvement of the basis of predictive modeling, one of the key instruments of planning open cast mines and their closure. This could become an excellent example of enhancing mining industry and academic collaboration (McCullough 2016).

We assume that we did not find all publications on meromixis in pit lakes from the last ten years. Therefore, we would be grateful to receive references for overlooked publications. A list of publications found by the authors will be made available at the web page of Martin Schultze and updated yearly. There are likely to be interesting case studies of meromictic pit lakes, and valuable experiences not available to the mine water community and the public yet. We would like to encourage the owners, the consultants, and the authorities to be less hesitant in publishing their results and experiences for the mutual benefit of all.

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Quantification of Acidity Deposition in the Sediment of a former lignite mining lake in the Wackersdorf Mining District (Eastern Bavaria)

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Abstract

From 1982 to 2001 acidic conditions prevailed at former lignite mining Lake Knappensee. Since 2001 the acidity of the lake water continuously decreased reaching circum-neutral pH conditions in 2010.

Based on acidity time series of the lake water in combination with water budgets derived from a regional groundwater model the cumulative acidity loss in the lake for the time span from 2001 to 2015 can be estimated to be 8400 kmol.

Internal neutralization by biogenic sulfate reduction with consecutive deposition of reduced sulfur in the lake sediment was supposed to be the crucial process leading to the observed decrease in lake water acidity. In order to test this hypothesis elaborate quantitative field and laboratory investigations were launched in December 2014.

15 sediment cores distributed over the lake`s area were sampled and analyzed for reduced sulfur species at the hydrological laboratory of the University of Bayreuth. The measured sulfur contents were converted into deposited proton equivalents and finally the results were extrapolated for the total lake sediment.

The amount of at least 6400 kmol of acidity deposited and fixed in the lake sediments estimated with this procedure compares well to the acidity-loss of 8400 kmol which was calculated for the lake water as mentioned above.

Measurements and data evaluation allowed for identification of naturally occurring internal neutralization to be the major process for the observed acidity decrease in the lake water. The internal neutralization processes are not only beneficial to the lake water quality, but are also of great practical importance for the assessment of the hydrochemical state of the lake.

The methodology applied to Lake Knappensee consisting of field scale sediment investigations combined with water budgets gained from regional groundwater modeling could also be used for the assessment of the hydrochemical state of other mining lakes.

Key words: Lignite mining lakes, internal neutralization, field scale studies, sulfur deposition

Introduction

Lake Knappensee is located in the former lignite mining area of Wackersdorf, Eastern Bavaria (Germany). The lake has an extension of 52 ha and is embedded in the regional ground and surface water flow regime.

Until the year 2001 the acidity in the lake`s water body amounted to more than 0.5 mmol/l. Lake Knappensee was therefore clearly affected by acidification processes as a result of former lignite mining. As of 2001 lake water acidity continuously decreased reaching acidity values of about zero mmol/l in 2010. Since then the lake water is practically acidity-free (fig. 1). The decrease in acidity also appears in a drop of lake water pH. After remaining at values of about pH=3.5 for many years, it increased to meanwhile neutral values around pH=7 since 2001.

Based on the acidity time series in combination with water budgets derived from a regional groundwater model for the site the cumulative acidity loss in the lake water for the time span from 2001 to 2015 can be estimated to be 8,400 kmol. Constant acidity load from the inflowing groundwater into the lake was assumed for this period.

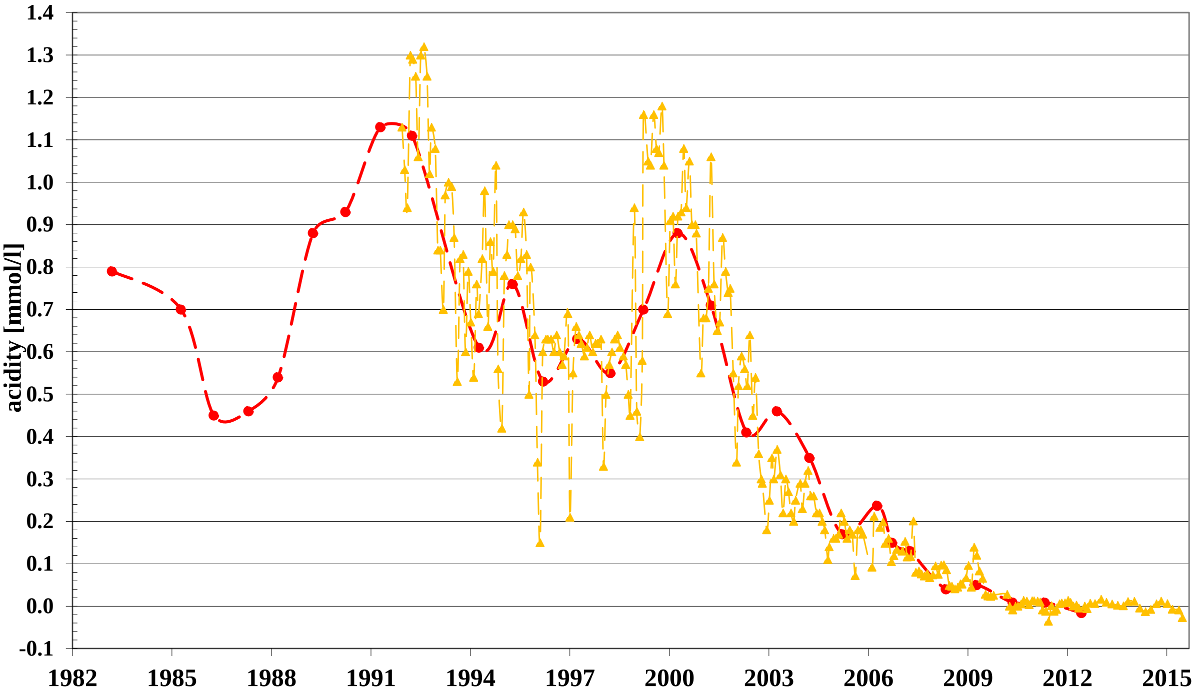

Figure 1 *Time series of acidity values in Lake Knappensee from 1982 to 2015. Red dots show acidities based on measurements from Landesgewerbeanstalt Bayern,yellow triangles are based on measurements from E.ON Kraftwerke*

Processes

Basically several processes could have led to the observed decrease in acidity. In the following these processes are assessed concerning their possible significance for the de-acidification.

First, the assumption of continuous acidity inflow from the surrounding aquifer could be wrong, i.e. the decrease could be caused by decreasing acidity of the inflowing groundwater (flushing of the mining dumps). However, this process is not likely to be the cause of the acidity decrease, as the time scale of the typical residence time of groundwater in the dumps is much larger (> 20 years) than the time scale of the decrease in the lake water (10 years). Furthermore the acidity in the surrounding groundwater entering the lake does not show any decrease since 2001 but is continuously high (> 6 mmol/l). Therefore internal neutralization processes remained as the most likely explanation for the acidity decrease in the lake water.

Transport simulations with a regional scale numerical groundwater/lake model corroborated this assumption. Taking a groundwater inflow showing the acidity observed in the surrounding sampling wells acidity in the lake should remain in the order of 1 mmol/l instead of being neutral. The only way to reproduce the observed acidity decrease in the model was to assume a sink term in the lake itself.

This sink term could be accomplished in principle by alkaline fluids leaking from red mud depositions below the lake bottom. The red mud originated from a nearby aluminum plant and was dumped in the former open pit from December 1965 to April 1973. Later on the red mud depositions were covered by ash layers of up to 20 m thickness. However, the red mud fluids show extremely high pH-values of up to pH=14, while the pH-increase in the lake stopped at circum-neutral pH-values. Thus, it is not very likely that leakage from red mud depositions are the reason for the neutral pH-conditions in the lake. Moreover, red mud influenced fluids should contain high amounts of sodium, but a sodium increase along with the pH increase was not observed in the lake. Finally, the hydraulic situation in the groundwater surrounding the lake with downward hydraulic gradients in the area of the red mud depositions would not allow for flux from red mud into the lake water.

In the end, biogenic neutralization remains the only probable mechanism that could act as an acidity consuming sink term. The northern half of the lake is characterized by low water depth (mostly < 2 m) and an extensive growth of partially submersed bulbous rush (*Juncus bulbosus*). Therefore a large amount of organic matter is produced and organic debris can accumulate at the lake`s bottom. The decomposition of this organic litter will lead to chemically reducing conditions including sulfate reduction. The sulfate reduction together with sulfur and sulfide mineral precipitation is in turn linked to proton consumption and thus to an increase in pH. The conditions for sulfate reduction und sulfide precipitation are especially favorable in the Lake Knappensee as the water shows elevated sulfate levels of about 700 mg/l and also elevated ferrous iron contents (e.g. from former pyrite oxidation).

The transformations can be described by the following net reaction equations:

Formation of elementary sulfur S^0

$$3CH_2O + 4H^+ + 2SO_4^{2-} \rightarrow 2S^0 + 3CO_2 + 5H_2O$$

Formation of iron monosulfide FeS

$$9CH_2O + 8H^+ + 4SO_4^{2-} + 4FeOOH \rightarrow 4FeS + 9CO_2 + 15H_2O$$

Formation of iron disulfide FeS_2

$$15CH_2O + 16H^+ + 8SO_4^{2-} + 4FeOOH \rightarrow 4FeS_2 + 15CO_2 + 25H_2O$$

CH_2O stands for organic material in the sediment; FeOOH denotes three-valent iron minerals.

As can be seen from the stoichiometric expressions shown above 2 moles of protons are neutralized per one mole of reduced sulfur produced from sulfate. Essential for a long-lasting de-acidification by this mechanism is that the reduced sulfur species are buried in the sediment, preventing them from being re-oxidized.

Methods

Exploratory investigation in 2011 revealed that layers with sulfide minerals covered by a thin oxic layer can be found in the sediment of the Lake Knappensee. The sulfide minerals were identified qualitatively by release of hydrogen sulfide after treatment with 0.1 molar hydrochloric acid.

In order to test the hypothesis of sulfate reduction and reduced sulfur deposition being the key process promoting in-lake neutralization, elaborate quantitative field and laboratory investigations were launched in December 2014.

15 sediment cores were sampled by lowering plexiglass liners of 6 cm diameter and 1 m length into the lake bottom. The locations of the sampling points are displayed in fig. 2.

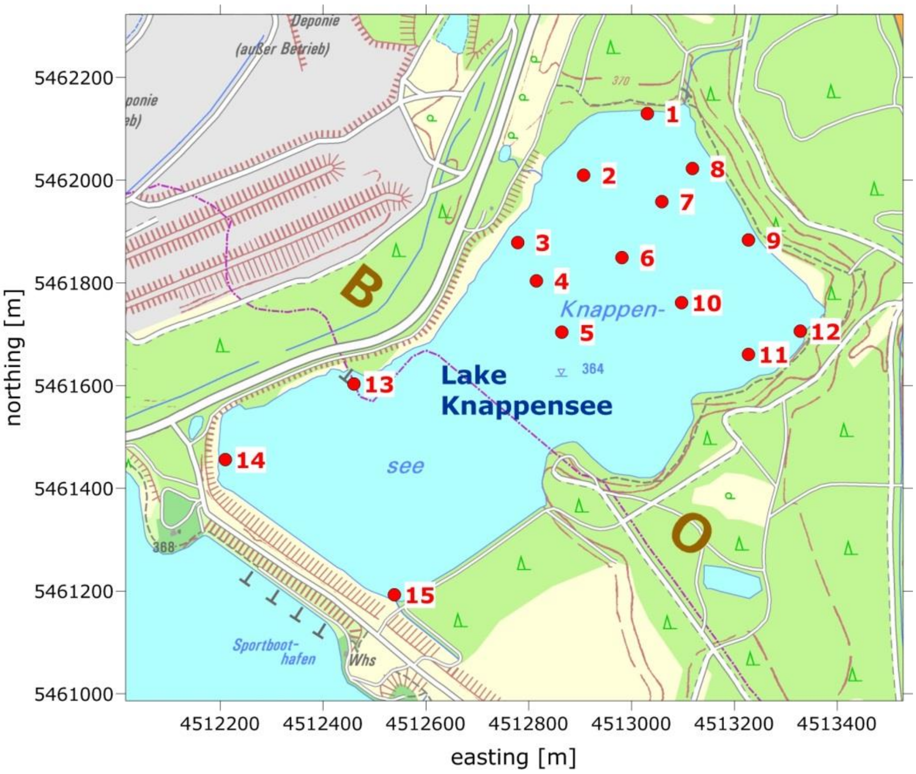

Figure 2 *Location of the sediment cores gathered from Lake Knappensee (map from Bayerische Vermessungsverwaltung).*

The sampling tubes were driven manually into the lake sediment until the compact underlying ash layer was reached. The tubes were then sealed with rubber plugs. The thickness of the black-colored organic-rich surface layers varied between < 1 cm and 29 cm, the total thickness of the cores (surface layer + ash) varied between 25 cm and 61 cm.

The cores were immediately delivered to the hydrological laboratory of the University of Bayreuth maintaining strictly anaerobic conditions during transport and storage. In the glovebox of the lab several samples were taken from the organic-rich surface layer of each core and analyzed for their content of elementary sulfur (S^0), acid volatile sulfide AVS, and chrome-reducible sulfur (CRS).

AVS is mainly made up of iron monosulfide, while elementary sulfur and disulfide sulfur are captured by the CRS method. The disulfide content of the sample can be calculated as the difference between CRS and S^0.

Besides sulfur species the dry matter content of the original sediment and the thickness of the organic surface layer were determined.

An overview on the mean observed sulfur contents of the individual cores expressed in mmol sulfur per kg dry matter is given in fig. 3. Obviously, appreciable amounts of reduced sulfur species were found in most of the samples. The relatively high content of AVS is a hint at recent sulfate reduction and sulfur deposition occurring in the lake and the sediment.

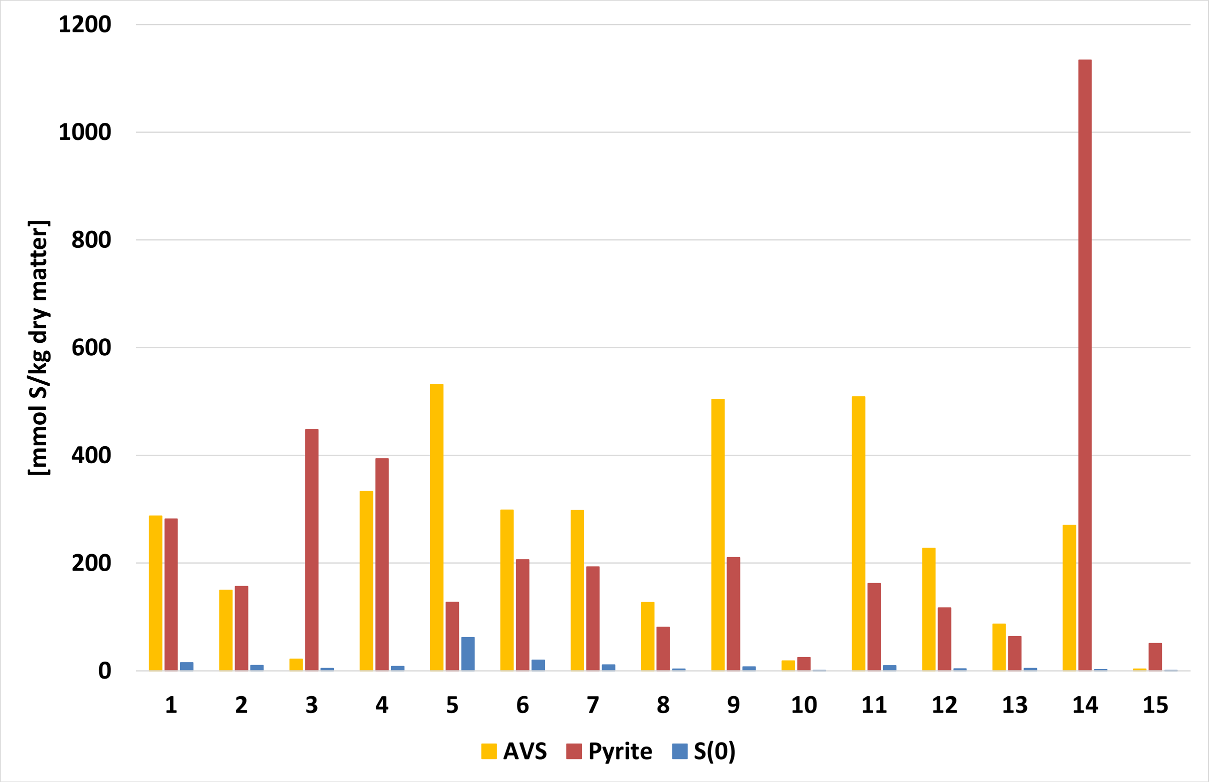

Figure 3 *Mean sulfur species contents at the 15 sediment sampling locations. Sulfur values are based on dry matter mass of the surface layer.*

Results

The first step in evaluating the field data consisted in calculation of proton (acidity) equivalents from the measured sulfur species content according to the stoichiometric relations given in the equations shown above. Sediment cores 3, 10 and 15 were not considered for proton equivalent calculations, as no clear organic surface layer could be identified for the three cores. The results of the calculations are displayed in tab. 1.

Table 1 *Proton equivalents calculated from measured sulfur species.*

mean sulfure species contents [mmol/kg]				**calculated proton equivalents [mmol/kg] from…**			
core no.	S(0)	AVS	disulfide-S	...S(0)	….AVS	….disulfide S	sum
1	14.9	287.3	282.0	29.8	574.6	563.9	1168.4
2	9.6	149.5	156.4	19.2	299.0	312.9	631.1
4	7.9	332.8	393.6	15.8	665.5	787.1	1468.4
5	61.5	531.3	126.9	122.9	1,062.5	253.7	1439.2
6	19.6	298.3	206.0	39.2	596.7	412.0	1047.9
7	10.7	297.6	192.7	21.4	595.3	385.3	1002.0
8	3.3	126.6	80.8	6.7	253.1	161.5	421.3
9	7.3	503.9	210.2	14.6	1,007.8	420.5	1442.9
11	9.4	508.5	161.8	18.7	1,017.0	323.6	1359.3
12	3.6	227.3	116.6	7.2	454.7	233.2	695.1
13	4.3	86.5	63.4	8.5	173.0	126.9	308.4
14	2.0	270.0	1134.0	3.9	539.9	2,268.0	2811.9

With the help of the calculation steps shown below the proton equivalents determined for the individual sampling locations were extrapolated for total proton equivalent mass in the lake sediment.

At first specific dry matter mass per unit surface area was calculated from dry matter content of the sample and the thickness of the organic surface layer.

Multiplying proton equivalents of dry matter with the specific dry matter mass per unit surface area yields the specific proton equivalents per unit surface area of the sediment.

Finally the specific proton equivalents have to be multiplied with the surface area attributed to the respective sampling location. The attribution of a surface area was performed graphically with the help of polygons surrounding the sampling locations (fig. 4).

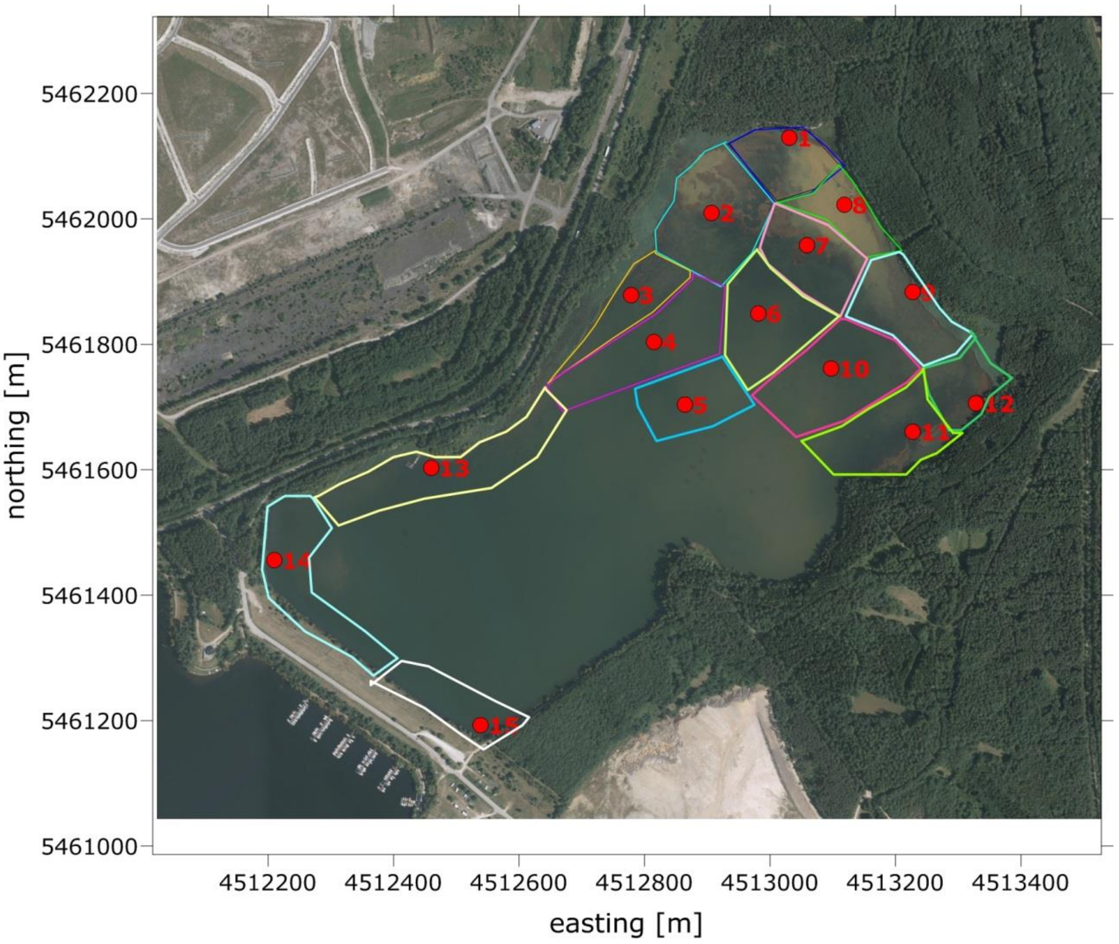

Figure 4 *Polygons attributing surface areas to the individual sampling location (aerial photograph from Bayerische Vermessungsverwaltung).*

The transformation of the proton equivalents derived from measured reduced sulfur contents to specific proton equivalent masses and their extrapolation to total proton equivalent masses is shown in tab. 2 and exemplified in the following for sediment core no. 1.

The samples from the organic-rich surface layer of core no. 1 yielded a mean dry matter content of 10.9 % (column 2 in tab. 2) and a corresponding water content of 89.1 %. The density of the dry matter was estimated to be 1.5 kg/l assuming dry matter being a mixture of organic and mineral compounds.

The bulk density of the surface layer (dry matter + water) is then 0.109 x 1.5 kg/l + 0.891 x 1 kg/l = 1.05 kg/l = 1050 kg/m^3 (1 kg/l being the density of water).

The thickness of the organic surface layer in sediment core no. 1 was 130 mm = 0.13 m. The specific mass of the surface layer per unit sediment area is then 1050 kg/m^3 x 0.13 m = 137 kg/m^2. Multiplying the specific surface layer mass with the measured dry matter content of 10.9 % (0.109) yields a specific dry matter content of 15 kg/m^2.

Table 2 *Extrapolation from specific to total proton equivalents*

sediment core no.	dry matter content [%]	densitiy of the surface layer [kg/l]	thickness of the surface layer [mm]	specific dry matter mass [kg/m^2]	proton equivalent based on dry matter mass [mol/kg]	specific proton equivalent [mol/m^2]	attributed area [m^2]	total proton equivalents [kmol]
1	10.9	1.05	130	15.00	1.17	17.53	13015	228
2	17.7	1.09	180	34.59	0.63	21.83	27095	591
4	10.3	1.05	290	31.50	1.47	46.25	27348	1265
5	13.0	1.07	170	23.59	1.44	33.95	15265	518
6	15.7	1.08	125	21.14	1.05	22.15	22193	492
7	14.8	1.07	150	23.77	1.00	23.82	17879	426
8	23.7	1.12	175	46.47	0.42	19.58	11166	219
9	11.5	1.06	120	14.65	1.44	21.14	19390	410
11	14.2	1.07	210	32.05	1.36	43.56	21635	942
12	19.9	1.10	200	43.70	0.70	30.38	11905	362
13	29.8	1.15	70	23.98	0.31	7.40	25698	190
14	12.6	1.06	85	11.40	2.81	32.07	22643	726
sum								**6369**

The proton equivalent of dry matter of core no. 1 calculated from measured reduced sulfur was 1.17 mol/kg (cf. last column in tab. 1). Multiplying the dry matter proton equivalent with the specific dry matter content of core 1 of 15 kg/m^2 leads to a specific proton equivalent mass per unit area of 1.17 mol/kg x 15 kg/m^2 = 17.5 mol/m^2.

A sediment surface area of 13015 m^2 was attributed to core no. 1 (see also fig. 4). Multiplication of the specific proton equivalent mass per unit surface area of 17.5 mol/m^2 with the attributed area of 13015 m^2 provides a total proton equivalent mass of 17.5 mol/m^2 x 13015 m^2 = 228 kmol (last column of tab. 2) for the area represented by core no. 1.

The calculating steps exemplified for core no. 1 were performed for all other cores except for cores no. 3, no. 10 and no. 15. As mentioned above, those cores were not considered for total proton equivalent calculations as no clear organic surface layer could be identified.

Highest amounts of proton equivalents were found for sediment core no. 4, mainly owing to the thick organic surface layer observed for this core.

The 12 polygons considered for proton equivalent calculation cover a surface area of 235232 m^2. This area makes up about 45 % of the total surface area of the lake. It was assumed that the remaining sediment area of the lake does not provide significant additional amount of proton equivalents. This is a conservative estimate with regard to the total acidity equivalents buried in the lake`s sediment.

The total proton equivalent mass buried in the sediments of Lake Knappensee was estimated to amount to 6369 kmol (cf. tab. 2). This value fairly matches the acidity loss of 8390 kmol which was calculated based on the acidity evolution in the lake since 2001 and water budgets derived from the regional groundwater model (see above).

Discussion

Estimations for total masses or charges for large natural objects like Lake Knappensee are always afflicted with various uncertainties. They may arise from spatial and temporal variations in the underlying processes and parameters, which often are only roughly encompassed.

Considering the acidity losses calculated for the lake water it is mainly the acidity of the inflowing groundwater which gives rise to uncertainty. Here we assumed the hypothetical acidity resulting from pure mixing of acidic groundwater entering the lake with neutral surface waters discharging into the lake to be 0.8 mmol/l (cf. fig. 1). If the hypothetical acidity of the lake water without internal neutralization processes was higher or lower, higher or lower acidity losses were estimated respectively.

Furthermore, the onset date of de-acidification processes is not precisely known. In our case, we assumed the processes to start in the year 2001, but neutralization process might as well have started a few years earlier.

While the proton equivalents calculated from sulfur measurements constitute relatively hard data, it is mainly the spatial heterogeneity of the parameter distribution providing a source of uncertainty for estimation of the total masses. Despite the relatively high number of 15 sediment cores and the appreciable effort which was taken for data analysis only a coarse picture of the real spatial distribution pattern of lake sediment parameters could be gained.

The estimated total proton equivalent of 6369 kmol buried in the lake sediment most probably provides a lower limit for the internal neutralization capacity of the lake, as only roughly half of the sediment area was considered for the calculations. Assuming that the proton equivalent mass in the order of the mean value of 30 mol/m^2 (cf. tab. 2) prevails in the remaining sediment area (about 200000 m^2), an additional amount of 30 mol/m^2 x 200000 m^2 = 6000 kmol of proton equivalents could be expected. The total amount of proton equivalents in the lake sediment would then increase to about 12000 kmol.

Conclusions

In spite of the uncertainties concerning detailed parameter distribution, results from the sediment studies prove that appreciable amounts of reduced sulfur compounds are buried in the Lake Knappensee sediments.

An important finding is that the acidity loss that is linked to the reduced sulfur fixation in the sediment is in the order of magnitude of the acidity loss derived from a mass balance approach in the lake water.

That means that the acidity stored in the sediment is sufficient to explain the de-acidification observed in the lake water since 2001. Naturally occurring internal neutralization could therefore be identified to be the key process leading to neutral pH-conditions in the formerly acidic lake.

The storage of large quantities of acidity equivalents in the sediment reveals to be the process underlying the sink term used in the transport model. This sink term was necessary to reproduce the observed neutral pH-conditions in the lake which is continuously fed by strongly acidic ground water to the day.

The internal neutralization processes in Lake Knappensee are not only beneficial to the lake water quality, but are also of great practical importance for the assessment of the hydrochemical state of the lake. One of the consequences for future management strategies of the lake should be that water level changes should be strictly avoided, as e.g. water level decreases would trigger re-oxidation of sediment areas exposed to the atmosphere and therefore initiate acidity pushes in the lake water. Overall the results suggest that Lake Knappensee contributes decisively to the partial neutralization of the acid mine drainage of the Wackersdorf lignite district.

The methodology consisting of field scale sediment investigations combined with water budgets gained from regional groundwater modeling applied to Lake Knappensee could also be used for the assessment of the hydrochemical state of other mining lakes.

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Varve formation in the acidic (pH 2.7) pit lake 111 (Lusatia, Germany)

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Abstract

Sediments from the north basin of Lake 111, a small but very well studied lake resulting from lignite mining in Lusatia, show a pronounced fine layering. This layering can be found in several lignite pit lakes, but mechanisms to explain it have not been investigated with respect to the specific hydrology and chemistry of acid pit lakes.

The north basin of Lake 111 is flat-bottomed, dimictic, and bioturbation can be neglected. Physical and chemical characteristics, sedimentation rates and composition of settling material have been monitored over two years and large thin sections of sediment cores were analysed microscopically to identify fine sediment layering as annual.

Total sedimentation rate was highest in winter, partly due to storms, while sedimentation of particulate organic matter showed peaks in May. Sedimentation of chrysophyte cysts occurred mainly in summer and autumn. Regular bands of chrysophyte cysts were detected, and comparison with the documented history of the lake substantiated that the observed lamination formed annually. To the best of our knowledge, this is the first report on varve formation in an extremely acidic lake which is not governed by fumaroles at the lake bottom.

Key words: acid pit lake, sediment, varve formation, chrysophyte

Introduction

Pit lakes or mining lakes form in many parts of the world as a consequence of opencast mining. In many cases, sulfide minerals in the dumps are oxidized upon contact with air, producing metal oxides and sulfuric acid. After mining the open pits fill by re-ascending groundwater or rainwater, which flush the acid and metals from the dumps into the lake water. This results in severe acidification of these lakes (pH 2-3) and high sulfate and metal concentrations. Such lakes are extreme ecosystems with respect to their chemical composition and their biocoenoses, which are practically devoid of higher organisms and poor in zooplankton species (Rodrigues et al. 2009, Belyaeva and Deneke 2013) and show low phytoplankton diversity and primary production (Lessmann and Nixdorf 2013). The most widespread phytoplankton genera comprise Chrysophyceae of the genus *Ochromonas*, Chlorophyceae of the genus *Chlamydomonas*, and Bacillariophyceae of the genus *Eunotia*. Their primary production is limited both by phosphorus and inorganic carbon (Lessmann and Nixdorf 2013), which is a consequence of high iron concentrations and extreme acidity.

Annual/seasonal laminations (varves) may form in lake sediments in the absence of significant water movement, bioturbation or gas bubbling. They reflect seasonal changes in sedimenting material. In lakes with a large catchment or with unstable soils in the catchment, the seasonal variation in sediment supply leads to clastic laminations, while a seasonal cycle of production and sedimentation brings about biogenic laminations (O'Sullivan 1983). Phytoplankton production can be traced in the sediment record using diatom frustules and chrysophyte stomatocysts (e.g. Hobbs et al. 2010). Lakes with high internal carbonate loading often possess calcareous laminations, which are triggered by rising temperature and algal uptake of CO_2. In humic lakes, ferrogenic lamination caused by seasonal Fe(II) oxidation may occur (O'Sullivan 1983). Counting and analysis of varves can be used to estimate the age of certain sediment layers and to elucidate specific situations or gradual development in the past of a lake and its catchment. However, this approach has apparently not been applied for mine pit lakes so far.

A fine layering has been reported to be common in sediments of Lusatian pit lakes (Friese et al. 2013), but the processes governing its formation have not been studied yet. Since calcite precipitation, a typical process causing sediment lamination (Scharf et al. 2009) cannot occur in an acidic, carbonate-free lake, it remained an open question if the laminations represented annual cycles (varves) that can be used for age determination of acidic pit lakes. Pit lakes are often situated in remote areas and not regularly monitored. A means to determine the age of sediment layers would allow to elucidate distinct events and processes in the past of these lakes or in their catchments, such as physical disturbance events, progress of landscape reclamation, or land use changes. Seasonal lamination of sediments has been documented for the very acidic and dimictic crater lake Katanuma (Satake and Saijo 1978), but the underlying mechanism requires the presence of fumaroles at the lake bottom.

Lake 111 is a small acidic (pH 2.7) pit lake in Lusatia, East Germany (51°29’ north, 13°38’ east). It started to form after closure of the lignite mine Agnes which was operated between 1929 and 1958 (Koschorreck 2013). Because of its high sulfate concentrations (1050-1600 mg L^{-1}) and the absence of surface inflows or outflows the lake served as a model site for testing passive bioremediation and the application of in-lake sulfate-reducing bioreactors (Koschorreck 2013), so its bathymetry as well as water and sediments have been thoroughly studied. The north basin is flat-bottomed, has a maximum depth of 6 m and is dimictic. Lake 111 water is low in nutrients and carbon (table 1). Its phytoplankton community is restricted to unicellular flagellates of the genera *Chlamydomonas* (Chlorophyta) and *Ochromonas* (Chrysophyta) which are present through the whole growing season (Kamjunke et al. 2004). Lake sediments are also acidic (pH 2.7-3), and sediment cores regularly showed a finely laminated structure, especially in the upper centimeters (Wendt-Potthoff et al. 2010; Friese et al. 2013).

Table 1 *Water chemistry of Lake 111 between 1999 and 2008. Data were compiled by Koschorreck (2013) using 143 to 287 single measurements. TIC total inorganic carbon, TOC total organic carbon.*

Parameter	Unit	Value	Parameter	Unit	Value
$KB_{8.2}$	mmol L^{-1}	17 ± 2	Cu	µg L^{-1}	6.4
Ca^{2+}	mg L^{-1}	219 ± 33	Ni	µg L^{-1}	200
Mg^{2+}	mg L^{-1}	30	NH^{4+}-N	mg L^{-1}	2.8 ± 0.5
Na^{+}	mg L^{-1}	7 ± 1	NO_3^--N	mg L^{-1}	0.3 ± 0.1
Fe	mg L^{-1}	171 ± 70	Total P	mg L^{-1}	0.009
Al	mg L^{-1}	38 ± 5	Si	mg L^{-1}	17.9
Mn	mg L^{-1}	3.1 ± 0.4	TIC	mg L^{-1}	6.1 ± 9.2
Zn	mg L^{-1}	1.08	TOC	mg L^{-1}	2.1 ± 1.8

The aim of the present study was to clarify whether the laminations represent varves. As the key to understanding varve formation is the study of modern lake processes (Tylmann et al. 2012), we combined the microscopic analysis of thin sections of a sediment core with sediment trap studies over 28 months from August 2006 to January 2009, and with documented facts about the history of this young anthropogenic lake.

Methods

Sediments were obtained in September 2002 by gravity coring (Uwitec, Mondsee, Austria). Cores sampled with pre-cut liners fastened with waterproof tape were sectioned vertically in the field for documentary purposes. One half of a 51 cm long sediment core was transported intact to the laboratory within the plastic liner and then embedded for thin sectioning following Röhrig and Scharf (2006). Briefly, samples were dehydrated by immersion in acetone. Then acetone was replaced by Palatal, a polyester resin. The resin was allowed to harden for approximately two weeks and finally cured at 60°C for 48 h. Large thin sections were prepared by Thomas Beckmann (Dünnschlifflabor

Schwülper-Lagesbüttel, Germany). Thin sections were analyzed using a Zeiss Axiolab microscope with a Nikon (Coolpix 990) camera for documentation.

Sedimentation rates were determined using two parallel sediment traps (Uwitec, Mondsee, Austria) which were exchanged approximately every two weeks from August 2006 to December 2008. Aliquots of the homogenized sediment trap contents were fixed with Lugol's solution. The sediment trap flasks were kept refrigerated and the remaining material was analyzed the following day. The contents were again carefully homogenized before filtration. Pre-washed and weighed membrane filters (ME24) were used to determine total sediment mass from 150 mL of sediment trap material. Pre-combusted glass fibre filters were used to determine particulate organic carbon (POC) from 200 mL of sediment trap material. All filters were dried for 2 h at 60°C. POC was determined with a TOC analyzer (Vario EL, Elementar, Germany). The sediment from the traps was also regularly inspected by light microscopy using 400 x magnification, and photographs were taken using an AxioVision camera and software (Zeiss, Germany).

To facilitate counting of chrysophyte stomatocysts in sediment trap material, organic matter from Lugol-fixed samples was removed by incubation and boiling with H_2O_2 and subsequent potassium dichromate treatment. After three washing steps with water, samples were again fixed with Lugol's solution. Chrysophyte cysts were then counted using sedimentation chambers and an inverted microscope.

Results and Discussion

Regarding recent sedimentation, a yearly cycle of gross sedimentation rate and POC content of the sedimenting material was evident (fig.1), with maxima of gross sedimentation rate in winter and summer and highest POC sedimentation in the summer. Minima of gross sedimentation occurred in late autumn. After the severe winter storm Kyrill on January 18 and 19, 2007, the sedimentation rate was 1.5fold higher than the other maxima. Living specimens from January 31 also contained empty cysts in addition to those with still visible cell contents, which indicates sediment resuspension. However, dump erosion may have been of key importance, as the eastern and southern shore of Lake 111 are still poorly covered by vegetation. Chrysophyte cysts were detected almost throughout the year and their counts had maxima in spring and late summer (fig. 1), but counts were also high around 10^{10} cysts m^{-2} a^{-1} at the end of the year. This appears unusual, however, maxima of cyst deposition in other lakes have been observed both in autumn (Smol 1988) as well as in winter or late spring/early summer (O'Sullivan 1983). Cysts in Lake 111 were 5-7 µm in diameter, their surfaces appeared rather smooth, and their collar was not pronounced (fig. 2), however, electron microscopy would be needed to substantiate details. Given the limitations of light microscopy, the overall morphology agreed reasonably with stomatocysts of known *Ochromonas* species (Holen 2014), and no other chrysophyte genera were detected in Lake 111 during several years of study (Kamjunke et al. 2004, Koschorreck 2013).

Fresh sediment was soft, fine-grained and layered to a depth of approximately 22 cm. Greenish-yellow and brownish bands with varying thicknesses alternated (fig. 3).

Large thin sections of the sediment confirmed the lamination up to 22.3 cm. Yellow bands appeared gel-like and did not contain clastic material, while the brownish bands were more dense. The high iron concentrations of the sediments (Wendt-Potthoff et al. 2010, Friese et al. 2013) suggest that the gel-like material may consist of amorphous iron minerals. Below 22.3 cm few limnic remains were detected, but the mineral matrix contained lignite particles, fly ash spherules, splinters of charcoal and gypsum crystals (fig. 4). Surprisingly, no pollen grains were seen in the whole core. Presumably they had been mineralized in the extreme chemical matrix of the sediment, or they are masked by the optical properties of the polyester resin and/or the wall of the pollen grains. Sedimentological patterns underlying glacial varves result from regular seasonal processes at the front of a glacier. In contrast, the structures of Lake 111 sediments formed by sand and silt layers are caused by the management of the lake or extreme weather events. Limnochemical and -physical processes may explain layering, but they may occur several times in a year. Moreover, calcite and siderite precipitation can be exluded in the present chemical status of the lake. Other biological proxies are diatom frustules and chrysophyte cysts, the latter being more stable against chemical attack (Hobbs et al. 2010).

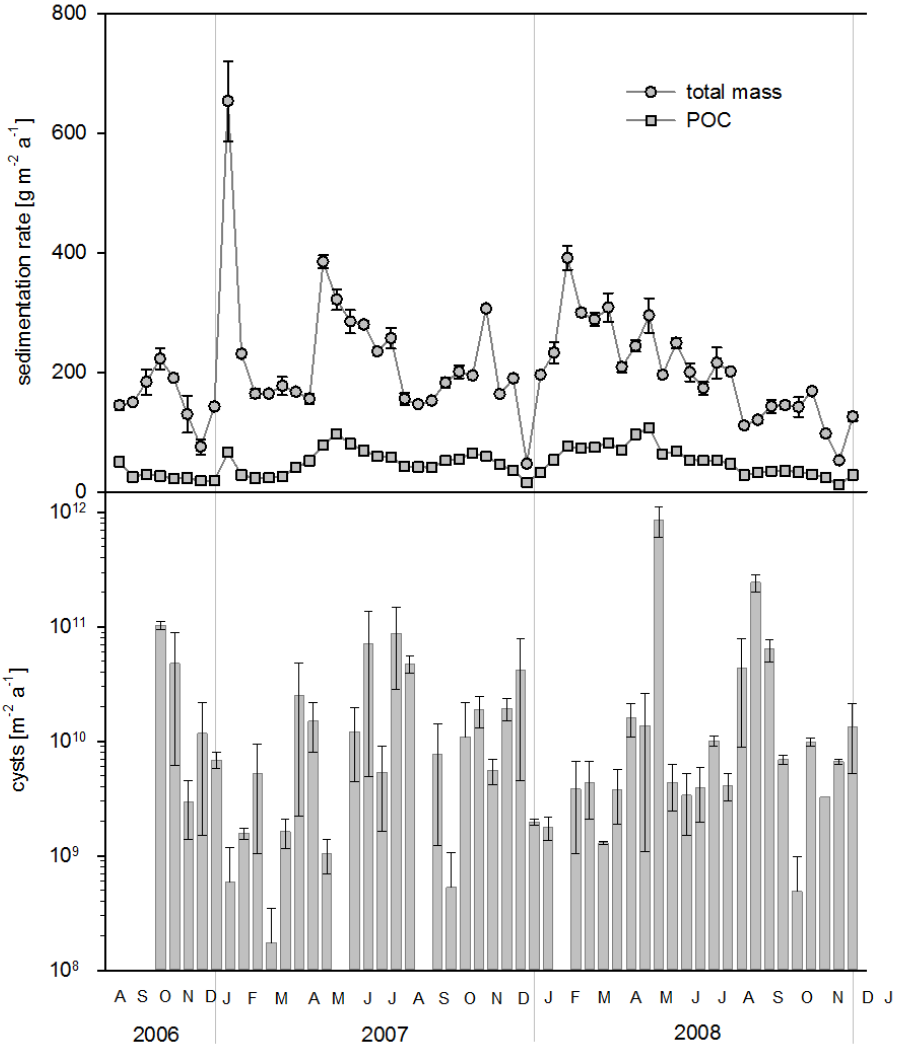

Figure 1 *Sedimentation rates of total solids, particulate organic carbon (POC) and numbers of chrysophyte cysts.*

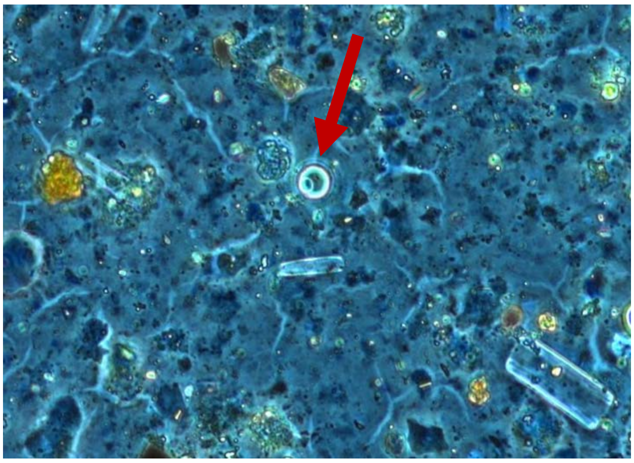

Figure 2 *Appearance of a chrysophyte cyst in sediment trap material after treatment with* H_2O_2 *and potassium dichromate.*

Indeed, rather well preserved frustules of the genus *Eunotia* and severely etched "ghosts" of *Navicula, Cymbella* and *Melosira* were detected, especially in the top 5 cm. Deeper in the sediment, they did not form clear and regular layers, and their numbers declined. This may be partly due to chemical degradation in the extreme chemistry of the sediment. Bands of chrysophyte cysts were found more regularly close to or in the yellow bands. In some cases, chrysophyte cysts were "missing", or it was unclear if two thin bands originated in the same year. There is one report indicating that *Ochromonas* might have been absent from Lake 111 in 1995, however, the authors could not rule out methodical problems (Wollmann et al. 2000). As chrysophyte cysts are typically better preserved in the sediment than diatom frustules, we assume that if only diatoms are detected in a defined layer, chrysophyte cysts have not been formed in the respective period. The formation of more than a single chrysophyte band is probably explained by intermittent intense sedimentation of other material.

Figure 3 *Vertically cut sediment core from Lake 111 with laminations.*

Assuming that formation of chrysophyte cyst bands formed annually in the sediment of Lake 111, the age of the sediment layers can be explained as follows:

The top 3 cm appear to be disturbed during sampling, probably due to the high water content and softness of the material. Down to 4.9 cm depth, the deposits of 4-5 years can be found. Further downwards to 6.8 cm, approximately 7 years are counted (altogether 11-12 years). The section between 6.8 and 8.2 cm represents 4 years. Between 9 and 10 cm depth, some uncertainty exists because chrysophyte cyst layers appear to occur in pairs. Taking this into account, the top 11 cm of sediment represent 23-26 years. Further downward, 4 cysts layers were detected until 12.7 cm, and another 0 to 2 unclear bands until 16.1 cm followed by 3 layers down to 16.6 cm (30-33 years in total). After another cyst band between 1.6. and 20.4 cm (summing up to 31-34 years), the sediment matrix was still layered but contained more plant particles and also diatoms. In one case the diatoms formed a band and were accompanied by scattered chrysophyte cysts. The seasonality remained unclear, as also signs of bioturbation were evident. We know that chironomid larvae colonize modern Lake 111 sediments (Rodrigues et al. 2009) and that their burrowing activity might be detected until 4 m water depth (Lagauzère et al. 2011). Maybe the water level was lower at that time, as the lake gradually filled with groundwater and precipitation is low in Lusatia. One or two additional years may be counted until 22.3 cm. The limnic regime must have been different below, and the contents of lignite, charcoal, glassy particles which probably represent fly ash, and gypsum crystals increased. These remains are associated with active mining in the area. Altogether, counting the chrysophyte cyst layers as annual laminations gives at least 32-36 years. Below, another 10 years of limnic sedimentation are estimated, giving at total lake age of 42-46 years at the time of sediment coring (2006). This corresponds well with the documented mine closure in 1958, assuming that it took at least two years to form a lake in the north basin of former mine Agnes.

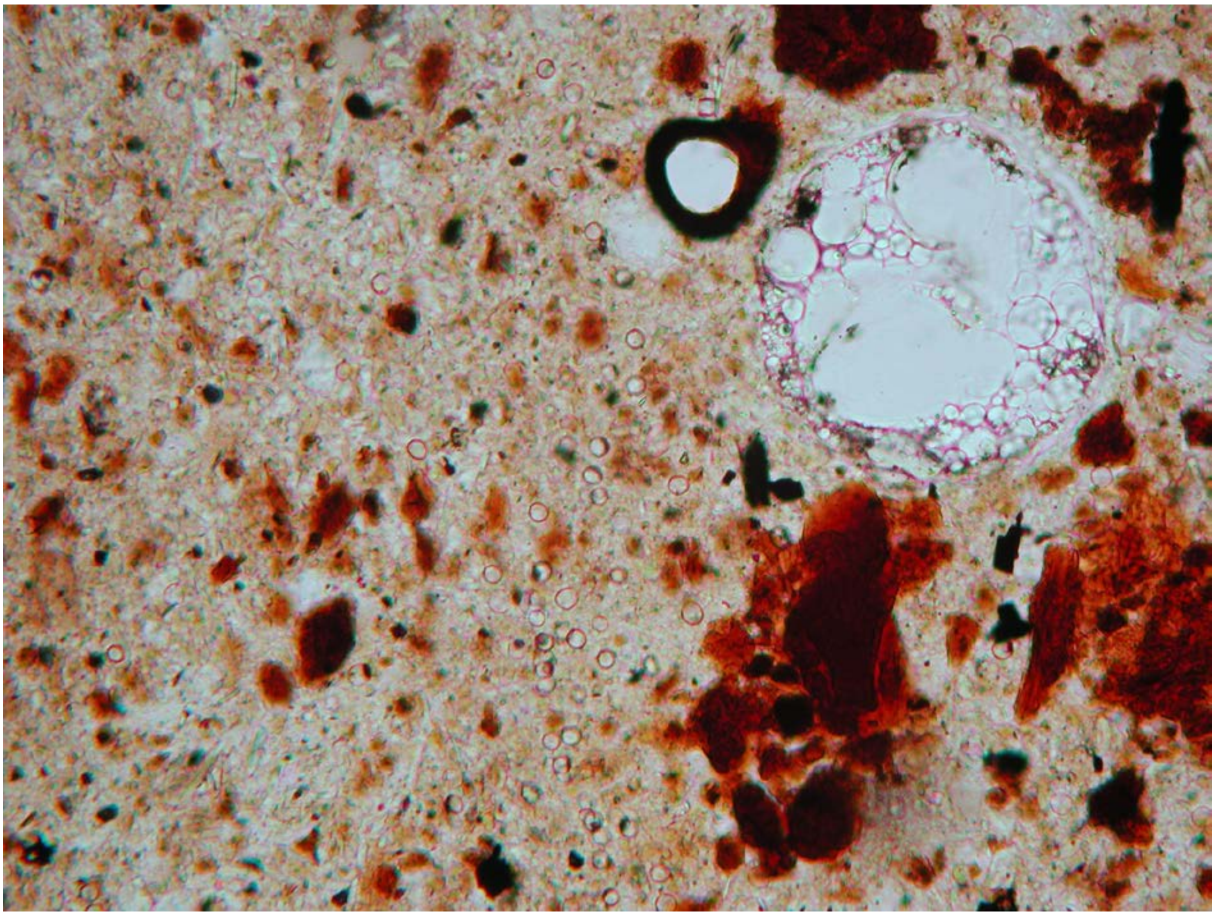

Figure 4 *Microscopic image of a layer with chrysophyte stomatocysts, a fly-ash spherule and coal splinters.*

Conclusions

Chrysophyte cyst layers in the sediment thin sections combined with the available information on the recent sedimentation and history of the lake clearly indicate that the fine laminations in Lake 111 sediment represent varves. To our knowledge, this is the first verification of varves in an extremely acidic pit lake. The cysts can be assigned to *Ochromonas* sp., since it was the only chrysophyte genus detected in Lake 111 and other acid pit lakes. Cyst formation was apparently not restricted to a defined season, as in many other lakes, but occurred more steadily with a bimodal maximum during summer. Only in some cases paired cyst layers were also seen in the sediment record. More detailed analysis of the sedimentation regime (e.g. iron sedimentation, re-dissolution processes) will be necessary to understand how the living planktonic cysts in the sediment trap finally form defined fossil layers in the lake sediment.

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Validation of Springer Pit Lake Water Balance and Water Quality Model, Mount Polley Mine, British Columbia, Canada

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Abstract

The Mount Polley Mine is a copper-gold mine consisting of three open pits and an underground operation, located in British Columbia, Canada. Following the failure of the glacial lacustrine layer beneath the perimeter embankment and the resulting breach of the embankment at theTailings Storage Facility on August 4, 2014, the Springer Pit has been used to store water draining from existing site facilities and submerged tailings. The Springer Pit continues to be used as a water storage facility under short-term restricted operations and discharge approvals, which also require the pit lake to be drawn down by treating and discharging the water to the receiving environment.

Water needs to be drawn down in the pit lake for two reasons:

- The mine has a positive water balance, so it has a finite capacity and consequently a finite amount of time before water begins to exfiltrate to groundwater and discharge to surface after the pit ultimately reaches its spillway elevation; and,
- The pit lake will need to be dewatered (and the tailings removed) to continue mining viable reserves, pending regulatory approval.

A stochastic water and mass balance model was developed for the Springer Pit to evaluate discharge water quantity and quality in the pit and at downstream receptors. Springer Pit water levels and water quality were simulated on a monthly time step from April 2015 to December 2016 to encompass the period of pit filling and restricted operations. The results of the model were also used to develop mine water management strategies, to provide a basis for selecting a water treatment technology, and to support permitting.

At present (May 2016), the pit lake has been filled to approximately 75% of its total capacity. Monitoring of the pit lake elevations and water chemistry have been ongoing and the empirical data provided an opportunity to validate model predictions. As noted in [2, 3], “two of the biggest problems with modern geochemical pit lake predictions are the challenge for model reviewers to independently repeat and check calculations, and the lack of understanding of the uncertainty associated with predictions.” This study addressed both of these problems and can be used to refine model inputs before extending the model for the next stages of mining. This is consistent with the recommendation provided in [4], that is “if the lake is in the filling stage, compare model predictions with observed data…validate and refine inputs to the model whenever information becomes available.” Moreover, it provides a counterpoint to critiques of pit lake modelling [5].

Predicted water elevation and concentrations were compared to observed data collected in the Springer Pit lake. In general, observed concentrations were within or below the range of predictions during filling, indicating that the model is performing well, particularly in light of challenges generally associated with pit lake models [3]. Three key factors that have led to a failure to predict mine waters elsewhere [6], particularly at copper mines, were favourable at Mount Polley: the predominance of non-acid generating material on site; the high quantity and quality of operational mine water data; and, the mine’s adherence to the water management plan.

Key words: pit lakes, modeling, validation

Introduction

The Mount Polley Mine (the mine) is a copper-gold mine operated by Mount Polley Mining Corporation (MPMC), a subsidiary of Imperial Metals Corporation. The mine is located approximately 56 km northeast of Williams Lake, British Columbia, Canada (Figure 1) and includes open pit and underground operations. Following the failure of the glacial lacustrine layer beneath the perimeter embankment and the resulting breach of the embankment at the at the Tailings Storage Facility (TSF) on August 4, 2014, the Springer Pit has been used to store water draining from existing mine facilities and tailings (both of which would previously have been stored in the TSF). A short-term water management plan was developed to manage a positive site water balance while drawing down water that has accumulated in Springer Pit since the breach.

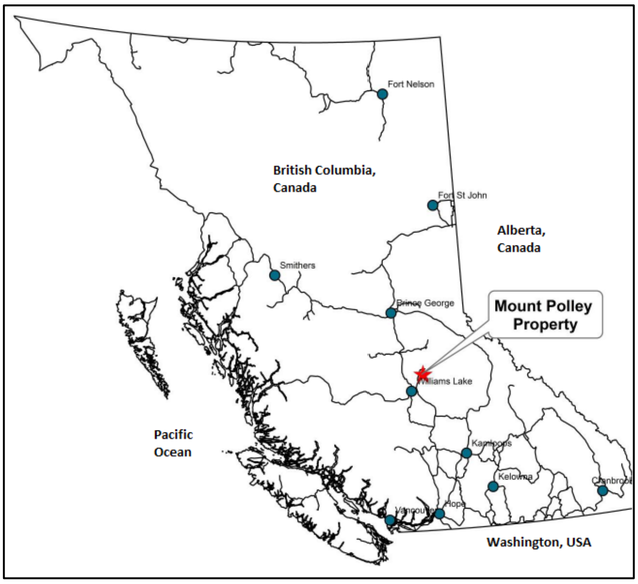


Figure 1. *Location of Mount Polley Mine, B.C., Canada*

As part of the water management planning, two models were developed to assess water quantity and quality in the Springer Pit lake:

1. **Site-Wide Water Balance Model (WBM):** the objective of this model was to simulate site water quantities, including Springer Pit volumes, under the current and proposed site water management plan.
2. **Mass-Balance Water Quality Model (WQM):** this model was developed to predict Springer Pit lake water quality for the purpose of estimating effluent quality and identifying constituents of potential concern in this facility and in discharge to the receiving environment.

The above models were developed using GoldSim™ Version 11.1 [1] and were internally linked. The WBM accounted for all flows within the mine as well as flows in local watercourses. The WQM accounted for mass transfers from each of the flows that could influence the water quality in Springer Pit.

To address uncertainty, the model was developed stochastically using a Monte Carlo approach. In the model, each input was defined as a probability distribution function that was randomly sampled over 1000 realizations. This approach provided a range of water elevations and qualities in Springer Pit at each timestep, which were subsequently used to calculate percentiles for each parameter at each model timestep. The predicted maximum of the 95th percentile constituent concentrations, projected over the duration of the model, were used to inform the water treatment plant design and to propose effluent limits for the short-term discharge permit. For additional detail on the WBM and WQM development, the reader is referred to the project Technical Assessment Report [7].

Water Balance Model

The pit lake is presently (as of May 2016) filled to approximately 75% of its capacity of approximately 15 Mm^3. Ongoing monitoring of pit lake water levels provided an opportunity to validate model predictions. The term "validation" as applied here refers to measurement of water levels and concentrations while the pit lake is filling, and comparing those measured values to model predictions that were generated before filling.

The water balance model has been updated regularly with measured climate and water level data since April 1, 2015 (Figure 2). The simulated lake elevations began to diverge in mid-June 2015, with the predicted lake elevation at the end of June 2015 being approximately 3.9 m higher than the observed value. Since July 2015, the simulated change in lake elevation has continued to diverge from the observed elevations at a slower rate. By the end of November 2015, the simulated Springer Pit lake elevation was 9.9 m higher than the observed level. This is equal to a total over-prediction between April 1 and November 30, 2015, of 2.8 Mm^3.

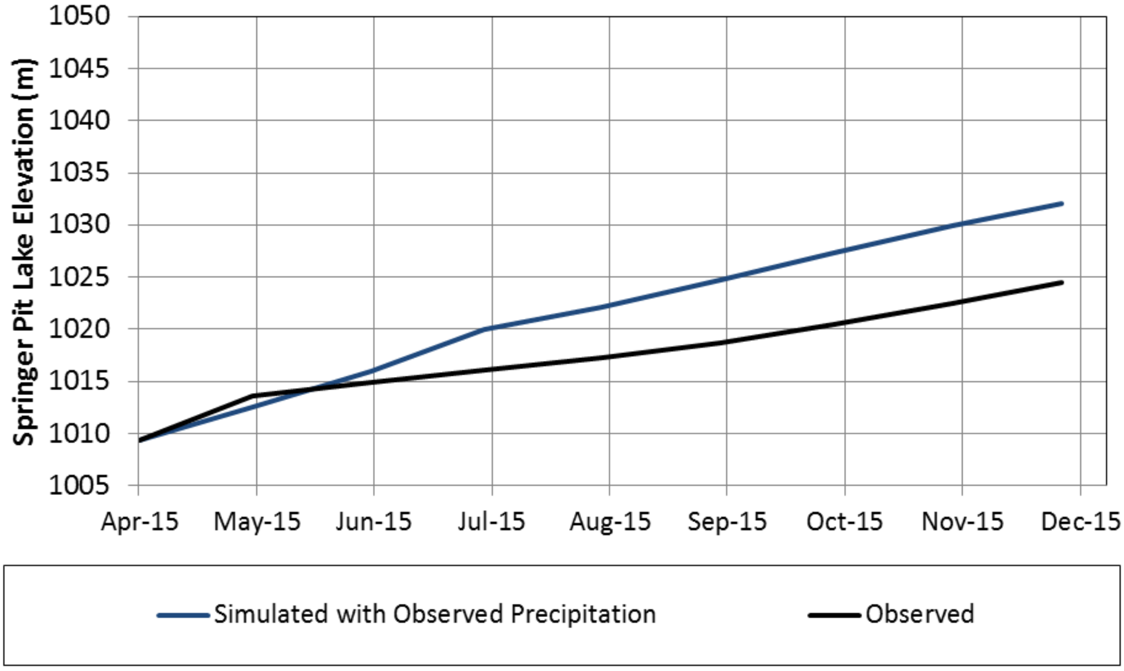


Figure 2: *Comparison between Observed and Simulated Springer Pit Lake Elevations (m)*

A review of the assumptions built into the WBM and the implementation of water management strategies during restricted operations revealed that the mill restart and the commencement of Springer Pit dewatering occurred at a later date than assumed in the WBM. The WBM was updated to reflect the actual timing of the mill restart and pit dewatering date. Predicted Springer Pit water levels, accounting for these updates, are presented in Figure 3. Water elevations are simulated in the WBM using stochastic climate values, and results are shown for the Average, and the 1 in 200-y Wet (99.5th percentile), and the 1 in 100-y Dry (0.5th percentile). Comparing the updated simulation that is based on measured climate inputs against the original, stochastic predictions, updated Springer Pit lake elevations have consistently tracked between the Average and 1:200-y Dry projections, and have climbed towards the Average projection over time (Figure 3).

Comparing measured water levels against both sets of model simulations, the observed Springer Pit lake elevations track consistently below the 1:200-y dry projection (Figure 3) from June 1 onwards. This is explained by the early snowpack depletion and extreme dry conditions experienced in early 2015. As of April 1, 2015, the snowpack at Mount Polley had essentially been depleted. Between the typical freshet months of April through June, a total of 105 mm of rainfall plus snowmelt was recorded. For comparison, the historic average rainfall plus snowmelt is 338 mm, and 176 mm for 1 in 200-y dry conditions. Therefore, runoff at the mine for the freshet period in 2015 (April through June) was compounded by a lack of April snowpack, plus the extreme dry conditions that remained close to 1:200-y dry conditions during May and June. For the remainder of 2015, the Mine has generally experienced more normal precipitation.

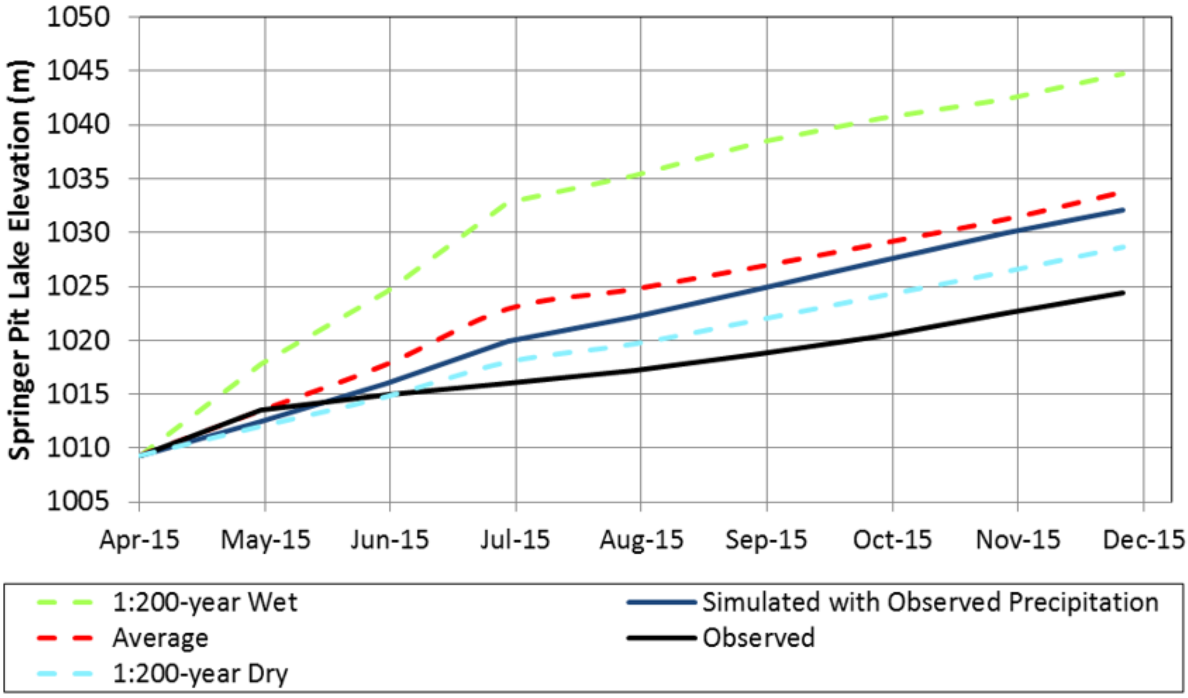


Figure 3: Comparison between Observed and Simulated Springer Pit Elevations with the TAR Predictions.

Water Quality Model

Water concentrations of forty modelled constituents were measured in Springer Pit lake during the period of July to December 2015, which included restricted restart of operations and pit filling. A comparison of the WQM predictions against measured concentrations shows that most constituent concentrations were either within or below the predicted range. Based on the comparison, predictions were grouped into three categories:

- **Over-predicted**: concentrations that were observed to be generally below the 5th percentile model predictions, including:
  - **Ions and nutrients:** chloride, ammonia, and total phosphorus;
  - **Dissolved metals:** aluminum, arsenic, cadmium, cobalt, manganese, and zinc; and
  - **Total metals:** aluminum, cadmium, chromium, cobalt, copper, manganese, silver, vanadium, and zinc.
- **Accurate**: concentrations that were observed to be between the projected 5th and 95th percentile model predictions including:
  - **Ions and nutrients:** total dissolved solids, calcium, sulphate, and nitrate;
  - **Dissolved metals:** antimony, boron, chromium, iron, molybdenum and silver; and
  - **Total metals:** antimony, boron and molybdenum.

- **Under-predicted**: concentrations that were observed to be greater than the 95th percentile model predictions, including:
    - **Ions and nutrients:** magnesium, and nitrate;
    - **Dissolved metals:** copper and selenium; and
    - **Total metals:** arsenic and selenium.

Figure 4 provides examples of select constituents that were representative of the above categories. Observed data on these plots are represented by samples from the Springer Pit dewatering sump, as well as samples collected within the pit lake near the surface and bottom.

Sulphate and molybdenum were two constituents that were observed to be within the WQM projected concentration ranges (Figure 4). The good agreement indicates that model inputs were well characterized and that these constituents were not sensitive to the differences in water management described above.

Observed concentrations of total phosphorus and copper in Springer Pit were below the WQM projected ranges (Figure 4). There are several reasons why the model may be over-predicting concentrations, including:

- The model was developed to predict water quality conservatively; where uncertainty existed in model inputs, the inputs were selected to minimize the risk of under-prediction.
- Metal concentrations that are far below detection limits may be skewed upward by model inputs where half-detection limits were applied.
- Processes such as uptake of nutrients, precipitation of dissolved species, and adsorption and settling of particulate materials were not accounted for in the model.

Although these factors may lead to over-prediction of concentrations, the model is considered valid for the purpose of developing permit effluent limits because the limits are also derived such that acute guidelines and Metal Mining Effluent Regulations limits are met at end-of-pipe and chronic guidelines are met within an Initial Dilution Zone in the receiving environment. By excluding the process of setting of TSS and particulate metals in the pit lake, the limits applied to the discharge cover a range of conditions, including worst-case conditions with respect to settling. Therefore, deviations in model predictions from observed conditions in this category tend to promote the ultimate objective of the model, which is protection of end uses in the receiving environment.

Nitrate and total selenium were observed to be above the projected ranges in the WQM (Figure 5). (*Note that other under-predicted constituents such as magnesium and dissolved copper were only marginally above predicted ranges*). A review of the WQM input assumptions and actual mine conditions (e.g., water management implementation, ongoing water quality monitoring), identified the following reasons that could result in an under-prediction of these constituents:

- the actual mill restart time (August 4, 2015) occurred later than was assumed in the WQM (June 1, 2015);
- increases in selenium concentrations were observed in one of the mine site facilities (the Northwest Sump) draining to the Springer Pit, at consistently higher concentrations than measured during the period when the water quality model input for this facility was derived (Figure 5);
- some oxidation of stockpiled ores may have occurred during the year that the mine did not operate following the TSF breach (August 2014 to August 2015), which could have increased the mass load of constituents upon restart of milling;

- some water transfers among site facilities differed from those projected at the time of model development (due in part to the unusual climate conditions in 2015 as described above); and
- a later than anticipated discharge approval date resulted in dewatering of Springer Pit commencing on December 1, 2015 rather than on July 1, 2015.

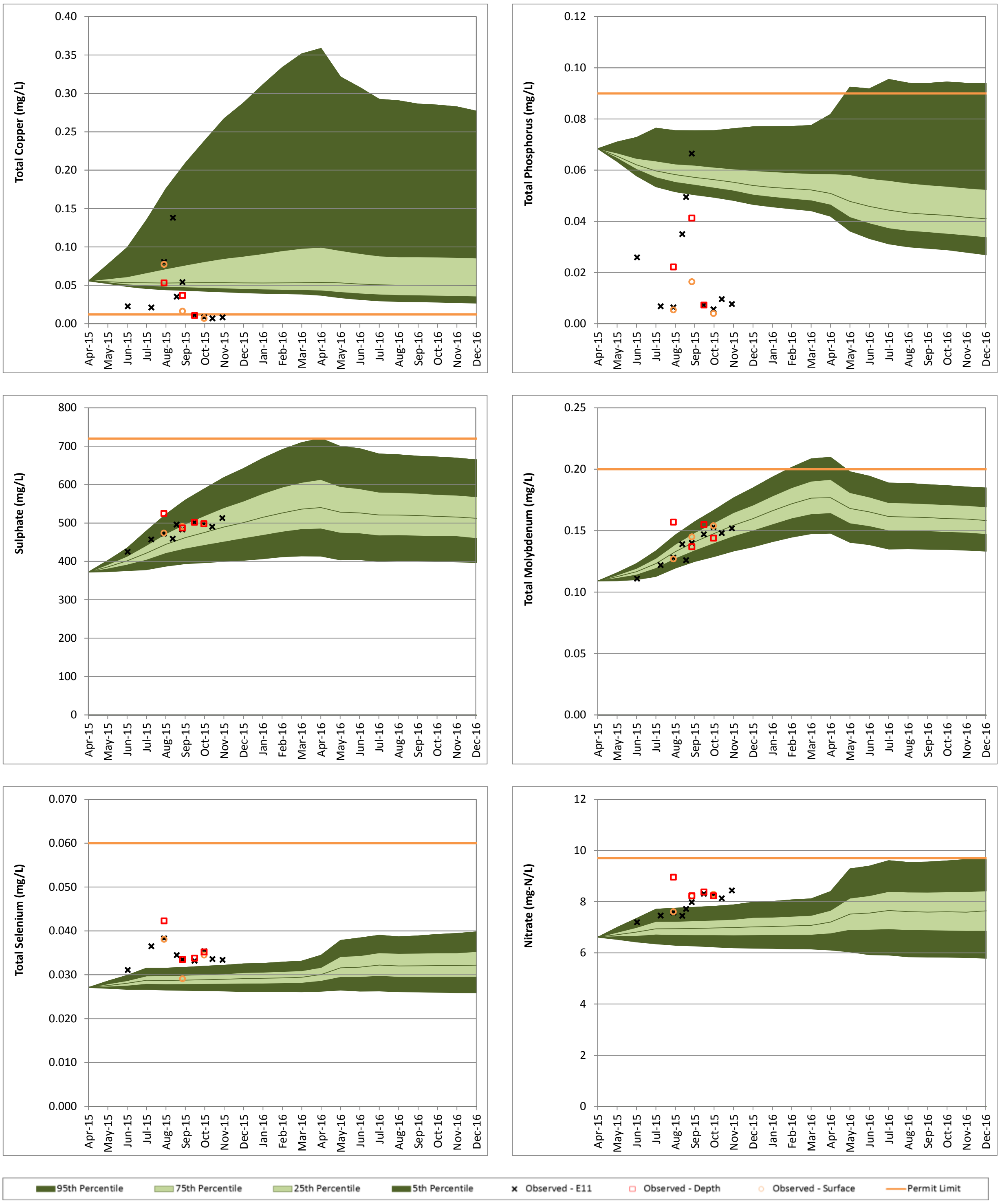
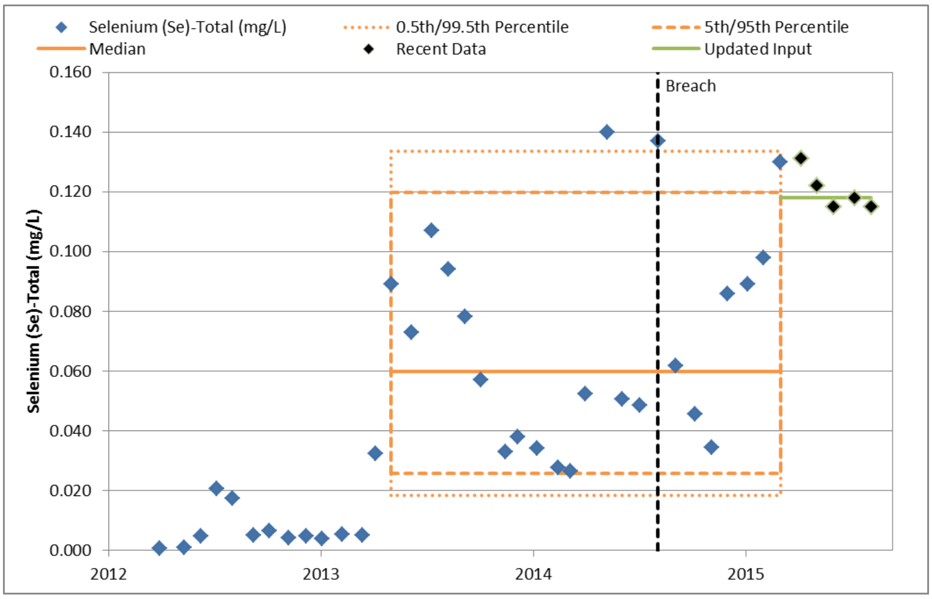


Figure 4: *Comparison of Observed Concentrations and Model Predictions for Select Constituents*



Note: Orange box indicates range of inputs used to derive inputs for model; green line shows mean of measurements after model predictions were generated.

Figure 5: *Monitored Total Selenium in the NW Sump and Water Quality Inputs Used.*

Model Refinements

After comparing observations to predictions and reviewing model inputs to identify the cause of any differences, the WBM and WQM were updated to improve future predictive ability. The main update was to align the water balance with measured flows on site, and the second was to update the water quality input for the Norwest Sump that collects drainage from the Temporary Potentially Acid Generating (PAG) Stockpile (in particular for selenium). Runoff for the period after model predictions were generated was observed to have higher concentrations (mean shown as the green line in Figure 5) than the previous period (shown in the orange box in Figure 5), which was originally used to derive inputs. Model predictions generated by re-simulating the same time period with these updates are shown in Figure 6. The update improved the comparison of measured values against model predictions (which are now hindcasts) for constituents that were under-predicted, but did not appreciably change those that were over-predicted. In the updated predictions, the uncertainty bounds were narrowed for most constituents.

Total selenium concentrations measured in the pit lake peaked in mid-August (Figures 4) and subsequently declined. Although the peak measured concentration of total selenium remained above the maximum of the updated model predictions, measured concentrations have decreased to be within the 5th and 95th percentile predictions, following this peak (Figure 6).

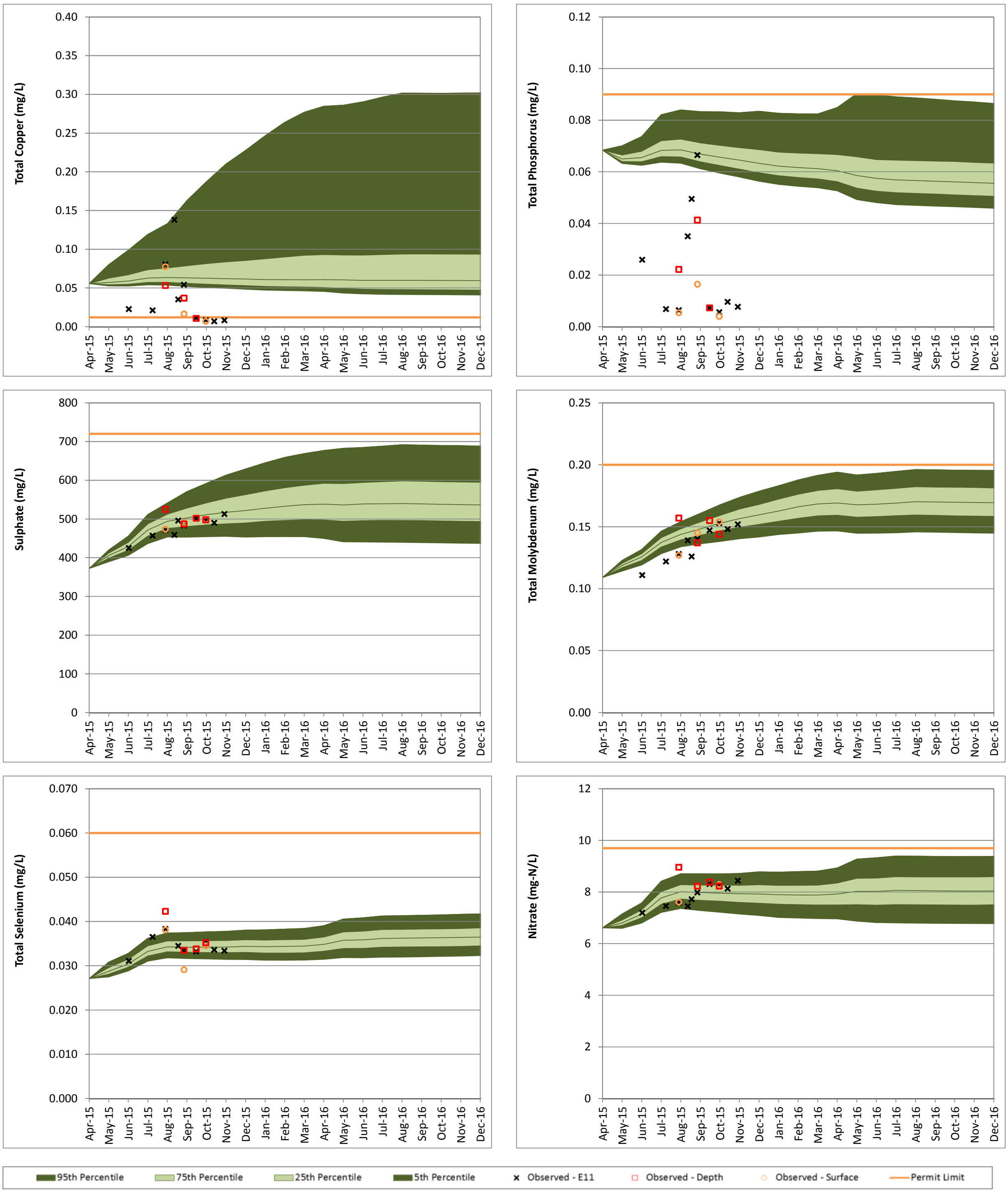


Figure 6: *Comparison of Observed Concentrations and Updated Model Predictions for Select Constituents*

Conclusions

A probabilistic WBM and WQM model were developed to predict water quantity and quality in the Springer Pit lake during restricted operations at the mine (contact water and tailings stored in the pit) [7]. At present (May 2016), the pit lake has been filled to approximately 75% of its total capacity. Monitoring of the pit lake elevations and chemistry have been ongoing and the empirical data provided an opportunity to validate model predictions.

Based on observed accumulations in Springer Pit, the WBM appears to be over-predicting water volumes. Although predictions have remained below average, the simulated water volumes inflows to Springer Pit since May 2015 have consistently exceeded the observed volumes. In light of these results, the model calibration parameters (runoff coefficients and base flows) will be reviewed and consideration given to atypical weather occurring during the validation period to improve model predictions. The model will be updated regularly to observed water levels for ongoing water management.

Based on a comparison of modelled to monitored concentrations in Springer Pit, most constituent concentrations were within or below predicted ranges. The model is presently being updated with geochemical source terms and a longer time frame of operations, and the differences identified during the model validation will be considered in the long-term update.

As noted in [2, 3], "two of the biggest problems with modern geochemical pit lake predictions are the challenge for model reviewers to independently repeat and check calculations, and the lack of understanding of the uncertainty associated with predictions." This study addressed both of these problems and can be used to refine model inputs before extending the model for the next stages of mining. This is consistent with the recommendation provided in [4], that is "if the lake is in the filling stage, compare model predictions with observed data…validate and refine inputs to the model whenever information becomes available." Moreover, it provides a counterpoint to critiques of pit lake modelling [5].

In general, the model is deemed to have performed well and achieved its objectives, particularly in light of challenges generally associated with pit lake models [3]. Three key factors that have led to a failure to predict mine waters elsewhere [6], particularly at copper mines, were favourable at Mount Polley: the predominance of non-acid generating material on site; the high quantity and quality of operational mine water data; and, the mine's adherence to the water management plan.

Water quantity and water quality models are a valuable tool that are commonly used to evaluate site effluent water quality and volumes for several purposes, including deriving mine effluent criteria and informing water treatment plant design. The validation of the Mount Polley WBM and WQM as part of the current study highlights the need to monitor, review and refine models after predictions are made to improve predictive ability when the model is applied to future iterations.

Acknowledgements

The authors wish to thank Mount Polley Mining Corporation for funding the model development and model validation. The authors appreciate comments by Lorax Environmental Services, who provided third-party review of the models on behalf of the BC Ministry of Environment, which prompted the model validation.

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Causes of an distinct metalimnic oxygen gradient in the pit lake Senftenberger See in summer 2013 as a case study

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Abstract

The lake Senftenberger See is a pit lake in the Lusatian lignite mining area in Germany and originated between 1967 and 1972 in the former lignite open cast mine Niemtsch. In summer 2013, a distinct oxygen gradient in the metalimnion with the oxygen concentration sharply decreased to 0 mg/L and in succession a high mortality rate in a fish farm was observed. At the same time, the Koschen channel with a lock connecting the nearby pit lake Geierswalder See started operation and increased the input of ferrous iron. In June 2013, a flood of the river Schwarze Elster passed through the lake.

The investigation of the causes of the observed distinct oxygen gradient was based on a systems analysis approach. All available meteorological, hydrological, limnological, hydrochemical, and biological data were analysed. A dynamic water balance model and a stratification model for the lake Senftenberger See were assembled. The stratification model was created as a 2D-model based on the model software CE-QUAL-W2 and was calibrated on the basis of measured temperature profiles.

The thermal stratification behaviour of the lake Senftenberger See was simulated for a time series. The effect of specific water balance variables on the water quality of the lake Senftenberger See was quantified by modeling the migration of a conservative tracer. The investigation results showed that the meteorological conditions in the year 2013 caused the distinct temperature and oxygen gradient in the metalimnion. The channel between the lake Geierswalder See and the lake Senftenberger See as well as the flood in June 2013 could be excluded as a cause. The long-term monitoring shows that the distinct metalimnic oxygen gradient was not a singular event in summer 2013. Similar conditions were observed in the lake Senftenberger See in previous years and in 2013 in other pit lakes, too.

It has been shown that the 2-dimensional limnophysical modeling with CE-QUAL-W2 is well suited to simulate the thermal stratification and the spatial migration of solutes in highly structured pit lakes. The simulated stratification of the Senftenberger See was in good accordance with the measured data. The model thus represents a good base for the further examination of additional water quality problems and its application to other pit lakes.

Key words: pit lake, metalimnic oxygen gradient, limnophysical modelling, solute transport modelling

1 Basics

The lake Senftenberger See is a pit lake in the Lusatian lignite mining area in Germany (fig. 1). The lake originated between 1967 and 1972 in the former lignite open cast mine Niemtsch. The Senftenberger See is a positive example for the post mining revitalization of the landscape and multivalent usage of a pit lake. On the lake Senftenberger See nature and landscape protection areas, sport and tourism as well as low water management, flood protection and fishery exist in parallel nearly without conflicts.

At the highest water level of +99.25 m NHN the lake Senftenberger See has a surface area of nearly 12 square kilometers and a total volume of 80 million m³. Thereof, around 16 million m³ are usable for water management. The lake Senftenberger See is divided into four deep basins: West, North, East and South (fig. 2). The first three basins are connected by shallow areas. The south basin, however, is connected only by a narrow and flat channel with the rest of the lake and largely hydraulically separated. In the middle of the lake Senftenberger See is an island with a large shallow bay. At the highest water level the lake is in average 6.2 meters deep and the maximum water depth is approximately 25 meters.

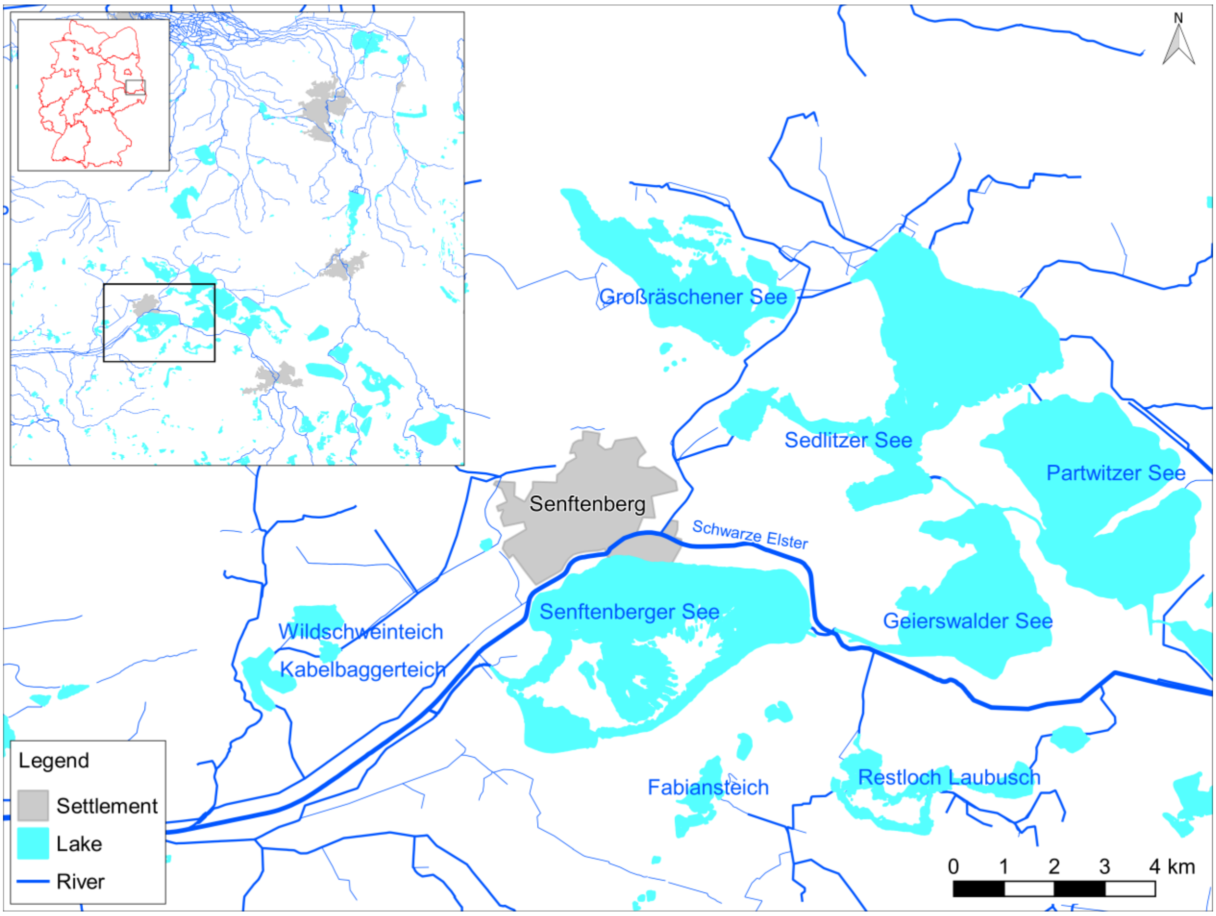

Figure 1: *Location of the lake Senftenberger See*

The lake Senftenberger See is located in the bypass of the river Schwarze Elster. The inlet from the river Schwarze Elster is located in the east and the outlet in the west (fig. 1). In July 2013, a traversable channel with a lock, the so called Koschen channel, started operation. The channel connects the nearby pit lake Geierswalder See with the lake Senftenberger See and increases the water inflow to the lake Senftenberger See.

The reservoir of the lake Senftenberger See is usually filled during the hydrological winter season (November to April) and discharged over the summer season. The water surface level of the lake Senftenberger See oscillates between +98 m NHN and +99 m NHN. The water level of +99 m NHN is only exceeded during flood events. In average of the years 1997 to 2012 approximately 0.80 m^3/s discharged into the lake Senftenberger See from the river Schwarze Elster and 0.79 m^3/s discharged back into the river Schwarze Elster. The average atmospheric water balance is with -0.02 m^3/s in deficit. Between June and November 2013 an average flux of 0.15 m^3/s discharged from the Koschen channel. Thereof a flux of approximately 0.05 m^3/s are originated from the lock operation itself and approximately 0.10 m^3/s from the lock bypass.

Since there were no data on the groundwater balance of the lake Senftenberger See, the net groundwater balance had to be determined as a residual of the sea water balance. By the year 2010, the Senftenberger See had a deficit in groundwater balance with a net loss of 0.1 m^3/s. Since then, the groundwater balance is excessive. For the year 2013 a net surplus of 0.3 m^3/s was determined. The change in the groundwater balance is a result of regional rise of the groundwater level subsequent to the restoration of former mining areas. The direct groundwater inflow to the Koschen channel is about 0.05 m^3/s. The average water balance of the lake Senftenberger See for the years 1997 to 2012 and in comparison the year 2013 is shown schematically in fig. 3.

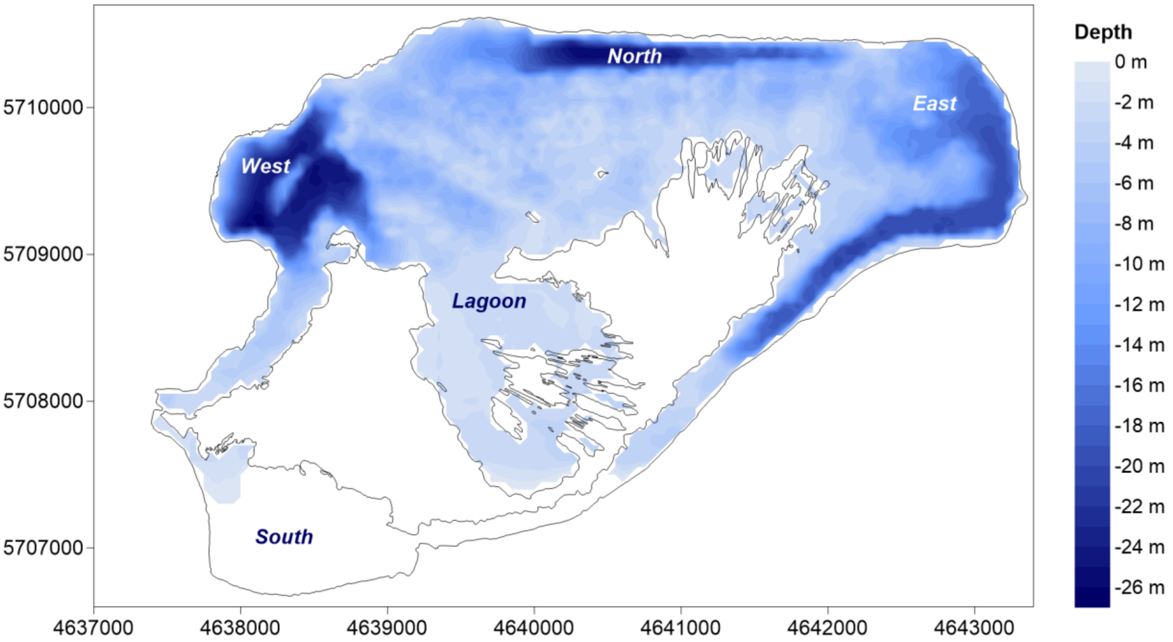

Figure 2: *Water depths in the lake Senftenberger See at a water level of +99.25 mNHN (There is no bathymetry data available for the south basin)*

In recent years, the lake Senftenberger See was only event-driven limnologically, hydrochemically and biologically investigated. In the hypolimnia of the deep basins oxygen-free conditions were recorded regularly in the summer months. Very low oxygen concentrations were also measured in the metalimnion of the lake repeatedly. This distinct oxygen gradient in the metalimnion is also observed in other pit lakes of the Lusatian area with similar limnological conditions. These lakes are characterized by a small hypolimnion volume and a significant groundwater influence.

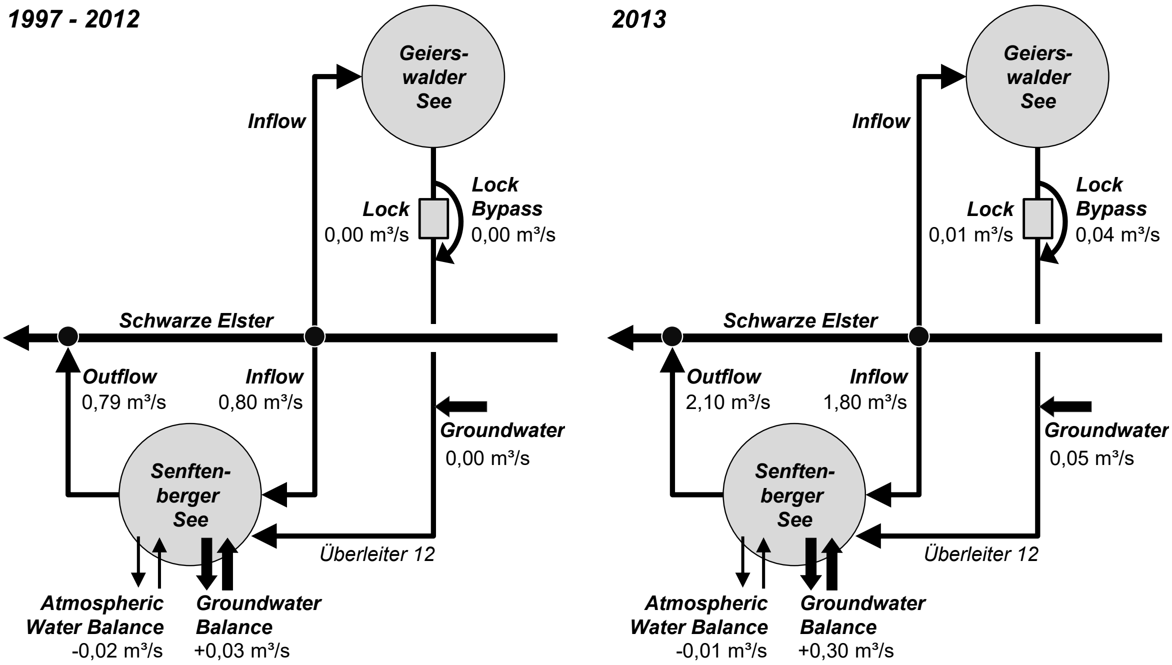

Figure 3: *Average water balance of the Senftenberger See for the years 1997 to 2012 (left) compared with the year 2013 (right)*

The groundwater that flows to the lake Senftenberger See from the surrounding former mining area has iron concentrations of 35 to 140 mg/L. The effects of iron influx are yet harmless and invisible. The water in the Koschen channel has iron concentrations between 1 and 5 mg/L. The oxidized iron settles as iron hydroxide along the channel and has a negative effect on the appearance.

2 Incidents in summer 2013

In summer 2013, a high mortality rate in a fish farm in the west basin of the lake Senftenberger See was observed. Subsequent measurements showed a distinct oxygen gradient in the metalimnion of the lake Senftenberger See, wherein the oxygen concentration sharply decreased to 0 mg/L. At the same time, the lock in the Koschen channel started operation. So the distinct metalimnic oxygen gradient and the high mortality rate in a fish farm have been associated with the increased iron input from the channel. Therefore the lock operations and the lock bypass were stopped by the authorities until the causes of the metalimnic oxygen gradient in summer 2013 are clarified.

3 Working hypothesis

For the metalimnic oxygen gradient in the lake Senftenberger See in early summer 2013 and the subsequent loss of fish, the following six events or their combination came into consideration.

1. The start of the regular lock operations in the Koschen channel.
2. The discharge of water from the Geierswalder See over the lock bypass.
3. The retention of a considerable amount of the flood in June 2013.
4. The stable thermal stratification of the lake under the influence of an unusually strong increase in air temperatures in spring.
5. The groundwater influx of ferrous iron into the Koschen channel and subsequently in the lake Senftenberger See.
6. The increasing groundwater influx of ferrous iron in the lake Senftenberger See from the surrounding former mining area.

4 Problem analyses

A systems analysis approach was used to investigate the causes for the observed distinct metalimnic oxygen gradient. All available meteorological, hydrological, limnological, hydro-chemical and biological data were collected and analysed.

The analysis of an 18-year meteorological data series showed, that the average meteorological conditions in the year 2013 were widely common. The weather of the year 2013 was characterized by a very cold March, a fast increase of air temperature in April, a stable warm weather period in the spring and six hot weeks during the summer from late June to early August.

In average of the year 2013 approximately 1.80 m³/s discharged from the river Schwarze Elster into the lake Senftenberger See and 2.1 m³/s discharged back into the river Schwarze Elster. In order to avert a flood in June 2013, about 2.9 million m³ were retained in the lake Senftenberger See within four days. From the Koschen channel on average 0.03 m³/s were discharged into the lake Senftenberger See. The net groundwater inflow was determined with 0.35 m³/s. The atmospheric water balance over the surface of the lake Senftenberger See was slightly in excess in the year 2013 (fig. 4).

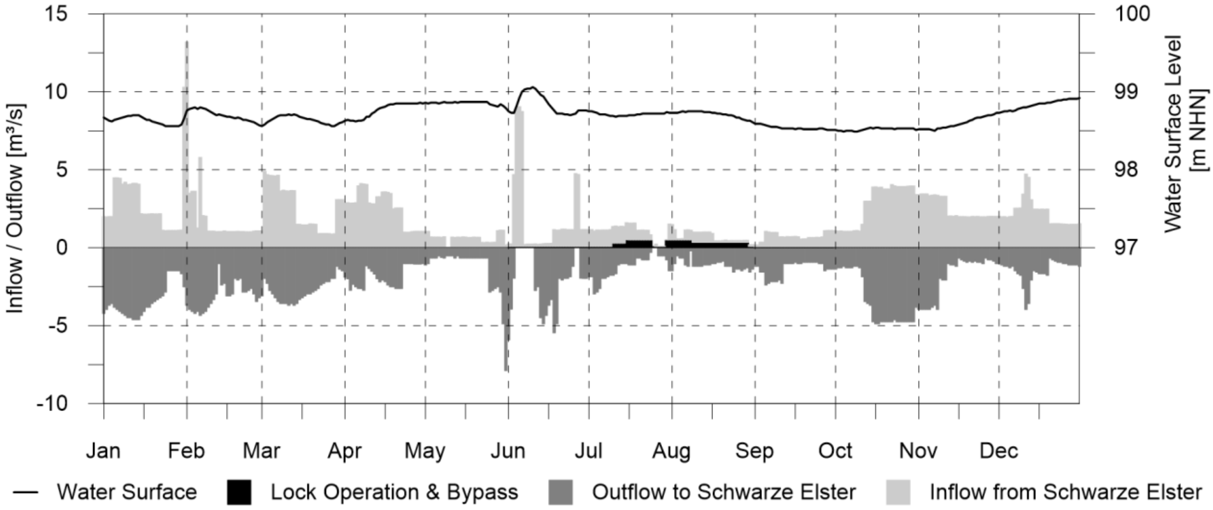

Figure 4: *Surface water balance of the Senftenberger See in the year 2013*

On average of the year 2013 only 3 % of the overall inflow to the lake Senftenberger See originates from the lock operation and the lock bypass in the Koschen channel and from the seepage of groundwater into the channel (fig. 4). If a representative iron concentration is assigned to every inflow component, an iron inflow balance can be calculated (see tab. 1). Accordingly, at least 46 % of the total iron input into the lake Senftenberger See comes from the seepage of groundwater and about 42 % from the discharge of the river Schwarze Elster. The iron input into the Koschen channel is around 157 kg/d. The vast majority of the iron already deposits as iron hydroxide along the Koschen channel, so that only a small fraction reaches the Senftenberger See. This iron is also highly oxidized and thus has a very low respiration potential.

Table 1: *Balance of the iron influxes into the lake Senftenberger See in the year 2013*

source	mean influx	representative iron concentration	mean iron load	
	m³/s	mg/L	kg/d	prop.
Net groundwater inflow into the Senftenberger See	> 0,300	25 2)	> 648	46,6 %
discharge from the Schwarze Elster	(1,800)		586 3)	42,1 %
groundwater inflow to the Koschen channel	0,050	36 1)	156	11,2 %
lock operation and bypass in the Koschen channel	0,050	0,5	1	0,1 %
Sum			> 1.391	100,0 %

1, 2) Averaged iron concentration of the groundwater in the specific inflow area

3) Mean annual iron load calculated by reference date measurements

The vertical temperature profiles for July, August and September 2013 showed a distinct temperature gradient between the epilimnion and the hypolimnion in the east, west and north basin and therefore a very stable thermal stratification of the lake Senftenberger See. The vertical profiles also showed a distinct oxygen gradient in the metalimnion, whereat in the north and west basins the oxygen saturation declined to 0 % below the thermocline (fig. 5). In contrast the pH-value, the turbidity and the electrical conductivity shows no significant vertical gradients.

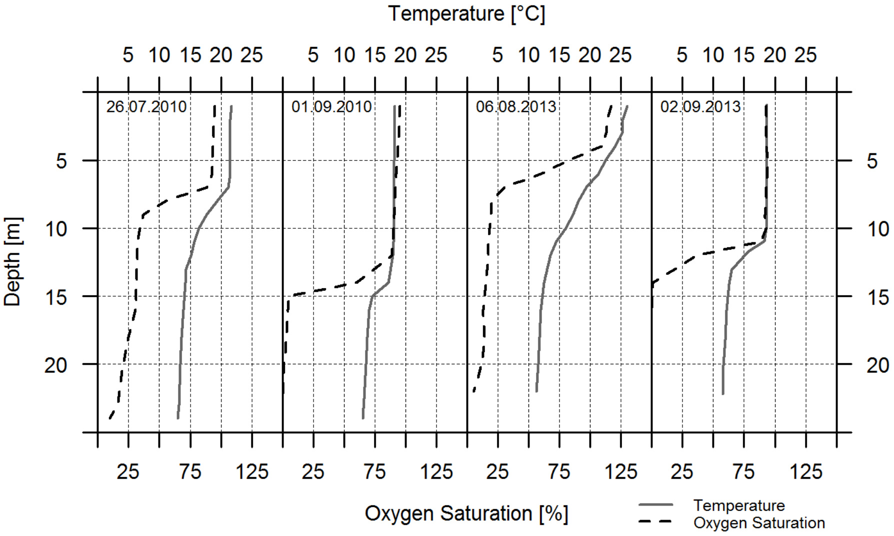

Figure 5: *Vertical profiles of water temperature and oxygen saturation in the northern sub-basin of the Senftenberger See*

5 A model for the lake Senftenberger See

5.1 Model assembly

For a more detailed analysis of the processes in the lake Senftenberger See and their interaction a two-dimensional thermal stratification model was assembled with the software CE-QUAL-W2. With this approach, the highly structured bathymetry of the lake Senftenberger See could be adequately taken into account. The developed stratification model consists of 15 longitudinal segments. The vertical discretization between the levels +99.5 and +97.5 m NHN was carried out in 0.1 meter intervals and below +97.5 m NHN in 0.5 meter increments. At a maximum water level of +99.0 m NHN and a maximum depth of +74 m NHN, the model has 62 vertical layers.

5.2 Model calibration

The stratification model was calibrated on the basis of measured temperature profiles (fig. 6). With the calibrated model the thermal stratification of the lake Senftenberger See was simulated for an 18-year time series (years 1997 to 2014) of meteorological and hydrological data. The model results showed, that the three relevant basins east, north and west have different vertical temperature gradients and circulation characteristics, although they are connected in the epilimnia. Because of the extended wind exposure of the east-west aligned north basin, the epilimnion and in particular the metalimnion are more spacious as in the east and west basin. The autumnal circulation reaches the ground in the north basin on average one month earlier than in the basin east. The full circulation in the basin west is delayed by one more month.

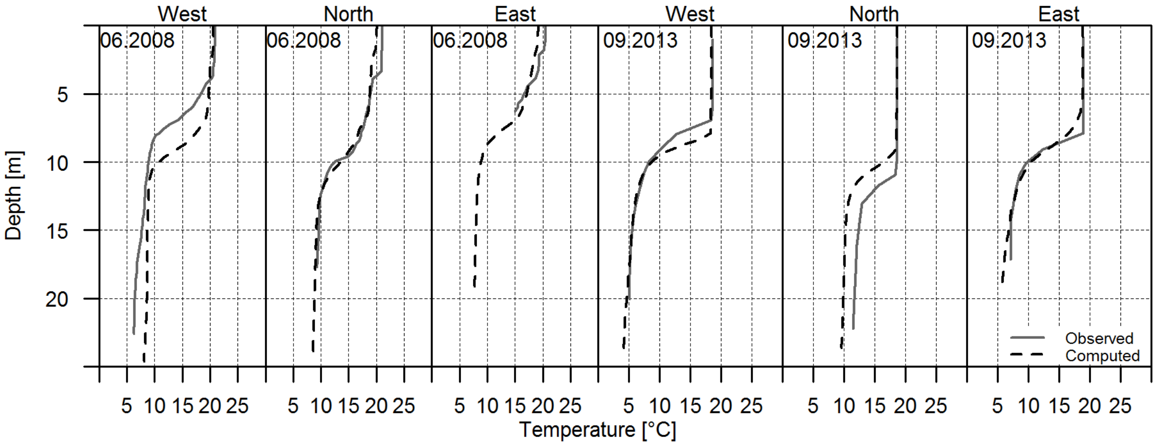

Figure 6: Comparison of the observed and modelled temperature profiles in the Senftenberger See

5.3 Model application

Model simulations using a non-reactive migration approach were run to understand the effects of selected boundary conditions (groundwater, flood from the river Schwarze Elster and the discharge from the Koschen channel) on the temporal and spatial changes of the water quality in the lake Senftenberger See. For that, each boundary condition was assigned a fictitious non-reactive solute concentration of 100. The water temperature of the selected inflow was set according to its natural conditions. The stratification of the boundary condition inflow depends on the water temperature.

5.4 Model results

By using a fictitious non-reactive solute concentration for the boundary condition inflow, the spatial and temporal spread of this inflow in the lake Senftenberger See under the hydrological, meteorological and limnological conditions in summer 2013 could be reproduced.

The inflow from the flood in June 2013 briefly reaches a maximal volume share of 15 % in the sub-basin east (fig. 7). Within 10 days the flood inflow reaches the sub-basin west with a maximum volume share of 8 %. The flood inflow in June 2013 had only a temporary effect on the lake Senftenberger See. On complete lake overturn in autumn, the volume fraction of the flood in the entire lake declined to less than 3 %. The nutrient influx of the flood is unknown. Due to the timing of the events and the high dilution in the lake the nutrient influx of the flood in June 2013 comes not in consideration as the cause of the metalimnic oxygen gradient that occurred in the early summer.

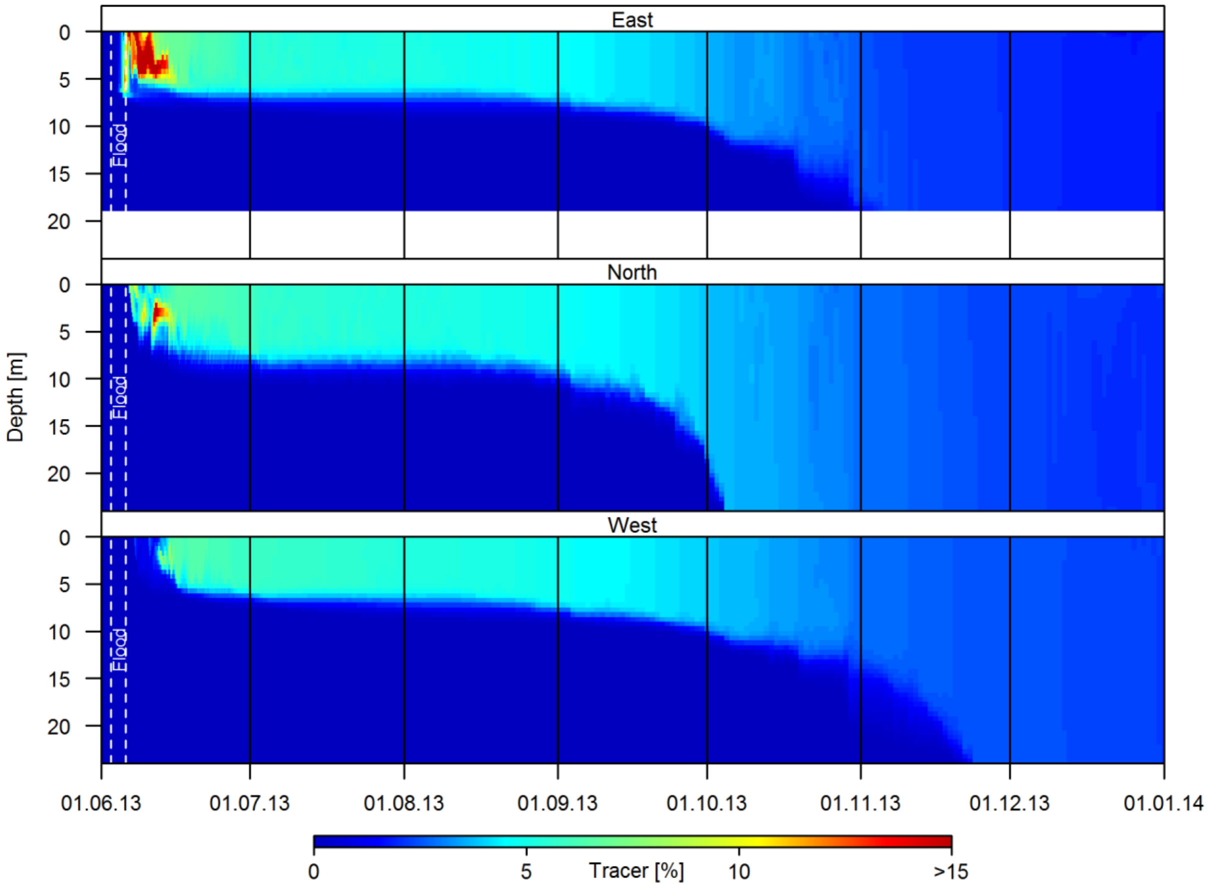

Figure 7: *The impact of the flood in June 2013 on the lake Senftenberger See illustrated by the spread of a non-reactive tracer (the color scale shows the proportion of river water in the three main basin of the lake Senftenberger See)*

The seepage of groundwater into the lake Senftenberger See comes from the surrounding former mining area and therefore is rich in ferrous iron. The groundwater exfiltrates due to the geohydraulic conditions mainly into the east sub-basin of the lake Senftenberger See. It mixes due to water temperature preferably in the metalimnion and could gain there a volume share of more than 25 %. In the hypolimnion the groundwater has an average volume share of 15 %. Due the distinct vertical temperature gradients in summer 2013 and the thereby inhibited vertical water exchange, the groundwater accumulated in the hypolimnion of all sub-basins to volume fractions of 20 % to 25 %. The iron concentration in the groundwater ranges from 35 to 140 mg/L. To fully oxidize this iron, between 5 to 20 mg/L oxygen is required. The accounting shows that the groundwater influx has a large fraction on the overall oxygen consumption potential in the lake Senftenberger See and is a possible cause of the metalimnic oxygen gradient.

For a short period of time the iron contaminated discharge from the Koschen channel gained a maximal volume share of 7 % in the sub-basin east. The discharge reaches the sub-basin west with a one month delay and gained there a maximum volume share of 4 % in September 2013. This effect is occurred three months after the high mortality rate in the fish farm and therefore could not be the cause of the distinct metalimnic oxygen gradient. The groundwater infiltrating in the channel of the Koschen channel has a ferrous iron concentration of less than 35 mg/L and therewith an oxygen consumption potential of 5 mg/L. At a maximum volume fraction of 3 % the potential oxygen consumption caused by the groundwater inflow is less than 0,15 mg/L. From a hydrochemical point of view, this low consumption potential could not be the cause of the metalimnic oxygen gradient. Furthermore the discharge from the Koschen channel mixes due to water temperature in the epilimnion of the sub-basins east and north and is oxidized there safely.

6 Interpretation

The analysis of the available long-term data showed, that a high oxygen consumption in the hypolimnion of mining pit lakes could cause a subsequent oxygen gradient in the metaliminion. Normally the oxygen concentration in the pit lakes does not drop below 4 mg/L (oxygen threshold value for fish). However, in summer 2013 the oxygen concentration undercut this limit in combination with the typical oxygen gradient in the metalimnion. For the first time, a water user was directly affected by such an event.

The measurement of the lakes stratification first started after the notification of the high mortality rate in the fish farm, so the event is not well documented. The actual public perception is dominated by the large-scale clogging of river waterbodies by iron hydroxide sediments as a result of the regional groundwater level rise after the closure of the nearby lignite mines. Therefore, a causal connection between the high mortality rate in the fish farm in the sub-basin west and the discharge from the Koschen channel into the sub-basin east was assumed.

Even if the oxygen consumption in the meta- and hypolimnion of the lake Senftenberger See is only caused by the oxidation of the iron input, the operation and bypass of the lock in the Koschen channel could be safely ruled out as a cause of the distinct metalimnic oxygen gradient in summer 2013. The discharge from the Koschen channel has an average share of 3 % of the total inflow. In addition, the groundwater exfiltration into the Koschen channel accounts for only around 11 % of the total iron input into the lake Senftenberger See. Furthermore, most of the inputted iron oxidizes and settles as iron hydroxide along the channel, so that only a small fraction of the inputted iron reaches the sub-basin east of the lake Senftenberger See at all. Compared to that, the iron input with the discharge from the river Schwarze Elster and the groundwater is three to four times as high (see tab. 1).

The modelling of the thermal stratification also showed that the discharge from the Koschen channel as well as the discharge from the river Schwarze Elster only mixes in the epilimnion of the sub-basin east, where a sufficient amount of oxygen is available for the iron oxidation. In contrast the groundwater due the water temperature preferably mixes in the metalimion of the sub-basins and has thus a significant share at the metalimnic oxygen consumption in the Senftenberger See.

A special weather-related characteristic of the year 2013 is the rapid warming of the lake Senftenberger See and the fast emergence of the epilimnion in the spring in succession of an extreme air temperature rise in combination with poor wind conditions. These conditions led to an exceptionally distinct temperature, oxygen and density gradient between the epilimnion and the hypolimnion.

The extraordinarily density difference between the epilimnion and the hypolimnion led to an accumulation of easily degradable products of primary production and a high intensity of heterotrophic processes in the metalimnion. This caused an extremely distinct gradient of oxygen concentration in the metalimnion. Furthermore, this effect benefited from the adverse limnological conditions in the lake Senftenberger See:

- the special bathymetry of the lake Senftenberger See with an adverse proportion of the epilimnia and hypolimnia volumes
- the increased discharge from the river Schwarze Elster and
- the associated increased nutrient input.

The evidence obtained point to a combination of several causes for the formation of the distinct metalimnic oxygen gradient in early summer 2013. The decisive factors were mainly the increasing ferrous iron input with the groundwater and the special meteorological conditions in 2013. The discharge from the Koschen channel could be definitely ruled out as the cause of the metalimnic oxygen gradient due the low iron load and the mixing into the epilimnion.

Acknowledgements

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Biogeochemical processes controlling density stratification in an iron-meromictic lake

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Abstract

In many mining regions on earth, pit lakes have been indentified where a permanent stratification creates an anoxic reductive deep water layer, the monimolimnion, with increased concentrations of dissolved gases and undesired ionic substances, e.g. heavy metals. We investigate one of the processes responsible for permanent stratification formation, the cycle of precipitation and re-dissolution of iron species due to changing redox conditions in different water layers. Hence, evaluating the relevant processes in these so called iron-meromictic lakes on their impact on density stratification helps to predict future water quality and to forecast potential turnovers.

We present an approach of quantifying the impact of iron-redox reactions on lake stability of a small well documented iron meromictic Lake called *Waldsee* in the lower Lusatian Mining district by summing up in-situ measured vertical electrical conductivity profiles. We used the derived “summed conductivity” as a measure reflecting the amount and seasonal mass-balance dynamics of electro-active substances in the lake. Furthermore we conducted a unique aeration experiment to physically reproduce the assumed chemical reactions in the lake.

Our findings showed that calculating “summed conductivity” revealed a seasonal oscillation in phase with the chemocline depth which indicates the transition zone between the two water layers. However, induced stratification was sustained throughout the observation period of four years. Mass-balance calculations revealed that the internal iron redox cycle alone was able to maintain the conductivity gradient. However, an inflow of significant amounts of ion rich groundwater seemed to be needed for the recovery of summed conductivity during times of rising chemocline in Waldsee. Aeration of deep water from the lake by the experiment lead to a change in water properties close to surface water layer properties of *Waldsee* and hence confirmed the occurrence of internal geochemical processes: iron removal, pH depression, DOC removal and CO_2 loss.

Key words: physical limnology; meromixis; mining lake; chemocline; column experiment

Introduction

Mining lakes, showing meromictic which means that a part of the lake (called monimolimnion) is not involved in the seasonal overturns of the lake (Boehrer and Schultze 2008) could be identified in several metal or lignite mining regions of the world, such the Iberian Pyrite Belt, Spain (e.g. Lake San Telmo (Cánovas et al. 2012) and Lake Conception (Santofimia and López-Pamo 2013)), Vancouver Island, Canada (Island Copper Mine pit lake (Wilton et al. 1998)), the Central German Mining District (e.g. Lake Wallendorfer See and Lake Rassnitzer See (Boehrer et al. 2014) and the Lower Lusatian Mining District, Germany (e.g. Lake Moritzteich (von Rohden et al. 2009)).Typically meromictic conditions in mining lakes are sustained by a continuous inflow of denser groundwater and surface water via streams or precipitation and the very low diffusion rate of substances via the zone of sharp gradients, the chemoline (Rohden and Ilmberger 2001). In some cases, stratification has even been implemented to restrict the vertical transport (Island Copper Mine pit lake in Canada, (Wilton et al. 1998)).

The volume ratio between the monimolimnion and the mixolimnion can show seasonal changes due to chemocline erosion by mixolimnion turnover (e.g. (von Rohden et al. 2009)) or by increased surface runoff, whereas increased groundwater inflow and higher surface evaporation (e.g. (Santofimia and

López-Pamo 2013)) as well as diffusive processes are able to cause a upward movement of the chemocline. Additionally chemical reactions such as trans-chemocline transport of iron species are able to sustain meromixis in mining lakes (Boehrer et al. 2009).

We use easily measurable vertical profiles of in-situ electrical conductivity as a quantitative bulk measure of solutes. similar to calculating salinity from electrical conductivity measurements in oceanography (e.g. Fofonoff and Millard (1983)). We sum up electrical conductivity over the vertical profile of *Waldsee* and use the derived “summed conductivity” as a measure for the amount of solutes within a pit lake, and give an approximate rough quantitative estimate for the re-dissolution of precipitated iron. Furthermore a lab experiment was conducted to physically reproduce the assumed chemical reactions in the lake in order to get evidence about the origin of the two different water types in the lake and the production of mixolimnetic water from monimolimnetic waters during periods of vertical chemocline propagation. For more detail on the study see Nixdorf and Boehrer (2015).

Methods

Site Description

Lake Waldsee is a shallow pit lake which has been formed by the collapse of underground mining structures after cessation of mining activities in 1948 (Schossig and Kulke 2006) (fig.1a). The lake has an area of about 2400 m² and fills a volume of 6500 m³. The maximum water depth is 4.7 m (Boehrer et al. 2009). *Waldsee* has no surface water inflow and is mainly supplied by local groundwater (von Rohden et al. 2009).

The physico-chemical profiles of *Waldsee* show a strong discrepancy in water parameters between the upper 1-1.5 m thick mixolimnic water layer and the monimolimnion below which additionally vary over the seasons (fig. 1b).

The mixolimnion is oxygenated and has an electrical conductivity which is approximately half of the related values for the anoxic monimolimnion (0.9-1.1 mS/cm). Due to the absent of large differences in pH value (Diesing and Boehrer 2010) this gradient can be mainly related to gradients in the concentrations of ferrous iron and bicarbonate (Dietz et al. 2012). Constituent concentration measurements in the mixolimnion and the monimolimnion have shown a difference in ferrous iron concentration of about 150 mg/l and in bicarbonate concentration of about 300-400 mg/l between both water sections (Boehrer et al. 2009).

The depth of the chemocline, which can be marked as the point of inflection of the κ_{25} conductivity profiles (figure 1b), varies with an amplitude up to 1 m due to seasonal changes. The lowering of the chemocline during the warm season is caused by wind driven nocturnal mixolimnic convection currents. On the other hand in winter, weakened erosive forces and significant net groundwater inflow lead to an increase of the monimolimnic water (von Rohden et al. 2009).

Additionally the density driven stratification of the two different water sections is maintained and stabilized by an internal iron redox cycle (Boehrer et al. 2009). The zone of iron hydroxide production is traceable by its increase in turbidity and is located slightly below the current chemocline height.

It is proposed that internal, trans-chemocline transport of iron species by oxidation, precipitation and re-dissolution, in combination with diffusive CO2 loss and regeneration, both triggered by changes in chemocline height, are able to maintain the density gradients between the two water layers and inhibit a complete mixing of this shallow lake (Boehrer et al. 2009).

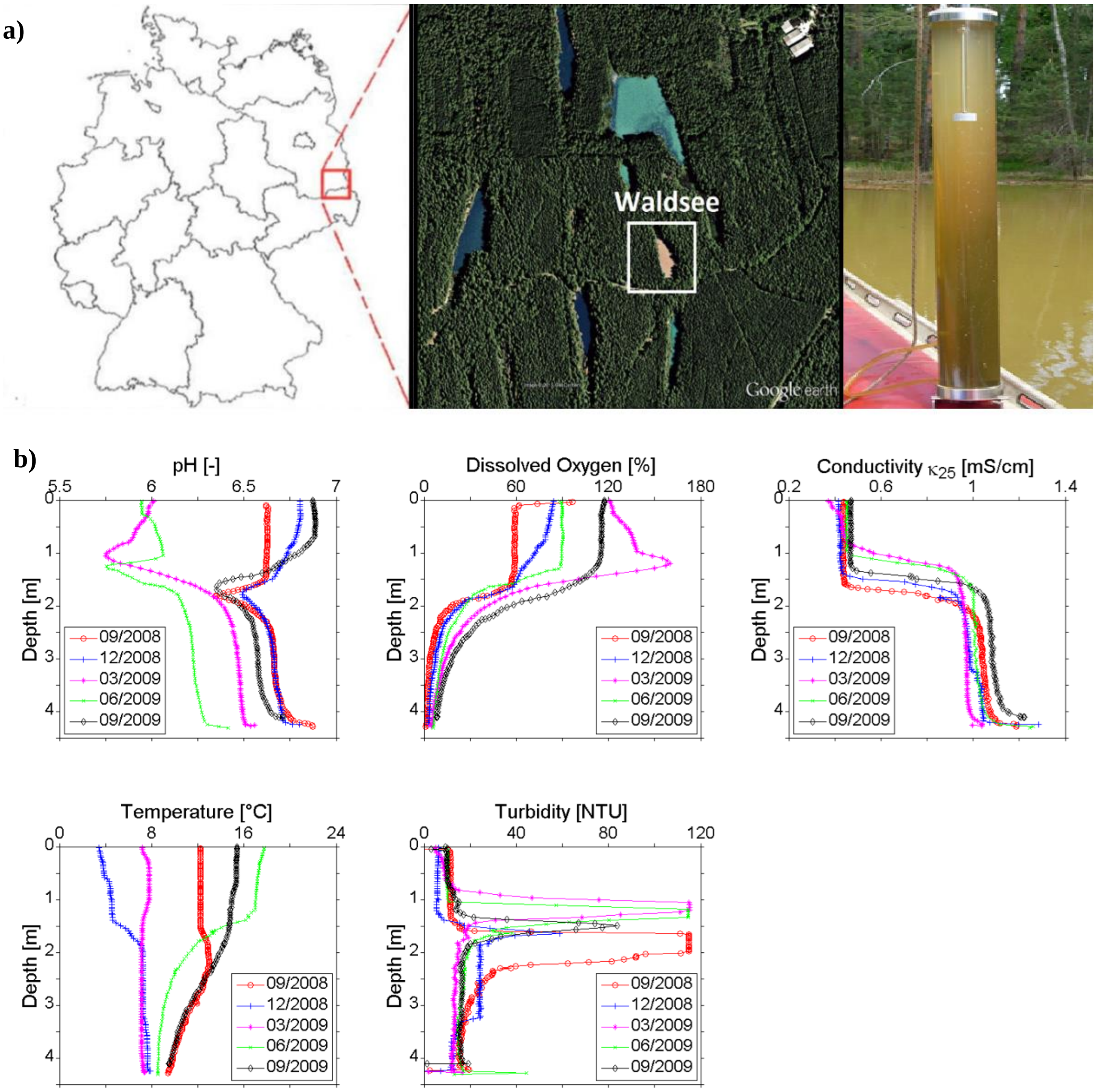

Figure 1: *a) from left to right: Location of the study site within Germany and within the local mining district, water sample containing both mixolimnion (yellowish color) and monimolimnion (darker colored) water. b) Hydrochemical profiles in Waldsee between 09/2008 and 09/2009 (from Nixdorf and Boehrer, 2015)*

Measurements and experimental set-up

45 monthly field measurements have been conducted in *Waldsee* between July 2006 and April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical conductivity (κ_{25}) were collected in *Waldsee* with a sampling rate between 1 and 4 Hz.

On May 18th 2011, mixolimnion and monimolimnion water were collected for chemical analysis in the laboratory including the determination of carbon (DOC; TIC, TOC) and iron species (ferrous and ferric iron) concentration.

For the column experiment, a 5 m high bluish-transparent PVC-column with an outer diameter of 20 cm and a wall thickness of 0.5 cm was installed and fastened at the technical hangar of UFZ Magdeburg. Prior to filling, the column was flushed with nitrogen gas to avoid initial oxidation of ferrous iron. The column was subsequently filled with 130 L of previously sampled monimolimnetic lake water to reproduce the maximum water depth of 4.7 m in *Waldsee*. We implemented an initial thermal stratification of the water and covered the column by PE-containing madrassas to prevent vertical circulation at the beginning of the experiment.

The aeration was accomplished with pressurized air at a water depth of 50 cm. The airflow was increased after 24 h of experiment time and additional 20 hours later the aeration depth was doubled in order to see the response of chemocline height in the water. At the end of the experiment, water samples were taken from the aerated top water layer and the bottom water and analyzed in the lab.

Conceptual electro-active species mass balance model

The total amount of electro-active constituents in the lake could be quantified by a parameter called summed conductivity $S_{\kappa 25}$. For each time of measurement it was calculated by multiplying the measured electrical conductivity κ_{25} with the corresponding water volume and subsequently integrating results over the complete water depth.

$$S_{\kappa_{25}}\left(t_i\right)=\sum_{j=1}^{n}\kappa_{25}\left(j,t_i\right)\cdot V_j=\sum_{j=1}^{n}\kappa_{25}\left(j,t_i\right)\cdot A\left(j\right)\cdot h_j \tag{1}$$

Therefore the lake was vertically portioned into j=1…n layers of volumina V_j where layer j=1 represented the bottom water layer. In the lake, the number of layers varied between 40 and 45 due to changes in water level whereas in the column experiment a constant value of 47 layers could be used in each time step. Each layer j had a respective height h_j of 10 cm. Furthermore, it was assumed that conductivity gradients in the planar directions were negligible.

Beside the assessment of the dynamics of the mass balance in the entire water body, calculating the spatially averaged conductivity of mixolimnion and monimolimnion for each time step allows to quantify changes in stratification stability.

Discrepancies between the measured dynamics of monimolimnion and mixolimnion conductivities and values calculated using a hypothetical scenario of a closed *Waldsee* represent the impact of cross-boundary mass fluxes on the electro-active species mass balance of *Waldsee*. For detail in the calculation see Nixdorf and Boehrer (2015).

Results

Column Experiment

Over the complete experiment time summed conductivity dropped by about 12 % from 13.44 $S\cdot m^2$ to 11.84 $S\cdot m^2$. This could be attributed to the expected oxidation and subsequent precipitation of iron hydroxide from the aerated part of the column. The precipitation process could be visually verified by a water discoloration to reddish brown and a settling of flocks within the column.

The results of the laboratory analysis showed that the aeration of the column's upper water changed the water characteristics significantly (fig. 2). Resulting upper water parameters approach in the direction of mixolimnetic water properties in *Waldsee* indicating the efficiency of the proposed iron hydroxide formation process. Similarly, changes of lower water properties during the experiment could be attributed to the impact of iron hydroxide reduction and re-dissolution process.

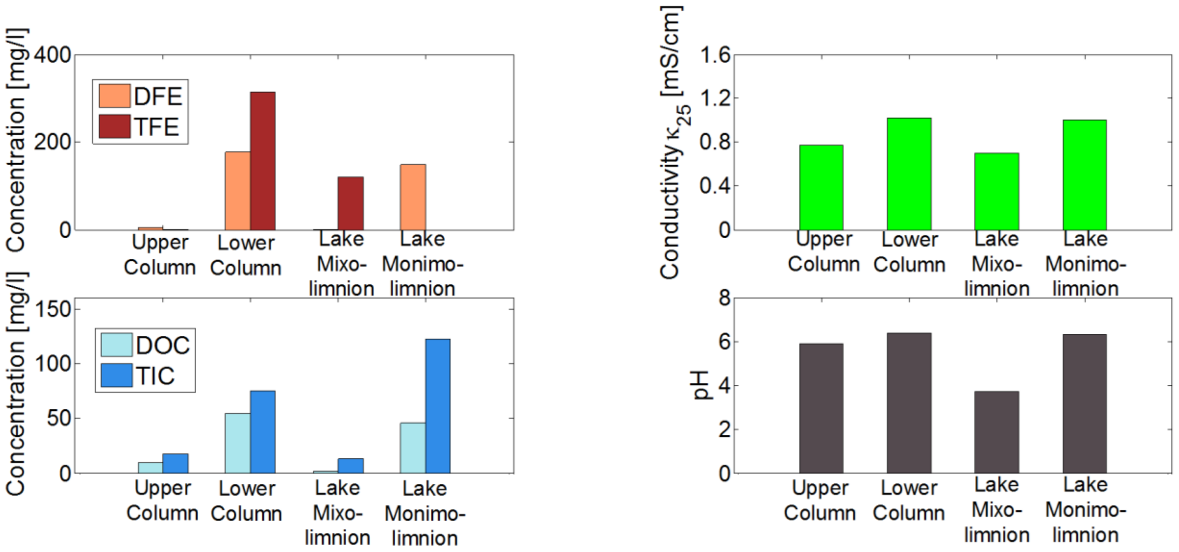

Figure 2: *Water properties of samples from different water layers in Waldsee and the water column. The determination of a plausible TFe value for the monimolimnion failed and was therefore excluded (from Nixdorf and Boehrer, 2015)*

Dynamics of chemocline height and summed conductivity in Waldsee

Over four years of monthly observation, a seasonal variation of the chemocline could be observed. (see also von Rohden et al. 2009). From April to October, the chemocline sank, while it rose during winter months (fig. 3a). The mean height above the lake bed was 2.86±0.29 m showing variations between 2.3 m and 3.5 m. Compared with the water level in *Waldsee* which was on average at 4.18 ±0.10 m this meant that the amplitude of the chemocline changes, expressed by standard deviation, were about three times higher than the observed variations in lake water level.

Similar to the behavior of the chemocline, summed conductivity of *Waldsee* underwent seasonal variations, within a range of 354 $S \cdot m^2$ and 468 $S \cdot m^2$. This means that about 25% of the summed conductivity disappeared over summer when the chemocline was moved downwards, but recovered again when the chemocline rose during winter months.

The initial summed conductivity of 465.18 $S \cdot m^2$ was only slightly different from the last measurement of 468.72 $S \cdot m^2$ indicating a similar amount of electro-active substances at the beginning and at the end of the observation period.

Impact of internal and external fluxes on stratification preservation

Within the observation period, measured averaged EC of the monimolimnion was in a range between 0.93 mS/cm and 1.09 mS/cm, having a temporal mean of 1.00 mS/cm and a standard deviation of 0.041 mS/cm (fig. 3b). In contrast average EC in the mixolimnion never exceeded 0.54 mS/cm. This confirmed that the permanent stratification of *Waldsee* was preserved during the entire observation period by the presence of conductivity gradients. An inverse relationship could be observed between variations of the average monimolimnion conductivity and variations of the chemocline. Assuming that groundwater showed fairly constant chemical properties, this indicated that internal physico-chemical processes were potential drivers of the monimolimnetic electrical conductivity variations.

We compared measured values with the calculated values of our simplified model of a closed system *Waldsee* in order to quantify the impact of internal processes versus external sources. The graph of the calculated values, which were in a range between 0.81 mS/cm and 1.25 mS/cm, showed that even in total absence of groundwater related ion exchange, the internal iron redox cycle alone was able to maintain the conductivity gradient. Although the curves resembled each other in terms of mean value and location of maxima and minima, the graph of the measured values showed, on average, only 47 % of the excursions found in the graph of the calculated monimolimnetic electrical conductivity values.

In conclusion, the electrical conductivity of precipitated ions from chemocline erosion partly re-appeared in the monimolimnion, but some iron was permanently deposited in the sediment. Correspondingly high iron mass concentrations of about 20 % could be measured in the sediment of *Waldsee* up to a depth of more than 10 cm (Friese 2004).

A less pronounced re-covering of electrical conductivity losses in the monimolimnion would lead to a continuous decrease in monimolimnion conductivity. For the chosen model, the calculated conductivity values dropped below the measured values significantly during periods of chemocline increase and additionally showed a long term decreasing trend. Excluding the temporarily storage of iron flocks on the side walls of being an efficient storage mechanism, the inflow of significant amounts of ion rich groundwater was the only remaining mechanism for the recovery of EC during times of rising chemocline in *Waldsee*. Finally, a net outflow of groundwater during periods of chemocline erosion (von Rohden et al. 2009) could also contribute to the less pronounced decrease of the measured monimolimnion conductivity in comparison to the results of the model.

It should be taken into consideration that the closed model silently assumed that the loss of the bicarbonate conductivity by CO_2 escaping to the atmosphere was entirely counterbalanced by CO_2 production as a by-product of the biochemically iron hydroxide reduction. At this point further investigations, e.g. by numerical geochemical equilibrium models, are needed to quantify the impact of the carbonate system on the electrical conductivity dynamics in *Waldsee*.

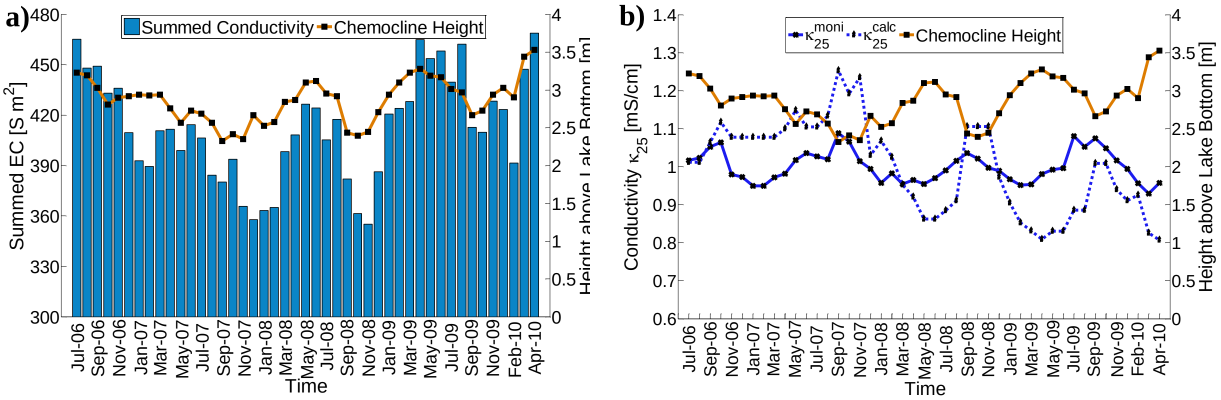

Figure 3: *a) Time series of chemocline height and summed EC at Waldsee between July 2006 and April 2010. b) Comparison of measured and calculated average EC in the monimolimnion (from Nixdorf and Boehrer, 2015)*

Conclusions

The present study provides an easily applicable approach to delineate and quantify the impact of internal geochemical processes, partial intermixing processes and groundwater flow on the dynamics of mining lake water properties by using spatial high resolution electrical conductivity measurements and simple one-dimensional algebraic equations.

Regular measurements of electrical conductivity could confirm that the induced stratification of *Waldsee* in two water sections is permanent and that the volume of both sections undergoes changes which follow a seasonal pattern with an increase of monimolimnion volume in winter and early spring and a decrease in the remaining months. However, it could be shown that the total amount of electro-active substance in *Waldsee* correlates significantly with the volume of the monimolimnion with variations up to 25 % within the observation period.

An aeration experiment in a 5 m high PVC column filled with monimolimnic lake water replicated the proposed dominating geochemical processes in *Waldsee*, first and foremost the iron-redox-cycle. The immediate precipitation of iron hydroxide flocs after the beginning of the aeration of the upper part of the column led to an approximation in electrical conductivity to the mixolimnion of *Waldsee*. This could confirm the previous research that the density-gradient in meromictic *Waldsee* is sustained by internally geochemical process and that, on principle, the water of mixolimnion and monimolimnion could both originate from local groundwater.

A comparison with an idealized model of complete retention of conductivity in the water body revealed that not all conductivity removed by chemocline erosion was lost, but about half of it reappeared in the monimolimnion. Though this number was affected by rough assumptions, it clearly indicated that re-dissolution was taking place, and this process must be considered as a factor for sustaining the density stratification. A groundwater inflow however was still required to balance the conductivity over the years in agreement with von Rohden et al. (2009).

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Challenges of pit lakes from a sociological perspective

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Abstract

The research main objectives is to analyze the social adaptation of a new pit lake near a mid-size and semi-rural community, the discourse of the main social actors involved and the controversies arise. The paper ambition to reflect on the sustainability of this and other post-mining regions, especially as they transition to natural resource-based tourism development. Research shows that endogenous factors of the community must also be taken into account in order to explain more thoroughly why transition may occur in some areas and not in others. Evidence suggests that certain conflicts and discourses condition the possibility and success of a new economic model around pit lakes regardless the ecological success of the restoration. Hence, the main challenges of pit lakes from a sociological perspective have to do with an appropriate social communication strategy and the adaptation to the social and economic system they are embedded in. Discourse analysis also shows an omission and/or non-rigorous use of the social dimension.

Key words: pit lakes, sociology, social constructivism, post-mining regions, environmental restoration, mining

Introduction

Mine waste and remediation has become the main challenge for many post-mining regions nowadays. Particularly relevant for the purpose of this study is the creation of artificial lakes by flooding the old mine holes and arising new natural habitats around. Pit lakes have been developed in the past internationally (Soni et al., 2014); e.g. Alberta Pit Lake in Canada, Sleeper pit lake, Nevada USA and Westfield pit lake, Scotland; and evidence suggests they are becoming one of the most recurrent end use of opencast mining. Geller et al. (2011) estimate the existence of at least 22 European regions with one or more pit lakes. In some of them, as in the so called New Lake District, in the southern parts of Leipzig, Germany, the transformation has led and is still leading to an entirely new landscape including 16 new lakes and natural habitats in a place where, until 1989, 60 million millions tons of coal per year were extracted. A similar scenario is currently emerging in several Polish regions (Gilewska and Otremba, 2015; Szczepinski et al., 2010) and will probably consolidate in the next decade in a context of ecological crisis and environmental concern. Moreover, with an increase in frequency and scale of mining activity in the global south, pit lakes will sooner or later become a common feature not only in the most advance but also in the currently emerging economies. The challenges faced by these and other "*pit lakes regions*" must be seen as the primary motivation for the current research.

Literature recognizes the existence of environmental risks of pit lakes (Soni et al., 2014; Gross, 2010, 2010b; Schultze et al., 2010; Doupé and Lymbery, 2005) which may have profound disadvantageous implications felt for many years, especially by local communities. These risks have to do with the post closure hazards such as excessive erosion and soil, unexpected flooding, leakage of pit lakes due to surface damage and land use, hazard due to proximity of other industries and slope failure, among others.

Especially relevant for the purpose of this research is that pit lakes appear to come not only with environmental risks but also with inherent social uncertainties. To be sure, all over the world, regions exist where human activities have led to vast changes in the landscape via industrial, military, and mining operations; urbanization, deurbanization and the conversion of agricultural land or land for leisure activities (Gross, 2010). These humanmade interventions have often triggered social tension between actors and groups with dissimilar interests and priorities in the local social structure. In other words, the same project may be perceived as either an opportunity or threat in accordance with the interest of the social actors involved (Gramling & Freudenburg, 1992). In this paper it is argued that pit lakes are not an exception, despite their value as natural resources for miscellaneous purposes.

By mean a social constructivist approach, this paper aims to study the social perception of the new pit lake in the municipality of As Pontes, Galicia, Spain, with particular attention to the conflicts arise in reaction to the new landscape and the challenges faced by the communities around. The As Pontes coal mine was exploited for 3 decades (1976-2007). During this time, more than 260 tons of coal were mined. The surface of the mine hollow and dump reached 38 million square meters (3,800 ha.). Filling began with rain water and water from the Eume (63% of volume), Illade and Meidelo rivers, various streams and run-off water (which circulates above the surface of a drainage basin). The final outcome is a water body with an 18 kilometer perimeter, 205 meters depth and with a beach of "500 meters in length to the practice of nautical sports or to sunbathe on the 370 meter shoreline" according to the mining company website.

It is important to throw into relief that the study of pit lakes from a sociological perspective may strongly vary from region to region. Some lakes occur close to large community centers, as they often do in Europe and Africa; while in Australia they tend to do it further (McCullough, 2011). In this sense, the pit lake studied in this paper is near a community of around 10.000 inhabitants. It is 65 km far from the nearest city, A Coruña and 500 km from the Spanish capital. Moreover, the community has experienced a strong socioeconomic transformation since the beginning of the mining activity in the late seventies, having double the population and moved from a primary sector oriented economy to a mining oriented one. Hence, this case it is an opportunity to assess the challenges of pit lakes located in semi-rural areas and particular those where the mining has supposed important changes in the community around.

In conclusion, the research main objectives is to analyze the social adaptation of a new pit lake near a mid-size and semi-rural community, the discourse of the main social actors involved and the controversies arise. By mean this analysis, the paper ambition to reflect on the sustainability of this and other post-mining regions, especially as they transition to natural resource-based tourism development.

Method

The presented example is part of a larger project on Impact of Large Scale Energy Mining Projects from a Sociological perspective (Pérez-Sindín, 2015a). In this project, the researcher conducted theory-informed case study on the social changes occurred in the municipality of As Pontes since the beginning of the mining activity up to date. Toward that end, the author undertook a mixed method based fieldwork consisting of the conduction of 19 in-depth interviews and two focus groups among the main social actors involved, postal self-administrated questionnaire among early retired miners, observation, particularly online observation, that is, the analysis of certain debates held in local Internet local forums, as well as secondary data collection, including both official statistics and relevant content from the main newspapers.

Thematic analysis is performed by a coding process divided in six phases: getting familiar with the data, generating initial codes, grouping codes into themes, reviewing the themes, defining and naming the themes and preparing the final report (Braun, 2006). This process was conducted by the computer program Nvivo. This research was based on the analysis of the codes related to the ecological restoration. Particularly, the aim was to identify the different opinions around the lake as well as the quantification of the most important. Especially noteworthy here was a debate held in the main local online community, composed by more than 2.500 members (25% of population). A total number of 38 comments were codified and classified in three main categories (neutral, critique and praising).

Results

1. *"Social openness could break out political riots"*.

The company has reported several times on the quality of water and its availability for human use. However, evidence suggests that the degree of social openness of the whole process is lower than in similar scenarios. Two objective facts indicate it. First of all, with regard to the very beginning of the restoration project, the final model of restoration was not the result of any competition or any sort of public exposition, but just the contracting of a German firm specialized in these types of projects (Bustabad, 2011). Hence, the model was planned by the own mining company and with the participation of external experts funded by the company. In other cases, as in the pit lakes occurred in the southern parts of the city of Leipzig, Germany, literature shows how the final model was first assessed in a process of both "public competition" and "citizen hearings" (Gross, 2010). Something similar had occurred around the pit lake located in Carmaux, France, where a public competition took place and government, several public services and citizens were involved in the whole decision making process (Pérez-Sindín, 2015b). Moreover, this fact is consistent with the stated by one of the engineer interviewed in 2008, during the years of flooding "openness could break out political riots" (Op. cit., p. 8).

2. Positive for the 60% of residents.

As far as the social acceptance of the new landscape, it is worth referencing the results of a survey performed during the years of flooding, in 2008 (Pérez-Sindín, 2015c). As observed in the table 1, up to a 60% of the respondents consider that the lake is something "very positive" or "positive". On the contrary, only an 18% of the total sees it as something "negative", "very negative". The results indicate the existence of a mostly positive opinion of the restoration process. However, it is important to note that negative options, indifferent and DK/NA/REF ratings sum up 40% of the total responses, which point towards the existence of certain social fragmentation. It is not easy to compare the results with other cases. The lack of equivalent question formulation and the different contextual factors make it complex to do consistent comparison. However, it is worth mentioning the results of a survey conducted in order to assess people opinion around the pit lakes occurred in the southern of Leipzig, Germany (Schmidt & Abel et al., 2014). In this case, respondents were asked about their willingness to use lakes and hardly a 10% of the total answer was negative. Assuming the contextual and methodological limitations, data shows a greater division in the case of As Pontes.

Table 1 *"In relation to the transformation of coal mine into a lake, you think that this is going to be for the town..." Fr., % of the total and cumulative.*

Options	Frequency	%	Cumulated %
Very positive	48	15,38	
Positive	141	45,19	60,58
Indifferent (Not mentioned)	20	6,41	66,99
Negative	32	10,26	77,24
Very negative	24	7,69	84,94
Dk/NA/REF	47	15,06	100,00
Total	312	100,00	

Source: Pérez-Sindín (2015c)

This fragmentation contrasts with the appropriation of the public opinion by certain institutional actors. Discourse analysis accounts for a tendency among certain decision makers to stand as representative of the whole community by publicly suggesting that "all town" is delighted, while no objective source is provided: *"you go to As Pontes and people are delighted with the mine"* Former mine director (Rodríguez, 2013) or "*Lake is a commitment of all the people*" As Pontes Major (La Voz de Galicia, 2013).

3. *"It is almost drinkable"* vs. *"10.000 times more acid than normal".*

The company has reported several times on the quality of water and its availability for human use. For instance, in April 2010, two years before the end of the flooding, the director of mine was interviewed in the Galicia Autonomous Community public television. In that occasion, the director assured that the water quality would be suitable at the end of the process. This information was also upheld in subsequent years up to date in different Galician and Spanish level newspapers. Previous studies suggest the existence of certain distrust during the years of flooding, based on the lack of accurate information about the whole process, and encourage by certain ecological organizations (Pérez-Sindín, 2015b, Sierra, 2012). This skepticism could have fallen after the flooding and once the company appears in several occasions in media and the beach was made public. Indeed, most of the participants during the fieldwork even reproduce mining company´s statements *"you can almost drink it"*.

Nevertheless, the analysis throws into relief the persistence of a skeptical opinion about the quality of water among some of the participants in the fieldwork. This view could be fuelled by different sources, first of all, by ecologist groups who challenge the official version. They have criticized the project repeatedly. In august 2012, when the official inauguration of the lake took place, the main ecologist organizations in Galicia (ADEGA, Verdegaia and SGHN) put into consideration the quality of the water by showing the results of their own tests. Despite such parameters as ph level were acceptable in the beach and swimming are of the lake the acidity in the streams and run-off water is, they maintain, *"10.000 times more acid than normal"*. Secondly, the existence of informal information channels. Certain members of the community see the whole process with skepticism even when they are aware of quality test made public by the company. The bellow verbatim represents this perception. The way the participant expresses concern: *"someone who knows someone working in the company…"* it is truly indicative of the existence of informal channels that come to contradict the official version.

"No, no, let´s see, [someone_anonymized] who knows someone working in the company, says that bathing is not recommendable, that it was added don't know which substance, and it is not good, oh well". In-depth interview: local businesswoman and long term resident.

4. **"*…for me the lake is an illusion, it is a terrible passion*" vs. *"This f**** shit of lake that we see through a fence"***

Another attention-grabbing aspect is the existence of extreme views around the lake, as well as they way different community members project their own emotions when talking about it. The bellow verbatim illustrates the "*passion*" the lake is raising among certain members. Concretely, among those who were previously employed in the mining company.

"I think the lake is an attractive and that will bring jobs, and that will bring leisure things, and that will change the people way of living. I am absolutely convinced. I hope…for me the lake is an illusion, it is a terrible passion. But I think so, but like I see it eh… In-depth interview: mining company employee.

The emotional discourse is also present in the words of local politicians as it echoed media the day after the lake inauguration. Here, the major´s word emotively refer to the importance of the mine for the community, as well as the inhabitants who where resettled after mining activity buried their villages.

"The mayor of As Pontes, reminded" all of those whose more than 50 years ago began to exploit the mine and those who followed, and who make the memory of thousands of workers remain under the water". But above all, "the inhabitants of the parishes that disappeared with the mining and were expropriated…Thanks to those parishes that sleep their sleep under these waters," he added. EuropePress (2012).

This view contrasts with another emotional version, this time rather negative one, among certain members of the community. The critical and belligerent tone of the comments bellow is certainly illustrative in this regard. Participants in a local forum debate showed their discontent with the whole restoration project. Particularly, they complain against the limited accessibility to the lake. The company, claiming security concerns, has a policy that limits for great part of the year the access to the bathing areas, while the rest of lake remain completely closed. This has been criticized on numerous occasions.

*"That's really nice and not this f****** shit of lake that we see through a fence!!!! I've had it up to here with these f****** photos from…"*Long term resident. [Answering the previous comment] *"Agree with you somehow, they deceive us with the lake in front of our nose but the f****** multinational [In reference to the mining company ENDESA], let's see when they open it to the public, don´t think I can enjoy it while all this junk is there… paper havens…"*

5. *"As Ponte has an impressive potential around" vs. "…with the beautiful landscapes in Galicia, who really want to spend vacations just next to a power plant…"*

Both the power plant and coal mine were the main source of direct and indirect jobs. Such jobs, especially the direct ones, rapidly improved the income level of many families. This economic boom turned into "depression" as of the mining restructuring occurred in mid-90s, i.e. layoff, early retirement plan, problems of employment and demographic shrinkage. The social perception of the lake largely depends on its capacity to drive economic development and, therefore, return to the *"good times"*. In this context, one part of the population has a great hope on the lake. This hope is not only fuelled by the mining company but also by the local government. Moreover, the local government has performed important investment both in advertisement campaign and in the organization of sport events. It is worth mentioning the organization of a so called Ironman, a triathlon macro event that is usually organized in larger cities, but in this case, the determination of the local politicians and other stakeholders, together with relatively high incomes of the council thanks to the still active power plant make it possible.

> *"The new lake will be in a closer future than we now imagine a new economic alternative for many people".* As Pontes Major, La Voz de Galicia (2013).

This view becomes even more optimism when interviewing former employees of the mining company. They give hope for greater growth and employment in the future thanks to the lake and they express it enthusiastically, as suggested before. Not only for its potential for tourism or leisure, but also as an asset to attract new industrial projects.

"It is a necessary investment, a VAST INVESTMENT…because the lake itself can bring a leisure and touristic transformation, and it may also be an industrial transformation…because here, it was already spoken, perhaps…cellulose or other industries".

"I think the lake is an attractive and that will bring jobs, and that will bring leisure things, and that will change the people way of living. I am absolutely convinced.

"Well, I think As Ponte has an impressive potential around eh:::(0.1) THE LAKE. The lake and, ps! I say the lake together with everything, the power plant, the new recovered areas, EVERYTHING" [interviewer: But potential for what?] Potential to redesign an industry, something that does not damage the lake and the surrounding but that it can, at the same time, seize the content of the lake, I mean, an industrial project, mainly, we are talking…YEAH; YEAH, there is something in progress actually, well, someone told me…someone bring it up that a pumping plant, another biomass plant, and…"

There is, however, a whole counter narrative about the entire restoration process. Particularly, the discourse analysis shows the existence of a skeptical view toward the transition from an industry based to tourism based economy. This skepticism is based upon the incredulity about the possibility to create jobs out of the new restored area, despite the optimism of the official discourse. The bellow comment best illustrate this point of view. The proximity of more consolidated leisure, touristic and coast areas in the Autonomous Community of Galicia is seen as a drawback in order for the lake makes profit of such activities. Hence, it is seen as an attractive area for locals but with low capacity of local development.

"What is the aim of the lake? With the beautiful landscapes in Galicia, who really want to spend vacations or just next to a power plant? If people come is just for curiosity. So, what is the function of the lake to me? Just a leisure area for locals or young people without car that cannot head other places". Source: online community "As Pontes Politica e Sociedade.

"They aim to make As Pontes a touristic hotspot but they omit that we must be an industrial area, where are the thousands of visitors that were to visit the As Pontes thanks to the lake?" Source: online community "As Pontes Politica e Sociedade.

"It is obvious that the public investment will not have effect in the town, you've got to be joking, neither in the shops nor in the hostel industry. Ironman is a way to advertise the lake (not even As Pontes town), show it in the media and make it fashion for four curious that one Sunday come to

visit it because they saw it in the newspaper”. Source: online community “As Pontes Politica e Sociedade.

5. *“The largest artificial lake in Spain” vs. “Public investment will not have effect in the town”.*

The strong landscape transformation has also led to major changes in community identity terms. The lake has become a new identity symbol for one part of the community. This is reflected in, for instance, the growing number of Internet side and Facebook pages aiming at highlighting the beauty of the new landscape. But such transformations could have also led to a certain rejection among one part of the population, especially among long term residents, that is, those related to the pre-mining community. This divergence was evidenced on July 14, 2014, after a program broadcasted in one of the top audience television stations in the Autonomous Community of Galicia. The program had as its ultimate goal to promote both the industrial and tourist side of the town. This event may be seen as part of the local government strategy to project a post-industrial, modern and renovated image. Without having delved into the program content, suffice to say that the central figure of the show was undoubtedly the restoration process and, particularly, the lake and its "espectacularity". The format and content of the program is a clear attempt to project an image of modernity. In this image, the lake stands as centerpiece and other elements of the mining universe were also proudly mentioned, as the power plant chimney.

At the end of the program, one As Pontes neighbor posted a comment on the greatest local Internet Communities judging by the number of members (2,500 members in April 2015 in a town with 10,000 inhabitants); in which he criticized the program intended to give a picture of As Pontes exclusively associated with "chimney" with the "central" [power plant] and "lake" when “in fact" there is "something else" to finish by saying "I hope not disturb anyone with my opinion”. The publication gave way to 38 comments. Some of them claim that old symbols of the town, as the old town or river were overlooked.

“I do not think they refer to something unique or singular, but ENDESA, this is a very important part of our history, and it changed the town, but one misses to take care and put in value, for example the river, or the oldtown”.

As shown in Table 1, 23,7% of these comments had a critical attitude toward the attention given to the lake as new symbol of the town, while the majority of the people, around 61% showed a more positive view. The distribution of praising/critical attitude gets more equalized as regard to the number of likes, 53% against 41%. The same occurs according to participants. In this case, 44% of participants show a praising attitude, while 31% shows rather a critical view.

Table 2 *Attitude toward the lake as a new symbol of the town*

Attitude	Comments		Likes		Participants	
	Frequency	%	Frequency	%	Frequency	%
Neutral	6	15,79	4	5,33	4	25
Attitude of praise	23	60,53	40	53,33	7	43,75
Critical	9	23,68	31	41,33	5	31,25
Total	38	100	75	100	16	100

Source*: debate at Internet community “Eres de As Pontes si…” search under keyword “lake”, access April, 2015.*

6. Inter-community conflicts.

This study has mainly focused on analyzing the social perception of the lake among locals residing in the adjacent community around. Existent surveys and other sources indicate that the majority of population assesses positively the whole restoration project. Hence, despite the difference with regard to other cases studied, the social acceptance has been relatively high. Nevertheless, evidence suggests that the opposition to the whole project could be higher in further communities, particularly those located in the course of the Eume River in its direction to the estuary in the Atlantic Ocean. It is worth remembering that the mine itself has always been a reason of inter-communities conflicts since the beginning of the activity. The pollution of the natural habitats around and particularly, the River

Eume, has always been at the center of controversy. The mining company plan to drain to the river the sludge accumulated in the reservoir formed by the Eume River, which could have "moderate to severe" (Bustabad, 2011) negative impact on water, landscape and leisure activities on both Eume Natural Park and river estuary. Thus it could compromise the local economies around. Against this background, the perception of the lake in the whole region is inherently negative and could grow in the future. Lake was flooded by mean the channeling of water from the river. Water circulates above the surface and return to the river through output channels. Several events have been organized by ecologist organization to assess the possible impact. Furthermore, mining company engineers acknowledge the existence of additional menaces (personal conversation). New fungal and bacterial species may impact river native species as far as the leisure and the use of certain infrastructures is not regulated in the lake. Hence, greater tourism development around the lake could be at the expense of near local economies, thus raise new inter-community conflicts.

Conclusions

There is a tendency to think that the main explanatory factor of a successful restoration projects is ecology. In the best case scenario, economy is also estimated, that is, the existence or not of potential market to develop certain activities around the new landscape. Without denying the irrefutable influence of these aspects, this research shows that endogenous factors of the community must also be taken into account in order to explain more thoroughly why transition from mining to leisure or other alternative economies may occur in some areas and not in others.

Results come to confirm William Freudenburg theory on social impact assessment. Environment and society are "jointly constituted". Environment can affect and construct identities, but identities can also socially construct environment in one or another way. Pit lakes are not an exception. Certain local identities and discourses may condition the possibility and success of a new economic model around pit lakes. The new landscape may be seen as opportunity or threaten in accordance with different social groups interests. Neither one nor another view guarantees sustainability. The overestimation of the pit lake as an economic driver could lead decision makers to invest in the lake without bearing in mind environmental risks. On the contrary, an underestimation of the new lake for exclusively identity reasons could lead to a waste of resources and, in the worst case scenario, to an environmental degradation.

In this context and doing reference to the title of this paper, the challenges of pit lakes from a sociological perspective have to do with two main aspects:

1. Social communication. Further positivist research need to be undertaken in order to examine how environmental, social and economic risks are being socially communicated, how pit lakes are being treated by mass media and whether they acknowledge the existence of risk or not. Judging by the results of this research, evidence suggests that the social acceptance and appearance of extreme discourses could be explained by a closed communication strategy. This strategy may include both lack of permanent information channels, inappropriate mass media in terms of proximity with the locals and uneven and/or informal dissemination of the information. Permanent and reliable information channels need to be available for the whole society, which may also contribute to planning and development. This is consistent with Ulrich Beck idea of second modernity, i.e., when human society realizes that not all risks can be controlled and that they must be coped with and incorporated into planning and development.

2. Socio-economic embeddedness. Engineering of the pit lakes must be consistent with the social and economic system the lake is embedded in. To what extent can a pit lake achieve tourism development if it is located near a traditional touristic destination? How this and other factors affect the creation and design of certain elements as beaches, natural areas etc. Are engineer taking into account the economic model of the region. Are social scientists taking part of the pit lakes planning before the flooding in order to assess adaptation capacity to the local economy? What criteria are being used to design pit lakes? This may also affect decision making during mining activity and earlier. The lack of adaptation of a pit lake in a given region may discourage the beginning of an opencast mine.

This research also shows that pit lakes can also revive social and identity conflicts originated during the mining period. In the same token, it is pertinent to think that an appropriate social adaptation may be an opportunity to solve them. For this reason, the integration of local and pre-mining culture into the restoration process may reinforce social cohesion: place names, revaluation of old symbols, urban integration of new and old landscapes, extol the pre-mining history in the new landscape, etc.

3. Sociological rigor. Discourse analysis accounts for a either omission or misuse of the social aspects of pit lakes. The social dimension is often reduced to frivolous or even emotional statements. This contrasts with the often very technical jargon when addressing ecological and more technical aspects. Social communication of lakes must include rigorous social assessment of the public opinion.

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A new technology of pit lake treatment using calcium oxide and carbon dioxide to increase alkalinity

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Abstract

Pit lakes are often subject to acidic groundwater inflow and therefore prone to short term re-acidification. Hence, the increase of alkaline buffer capacity is the main treatment aim to develop stable pH-conditions that allow biological processes to take place.

To increase alkalinity in pit lakes one needs to apply alkaline materials in combination with CO_2. A test of this treatment approach that uses CaO (phase 1) and $CaCO_3$ (phase 2) in combination with CO_2 is presented in this paper.

The treatment process was established in a closed reactor system, which produces high alkaline waters. The treatment process itself consists of a standard lime slaking technology, which is only necessary in the case of CaO application, and a carbon dioxide dissolution reactor. The alkaline suspension (CaO or $CaCO_3$) and the CO_2 enriched water enter an HCO_3^- producing reactor. Since CO_2 is an expensive product, a gas recovery reactor (GRR) was installed downstream of the HCO_3-reactor. The produced HCO_3^- was then applied to the pit lake using an injection system based on submerged buoyant jets.

Between both test phases the acidic groundwater inflow caused a decrease in pH and alkalinity due to re-acidification. That period was closely monitored to determine the alkalinity decline and therefore the treatment success. Also, the impact of the processed water, which was discharged into the lake, on the lake water quality is described.

The pit lake chosen for the tests is called Drehnaer See. It is a small sized pit lake with a total volume of 13 Mio. m^3. The acidity before the treatment was between 3.4 and 4.1 mol/m^3. Prior to the actual test the lake was neutralised using lime (CaO). During this initial treatment step pH-values of the lake water increased from around 3.0 to 7.0. After the neutralisation the determined alkalinity was 0.3 mol/m^3.

The treatment process was successfully tested. Values between 20 and 30 mol/m^3 in the discharge of the closed reactor system (HCO_3-reactor) were measured. It was demonstrated, that it is possible to produce an almost clear and particle free solution with an alkalinity of 30 mol/m^3. Alkalinities of 40 to 50 mol/m^3 are possible as well, but could not be achieved with the treatment plant at the test site due to limitations in the CO_2-supply.

After a treatment period of just 3 months alkalinities in the entire water body were determined to be around 0.7 mol/m^3 in phase 1 and 0.9 mol/m^3 in phase 2.

Key words: Mine water, treatment technology, pit lakes, carbon dioxide, CO_2, lime, CaO, calcite, $CaCO_3$, alkalinity

Introduction

Pit lakes in Germany are often characterized by low pH values and elevated concentrations of Fe, Al, Mn and NH_4-N as well as a lack of organic and inorganic carbon. Therefore, the main aim of pit lake treatment is the neutralisation of the water body and the associated mineral precipitation of Fe, Al and Mn. While neutralisation with lime is no technological challenge anymore, buffer capacities of most lakes will not exceed values between 0.3 mol/m^3 and 0.4 mol/m^3.

Due to acidic groundwater inflow pit lakes are often subject to short term (months) re-acidification. Hence, the increase of alkaline buffer capacity is needed after the initial neutralisation is achieved to help trigger biological processes. For the long term stabilisation of pH-values the alkalinity needs to be elevated to levels of around 1.0 mol/m^3

In general several options to build up alkalinity are currently tested and available in pit lake treatment. The technologies can be divided into two approaches, based on the location where the main reactions take place. One approach is the use of the water body as the main reactor (open system). The second one is the use of a closed system, which is described in this paper.

In Germany and Sweden the application of alkaline solids for lake water treatment is mainly achieved by distribution of the reactants on the lake surface by small or medium sized boats or ships. Technologies that uses submerged jets were only tested in the last 5-10 years and show promising results, since the energy for mixing the reactants into the water body is more efficiently used, compared to the application of the reactants on the water surface. Since process efficiencies are higher and specific costs are lower, a submerged jet based units was chosen for the distribution of the process water discharge to the lake.

A variety of alkaline solids such as lime (CaO), hydrated lime ($Ca(OH)_2$) or limestone ($CaCO_3$) can be used to achieve neutral pH-values in acidic pit lakes. Due to the lack of inorganic carbon or kinetic constraints, the aforementioned materials are limited in the production of the aquatic species HCO_3^-..

This paper presents a closed treatment system that uses lime (phase 1) and limestone (phase 2) in combination with CO_2 with the aim to significantly increase the alkalinity of the lake chosen as a test site.

Methods

Study area

The pit lake Drehnaer See has a volume of about 13 Mio. m^3. The bathymetry of the lake and the cross sections A-A' and B-B' are shown in figure 1. Coal mining at the site produced long trenches in the northern and southern part of the lake, which are accompanied by a shallow area in its centre.

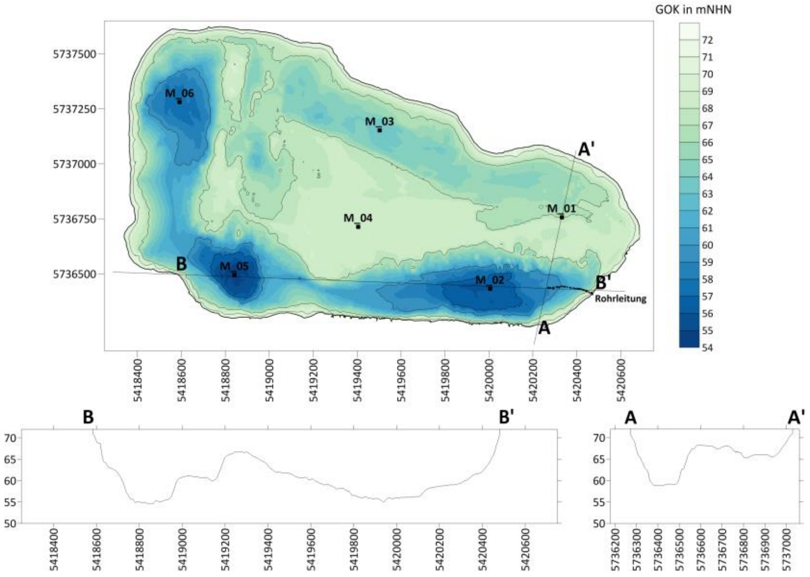

***Figure 1** Bathymetry and cross sections of the Drehnaer See.*

Lake water quality

The lake water quality before the treatment was typical for pit lakes in Germany. Measurements were conducted at six sampling points (M_01 to M_06 in figure 1) in varying water depths. The low pH-values (2.99 and 3.12) and high values of electrical conductivity (1660 µS/cm and 1670 µS/cm) derived from acid mine drainage. The corresponding lake water acidities were determined by titration and yielded values between 3.4 and 4.1 mol/m³. The acidity is mainly connected to iron (31.6 to 32.5 mg/L), aluminium (5.81 to 6.58 mg/L) and manganese (1.14 to 1.27 mg/L) as well as ammonia (1.5 to 1.6 mg/L). Low values for total organic (0.58 to 1.0 mg/L) and total inorganic carbon (0.2 to 1.1 mg/L) are characteristic for acidic pit lakes in Germany too.

Experimental design

The treatment test had several steps. First, the initial neutralisation was achieved by the application of a lime suspension. The pH-values of the lake water were increased from around 3.0 to 8.0 and higher. In a second step alkalinity was injected into the lake using the developed closed reactor system, which allows for intense chemical reactions between the solid phase ($CaO/(Ca(OH)_2$ or $CaCO_3$) and the gas phase CO_2 to produce the aquatic species HCO_3^-. After the successful increase of alkalinity re-acidification was monitored. In this period pH-levels decreased to values below 4, before test phase 2 was started. For the subsequent neutralisation limestone was used followed by test phase 2, were $CaCO_3$ and CO_2 were applied to increase alkalinity.

Closed reactor system

The applied treatment technology in a closed reactor system was developed in the GFI laboratory. The main aim of the research was to develop a technology that produces alkalinities above 20 mol/m³. The industrial scale reactor (figure 5 and 6) was designed based on successful tests with a batch reactor (figure 3) and in a small scale pilot plant (figure 4). In the small scale reactor alkalinities as HCO_3^- of up to 48 mol/m³ were repeatedly produced. Figure 2 shows the heterogeneous reactions and the components of the tested technology that were considered in the design.

The industrial scale reactor has several modules (figure 2 and 5). The modules can be operated semi-automatically on site or even from a smartphone. Module one (K1, K2a, K2b) is a standard lime slaking technology, module two is a carbon dioxide dissolution reactor (C2), module three is an alkalinity producing reactor (HCO_3-reactor), that was developed at the GFI Grundwasser-Consulting-Institut GmbH (GFI 2012). Comparable tests are described in Watten et. al (2007). The fourth module is a gas recovery reactor (GRR) and the fifth module is an injection system based on free, submerged buoyant jets (momentum discharge), that was applied to distribute the alkaline water in the entire water body from a single point close to the bank of the lake.

Sampling – lake water

The lake water was closely monitored fortnightly. At each of the six monitoring points vertical profiles for pH, specific conductance, temperature, O_2-concentration and turbidity were recorded. Further, water samples in 1, 8, 10, 13 and 15 m water depth were taken. The following parameters were determined: acidity/alkalinity, total Fe, dissolved Fe, Fe(II), Fe(III), Al, Mn, Ca, Mg, NH_4-N, NO_2-N, NO_3-N, SO_4, TOC, TIC.

Sampling – process water / closed reactor

During the process all relevant flow rates and mass fluxes were recorded. Water samples were tested for the same parameters as the lake water (see above). Sampling points were installed before and after the HCO_3^--producing rector (figure 6) as well as after the gas recovery reactor.

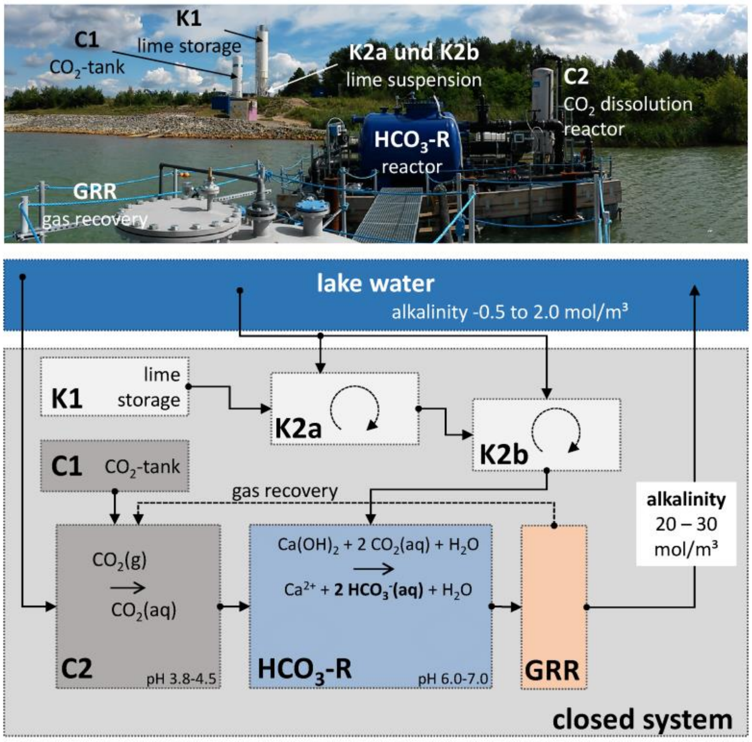

Figure 2 *Closed reactor system and heterogeneous reactions.*

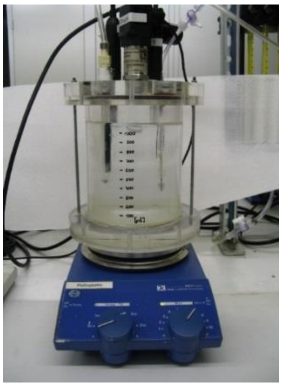

Figure 3 *batch scale reactor.*

Figure 4 *small scale reactor.*

Figure 5 *industrial scale reactor.*

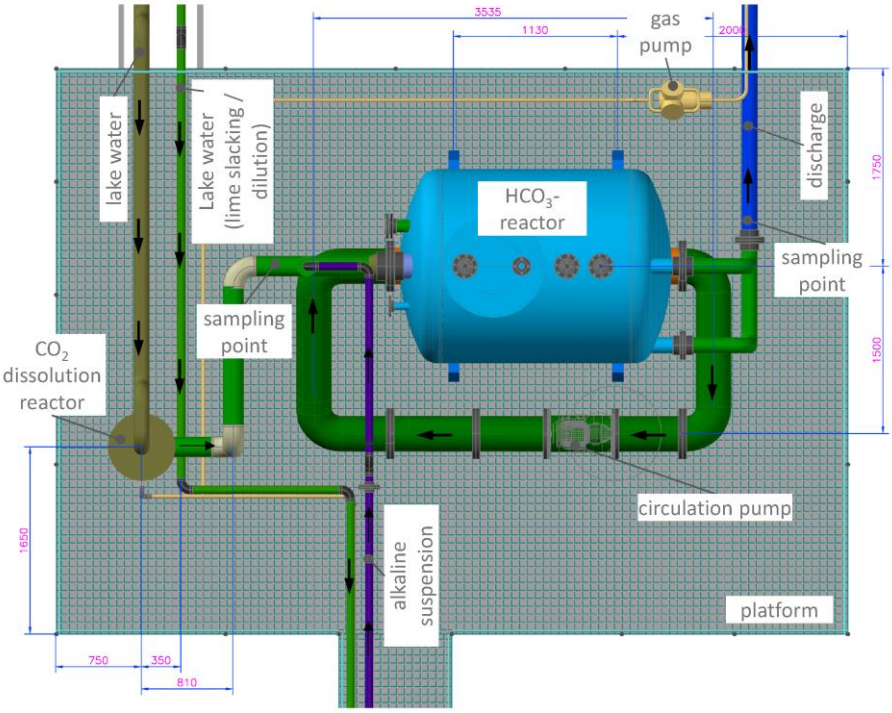

Figure 6 *flow directions of the closed system and location of sampling points.*

Results and discussion

The tested treatment process is influenced by multiple factors, e. g. the pH value in the HCO_3-reactor or the ratio of TIC flux to mass flux of the used alkaline solid (TIC/alk$_{solid}$). Further, the efficiency of the process is closely linked to the degree of calcite oversaturation and the CO_2-concentration of the water that enters the HCO_3-reactor. The experiments on the large scale reactor showed that the alkalinity produced by the process strongly depends on the energy input (mixing) and the reaction time. During a total of 52 tests alkalinities between 9.4 und 30.4 mol/m³ (see figure 7, phase 1, CaO / CO_2) respectively between 11.4 und 18.05 mol/m³ in 18 tests (see figure 8, phase 2, $CaCO_3$ / CO_2) were measured.

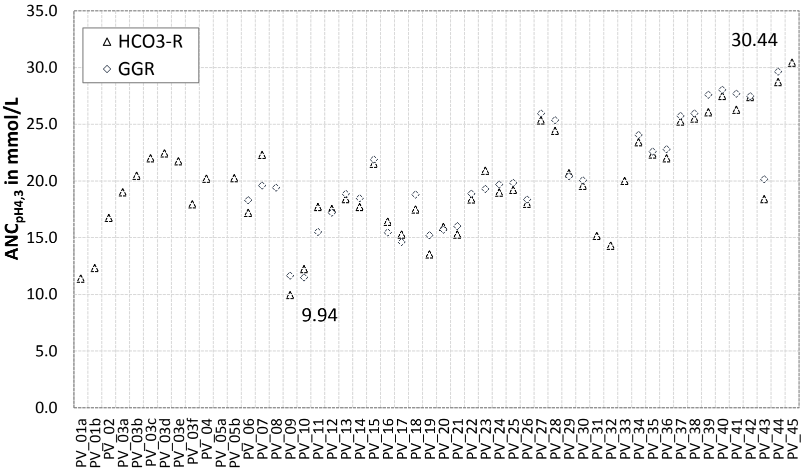

Figure 7 *Measured ANC downstream of the HCO_3- reactor and the GRR in phase 1 (CaO / CO_2)*

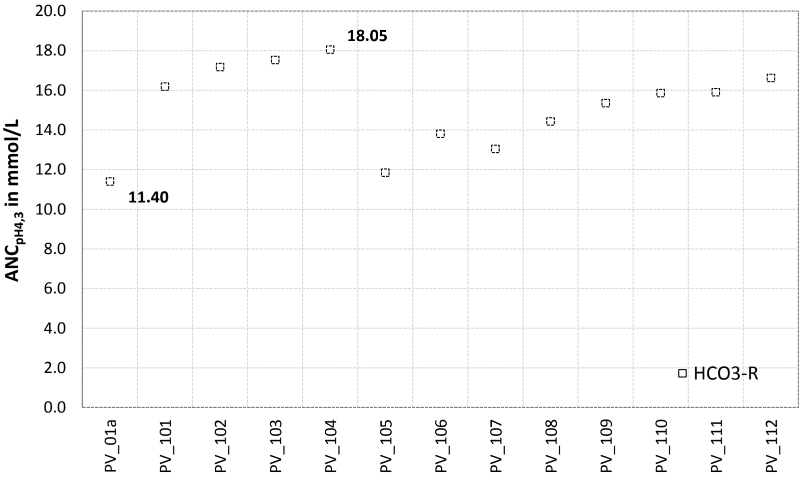

Figure 8 *Measured ANC downstream of the HCO_3- reactor in phase 2 ($CaCO_3$ / CO_2).*

reactor

The overall alkalinity production of the system was limited by the capacity of the CO_2-mass flux. With a maximum capacity of 340 kg/h and the flow rate of the system (108 m³/h) the CO_2-concentration could not exceed 71.5 mol/m³. As a result of the small scale reactor tests (see figure 4) a stoichiometric ratio TIC/alk$_{CaO}$ of > 1.8 needs to be specified to produce alkalinities around 50 mol/m³. Based on these findings the maximum achievable alkalinity is 39.7 mol/m³. All measured alkalinity values were below this level. Table 1 sums up the capacities of the installed technological units.

Table 1 *Capacities of the technological units.*

unit	unit is limited by	range	notes
system flow rate	pressure at desired flow rate	86-108 m³/h	max. CO_2-dissolution is determined by system pressure
CO_2-mass flux	water flux over CO_2-dissolution reactor	0-400 kg/h	limited by pressure of system
	evaporator unit	0-340 kg/h	max. CO_2-mass flux was limited by capacity of evaporator unit, design mass flux was not reached, installed capacity was not high enough
Energy input	circulation pump	0-550 m³/h	determines turbulence in HCO_3-reactor
HCO_3-reactor	pressure	1.0-4.5 bar	for safety < 5 bar
resulting HCO_3-producing capacity		*39.7 mol$_{Alk}$/m³*	*max. alkalinity at DIC/alk$_{CaO}$ ratio of (GFI 2012)*

mass concentration of suspension

The test results showed that with increasing mass concentration up to a value of 2.5 % (phase 1) and 8 % (phase 2) the HCO_3-concentration was increased too. Above the aforementioned values an alkalinity increase in the aquatic phase was not observed. These threshold values were caused by the CO_2 limitations of the installed unit (see table 1).

mixing energy

A set of tests were conducted to optimise the input of mixing energy into the HCO_3-reactor. During the these tests the parameters c_{CO2} (54.7 ± 1,5 mol/m³), c_{Alk_solid} (58,8 ± 0,2 mol/m³) and the mass concentration of the suspension (1,35 ± 0,1 Ma%) were fixed. The energy input was varied between 39.6 and 316.9 W/m³. The results of the tests PV_3a to PV_3f revealed, that increasing the energy input up to 250 W/m³ increase the alkalinity output. Higher inputs of mixing energy not necessarily increased the alkalinity of the discharge.

<u>calcite saturation</u>

All discharges were calcite oversaturated. The degree of oversaturation ranged between $0.05 < SI < 0.65$. With increasing saturation indices (SI) the observed alkalinities increased as well. The interesting fact is, that despite the oversaturation, calcite precipitation was hardly noticed in the system, when flushing intervals were implemented as part of the process control.

<u>efficiency of the process</u>

The process efficiency was defined by the ratio of filtered to unfiltered alkalinity in the process water downstream the HCO_3-reactor. Both were determined by titration. The unfiltered sample sums the alkalinity in the aquatic and in the solid phase. Determined efficiencies were between 5.3 and 50.5 %. Due to the fact that the closed system was limited to an alkalinity maximum of 39.7 mol/m³ by the CO_2 capacity, the process efficiency regarding the installed units are higher and ranged between 24.9 and 76.5 %.

The CO_2-limitation of the process proved an important point. The closed system can be operated with a stoichiometric ratio $\underline{TIC/alk_{solid}}$ of around 1 without severe calcite precipitation in the HCO_3-reactor. The application of this ratio significantly reduces the process efficiency, but increases the alkalinity load drastically while the pH values in the discharge stayed in the neutral range. Further, the particle size of the used alkaline solids is reduced, which is an advantage for the ongoing reactions that take place in the lake.

<u>pit lake water quality</u>

The development of the lake water alkalinity (ANC - acid-neutralising capacity) is shown in figure 8. The pH values during the course of the tests are presented in figure 9. For comparison both figures show the values during and after phase 1 und 2 (CO_2 application) as well as the values after the neutralisation (no CO_2 used).

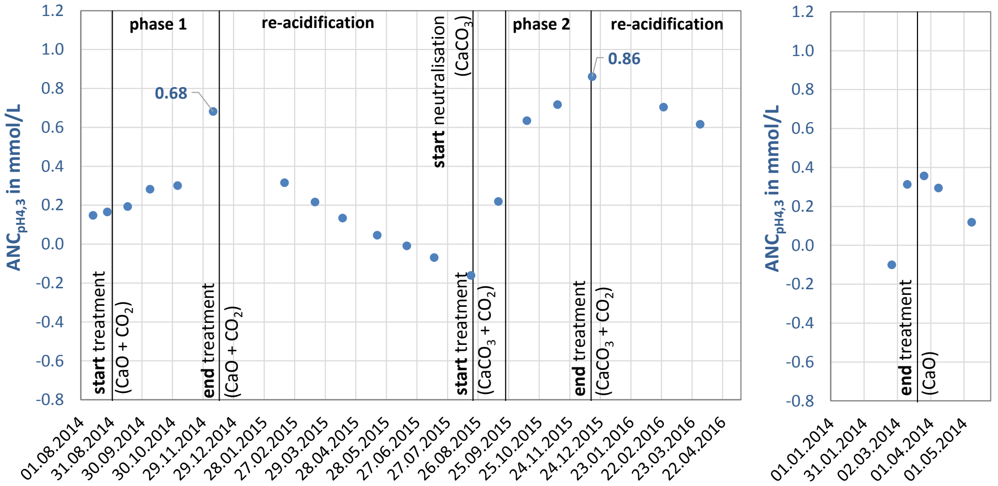

Figure 8 *Development of ANC in water body (volume weighted average), during and after phase 1 und 2 (left), after neutralisation (right).*

After phase 1 an ANC volume weighted average of 0.68 mol/m³ and after phase 2 of 0.86 mol/m³ was determined. Due to problems with the CO_2 unit, the treatment process in phase 1 only worked properly in the last third of the test period and limited the alkalinity.

The comparison of ANC and pH development after the tests with the period after the initial neutralisation of the lake shows that without the application of CO_2 and the related increase in alkalinity, pH values dropped below 6 in less than two months (figure 9, right). The alkalinity increase extended this period by roughly 6 months in phase 1. Three months after the end of phase 2 the pH values were still around 7 (figure 9, left). The pH values are expected to stay on that level over a period of 6-8 months.

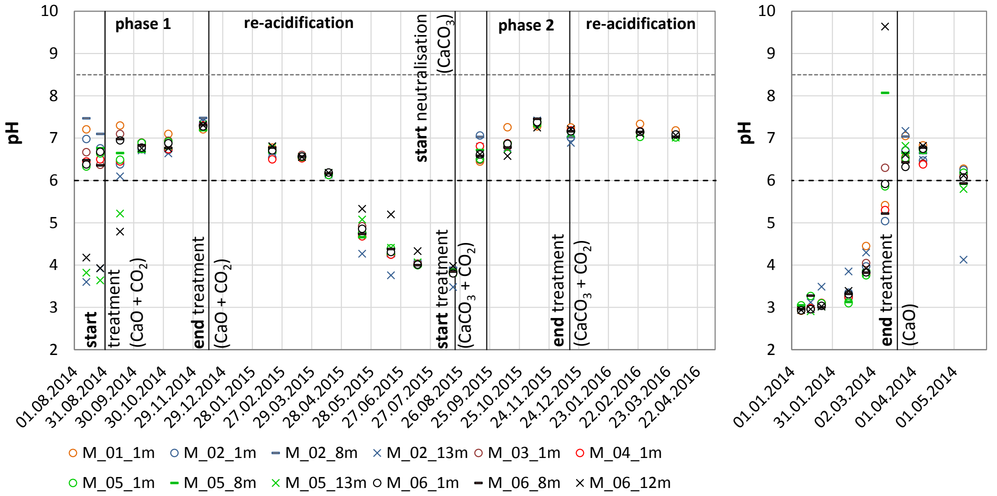

Figure 9 *pH values at sampling points during and after phase 1 und 2 (left) and after neutralisation (right)*

Conclusions

In the described tests it was shown that alkalinities of around 30 mol/m³ and 18 mol/m³ in the aquatic phase can be achieved using CaO or $CaCO_3$ in combination with CO_2 respectively. Higher alkalinities between 40 and 50 mol/m³ are possible using CaO and CO_2, but were not achieved in the tests due to limitations in the CO_2 supply unit. By application of $CaCO_3$ the alkalinity was limited around 20 mol/m³ due to smaller reactions rates of $CaCO_3$ compared to CaO.

The system can run in an oversaturated state for the mineral calcite, but needs to be automatically controlled, especially regarding the specified flushing cycles and pH values in the HCO_3-reactor. To run the process stable, with regard to the prevention of calcite precipitation and associated blocking of process units, pH values around 6.5 need to be maintained in the HCO_3-reactor.

If the process is used to treat a pit lake, the water body can and should function as a second reactor, where the additional reaction time can enhance the overall process efficiency. A direct application of CO_2 and alkaline solids is not favourable, since high CO_2 concentrations in the lake force a high degree of degassing and therefore the loss of a reactant. Due to the closed system approach the CO_2 loss to the atmosphere was minimised.

The process can be applied to other applications in which high alkaline water is needed. Depending on the application the gas recovery reactor can even function as a microflotation unit to reduce the amount of particles in the discharge to a minimum.

Acknowledgements

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Field experiments on subsurface iron removal in the Lusatian mining region

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Abstract

A series of field tests were carried out to explore the application of subsurface iron removal (SIR) for unfavourable hydrogeochemical site conditions. At two sites in the Lusatian mining region characterised by low pH (5.4 to 6.4) and low alkalinity ($K_{S4.3}$ = 0.39 to 0.85 mmol/L) together with high iron concentrations (9 to 47 mg/L) groundwater was treated using SIR. The results show that generally the technique can be successfully applied by adjusting the operational procedures to the specific site characteristics. Crucial for the application are an effective mechanical deacidification of the extracted groundwater, the use of technical oxygen and optimised interim periods between infiltration and abstraction. The application of sodium hydroxide to increase the pH and enhance the oxidation of iron was found to be of critical economic viability.

Key words: subsurface iron removal, pH, alkalinity, field test, efficiency coefficient

Introduction

Iron and manganese are commonly present in anoxic groundwater worldwide. Iron concentrations up to 3 mg/L are normally not harmful to human and animal health, but result in technical problems: clogging of production wells, precipitation and incrustation in the water supply distribution systems and orange/brown colour of water. According to the drinking water guidelines in many countries the total iron concentration should be less than 0.2 mg/L. As a result of pyrite weathering due to dewatering during mining activities very high iron concentrations of more than 100 mg/L can be observed. If groundwater has to be used for drinking water supply, industrial/agricultural water or so called eco-water for feeding wetlands in areas affected by mining, often iron removal is required. As an alternative to conventional iron removal, which uses filters in a treatment unit above ground, there is also the low-cost option of subsurface iron removal (SIR), which takes place directly in the groundwater (DVGW 2005).

As the efficiency of SIR depends on hydrogeological and hydrogeochemical site conditions, a reliable data base is required to design the scheme or it is advisable to conduct a small-scale pilot experiment to determine the suitability of the aquifer for the application of this technique (Ebermann et al. 2012; Rott et al. 2002). The process of subsurface iron removal is based on interacting redox reactions and ion exchange processes in a reaction zone formed around wells. When aerated or oxygenated water is infiltrated into a well, the oxidation process changes dissolved Fe(II) into less soluble Fe(III), mainly precipitating in the aquifer as iron(hydr)oxide. The iron hydroxide is stored in the pore space of the aquifer, providing adsorption sites. These sites are occupied mainly by calcium ions. When further Fe(II) ions enter the reaction zone during extraction, the adsorbed calcium ions are replaced. Infiltrated oxygen-enriched water leads again to oxidation of the adsorbed Fe(II) ions. Thus, a high adsorption capacity for Fe(II) is built up within the so-called reaction zone around the well. Periodic alternation between infiltration and abstraction eventually results in the production of iron-free water.

With atmospheric oxygen and concentrations up to 10 mg/L, a portion of the abstracted groundwater from one well is infiltrated into another well. A typical tool for the aeration unit is a water jet air pump. The selection of the oxygenation technique is based on the oxygen consumption in the reaction zone during the infiltration. The main oxygen consumers are Fe(II), Mn(II), ammonium and easily degradable organic compounds. Additionally, nitrite and sulphide consume oxygen depending on their concentrations. Conditions that hinder subsurface iron removal are low pH, low hardness, and high Fe(II), Mn(II), ammonium and sulphide concentrations.

The oxidation of Fe(II) to Fe(III) requires a pH value greater than 5.5 (Eichhorn 1987). During iron oxidation the pH decreases in accordance with the buffering capacity of the water-soil system. The efficiency of the SIR technique is determined as the volumetric ratio of the water extracted to the water infiltrated, which commonly is between 3 and 5, but could reach 10. This ratio is called the "efficiency coefficient" (DVGW 2005). A high efficiency coefficient is the aim of optimizing design and operation of the technique.

In 2014 and 2015, field experiments were conducted at monitoring wells at two sites in the Lusatian mining region to test if subsurface iron removal was applicable at low buffering capacities and low pH found in the groundwater. At the site Schleife the aim was to produce so called eco-water to feed a small pond during mining operations and groundwater lowering (Koch 2012). Eco-water should have an iron concentration of less than 1 mg/L.

At the site Spreewitz high iron concentrations of more than 100 mg/L occur in the groundwater, which discharges to a natural stream and causes iron sludge deposits, brown colour of surface water and limitation of aquatic life. Different remediation measures are planned to control the iron load to the stream. A field test was conducted at a single monitoring well to gain experiences with subsurface iron removal under hydrogeochemically unfavourable conditions.

Materials and Methods

At the site Schleife, a field test was conducted using two new observation wells (OW 1 & 2). The observation wells were used both as extraction and as infiltration wells. Extracted groundwater from OW 1 ($Q_{max} = 8.4\ m^3/h$) was discharged as eco-water to a nearby creek. A portion of the pumped water was treated in an aeration tower (d = 0.6 m, h = 3.1 m), enriched with technical oxygen using static mixing units (Sulzer chemtech GmbH, SMV DN 25, PP) and infiltrated into OW 2 ($V = 50\ m^3$). Following an interim period during which dissolved and adsorbed iron was oxidized and immobilized, water with a lower iron concentration was extracted from OW 2. A portion of the pumped water was enriched with technical oxygen and infiltrated into OW 1. Thus, by switching between extraction and infiltration, a continuous treatment and supply of eco-water was possible.

Temperature, pH, electrical conductivity and O_2 concentration were continuously measured using Multi 3430 and Multi 350i devices (WTW Weilheim, Germany). To gain first information on site, a field test kit (Merck-Aquaquant) to determine iron has been used. The analysis of total iron (Fe_{tot}), dissolved iron and major cations and anions was performed parallel in two independent laboratories (DIN EN ISO 11885 and DIN 38406-E1). Water was filtered through a 0.45 µm membrane filter (GD/X Whatman) directly after sampling to determine dissolved iron. All cations were determined by ICP-OES (Spektrometer Optima 4300 DV, Perkin Elmer). Anions were determined using ion chromatography (ICS 900, Dionex). Titration was used to determine alkalinity ($K_{S4.3}$; automated titration, G20 Compact Titrator, Mettler Toledo) and acidity ($K_{B8.2}$; manual titration with phenolphthaleine. Determination of NH_4^+ was by photometry (DIN EN ISO 11732, E32).

Selected groundwater quality parameters are shown in Table 1. The hydrogeochemical conditions were critical with low buffering capacity and a low pH (6.1 to 6.5). In total 30 cycles of infiltration and extraction were run. The oxygen concentration was controlled ($c(O_2) = 10 – 30$ mg/L), pH adjusted using NaOH (pH = 5.9 – 11.1) and the reaction time between infiltration and extraction varied (t = 0.2 – 15 h).

Table 1 *Groundwater quality data (Schleife 26/08/2013, Spreewitz 28/08/2014).*

Parameter	Unit	Schleife OW 1	Schleife OW 2	Spreewitz OW 6348
pH	-	6.4	6.1	5.4
EC	µS/cm	367	416	505
$K_{S4.3}$	mmol/L	0.75	0.39	0.85
$K_{B8.2}$	mmol/L	1.3	1.5	5.8
DOC	mg/L	2.1	1.7	8.2
NO_3-N	mg/L	<0.05	<0.05	0.3
NH_4-N	mg/L	0.26	0.12	0.4
SO_4^{2-}	mg/L	103	141	228
Fe_{tot}	mg/L	8.61	12.5	46.6
Fe_{diss}	mg/L	8.46	12.4	46.0

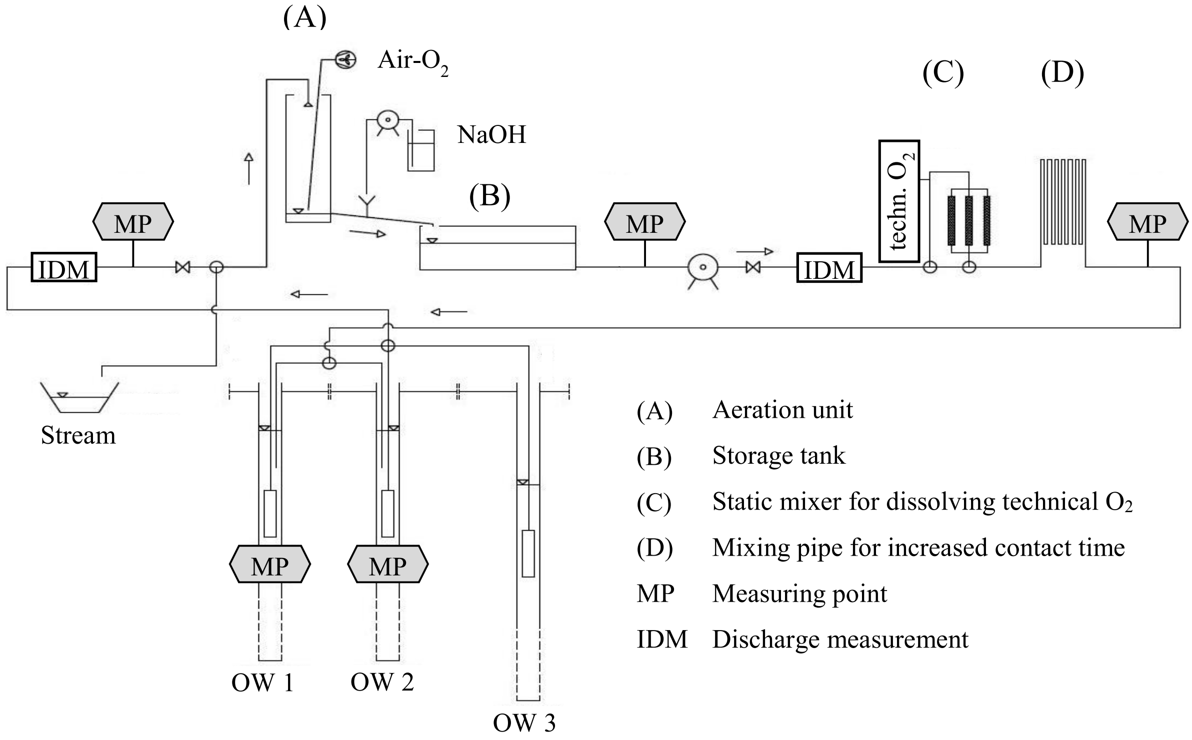

Figure 1 *Schematic of field test set-up.*

In Spreewitz, an experiment was carried out to test chemical deacidification using $Ca(OH)_2$. A 2-inch diameter observation well (OW 6348) was used for the experiment with permission from LMBV. The aquifer consists of coarse sand and gravel, covered by a 1.4 m thick silty fine sand layer. The filter screen is located between 2.3 and 4.3 mbgl. The groundwater level was found between 1.5 and 2.1 mbgl. The upper meter of the filter screen was separated using a packer system to achieve a more horizontal reaction zone during infiltration and an increase in radius. Groundwater and infiltrate was pumped using a centrifugal pump (Alko TDS 1001/3). Discharge was measured using an IDM (Siemens Sitrans FM MAG 5100 W). Technical oxygen from a pressurized gas bottle was added before a static mixer (PVC pipe, L = 50 cm, 4 static mixing elements, Sulzer chemtech GmbH, SMV DN 25, PP). The oxygenated water was passing a 100 L degassing tank (contact time 150 s) to further dissolve oxygen and to separate non-dissolved gas. The water was injected into OW 6348 via a PE hose connected to the lower end of the installed packer. If treatment of local groundwater is costly to run such an experiment, other water sources could be an alternative, as for example described by Rößner et al. (2013). In Spreewitz public drinking water from a nearby house was used as infiltrate, having a $K_{S4.3}$ of 2.3 mmol/L. In total 10 cycles of infiltration and extraction were monitored.

Results

At the site Schleife subsurface iron removal worked resulting in iron concentrations in the extracted water mainly below 1 mg/L (threshold value for eco-water), but higher than the technically required concentration of < 0.5 mg/L to prevent well clogging during long-term operation of such a scheme.

The development of iron concentrations in the pumped water of OW 1 shows characteristics atypical for the subsurface removal of iron (Fig. 2). Typically, the concentration of iron increases continuously during extraction. At Schleife, an initial increase was followed by a decrease in the concentration of iron then remaining at a level of 0.3 – 0.5 mg/L. During the initial phase of extraction the threshold value of 1 mg/L was partly exceeded. Increasing iron concentrations after reaching low values only occurred at pumped volumes of 200 – 250 m^3 corresponding to an efficiency coefficient of 4 to 5. The presence of pyrite indicated in the borehole profiles was confirmed by the analysis of sulphate together with the consumption of oxygen for processes other than the oxidation of iron. Fe(II) released as result of the oxidation of pyrite is the cause of the observed temporary increase in the concentration of iron during extraction. With the number of cycles the oxygen consumption for processes other than the oxidation of iron decreased. The stoichiometric comparison of the decrease in oxygen consumption against the decline in the sulphate concentration confirmed, that the oxidation of pyrite was the dominating process.

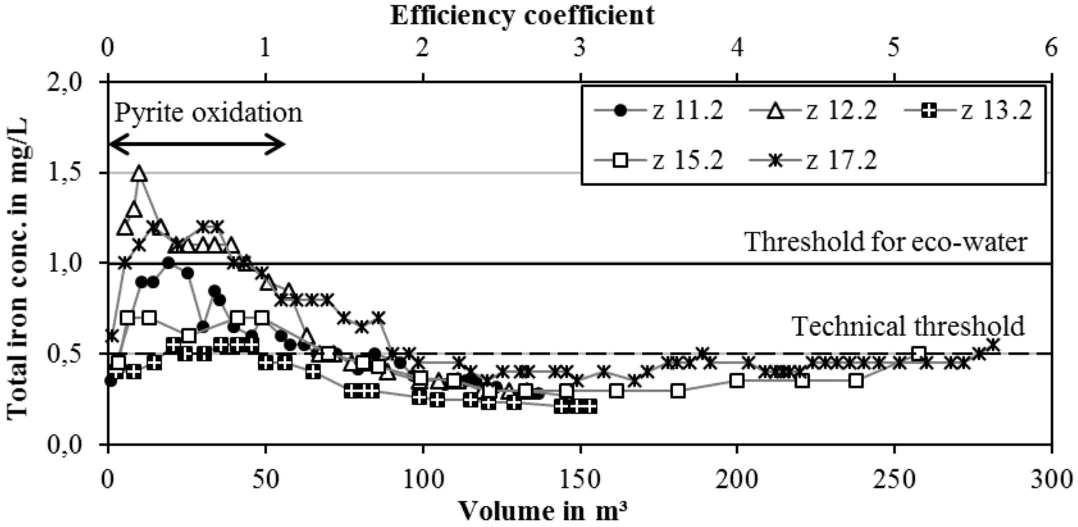

Figure 2 *Efficiency coefficients for cycles with technical oxygen at OW 1.*

The iron concentrations at OW 2 are characterised by the continuous rise in concentrations representative for the subsurface iron removal and are not affected by the oxidation of pyrite. Despite the application of technical oxygen, at an infiltration volume of 50 m^3 the threshold of 1 mg/L for ecological safe water was exceeded after only 45 m^3 (Fig. 3). Consequently the site represented by the observation well OW 2 has been considered unsuitable for the production of eco-water using subsurface iron removal techniques.

During cycles with aeration of the infiltrating water (O_2 = 9 – 10 mg/L) the oxygen consumption was independent from the contact time during the interim period between infiltration and extraction. About 94 % of the oxygen dissolved in the infiltrate was consumed. During cycles with added technical oxygen (O_2 = 26 – 33 mg/L) only 20% of the infiltrated oxygen was consumed for oxidation of iron, but 80% for other processes or was extracted back. A longer reaction time between infiltration of oxygen-rich water and abstraction of treated groundwater resulted in an increase in oxygen consumption for other processes, whereas for iron oxidation no more oxygen was consumed (Fig. 4).

Despite the unfavourable hydrogeochemical conditions, OW 1 is suitable for the application of subsurface iron removal using it alternately with a second well. Through a prolonged start-up phase with extended interim periods between infiltration and extraction, a decline of ancillary processes such as the oxidation of pyrite can be achieved resulting in the gradual reduction of the atypical high iron concentrations at the beginning of the extraction phase. During the start-up phase, the technical threshold for the operation of the system of 0.5 mg/L should be applied as criterion for the termination of the extraction phase. This criterion can be further adjusted, i.e. reduced once operating conditions have been established. For normal operation the interim periods between infiltration and extraction should be short as extended periods do not enhance the oxidation of iron. The application of sodium hydroxide to increase the pH and improve the oxidation of iron is not an economical viable solution. The effective mechanical deacidification of the extracted groundwater was found to be crucial for the application of the technique of subsurface iron removal. The long-term use of filter media (calcite, dolomite) to increase the buffer capacity of the infiltrate needs to be further explored in the context of the residual iron concentrations of > 0.2 mg/L which might lead to clogging of the filter.

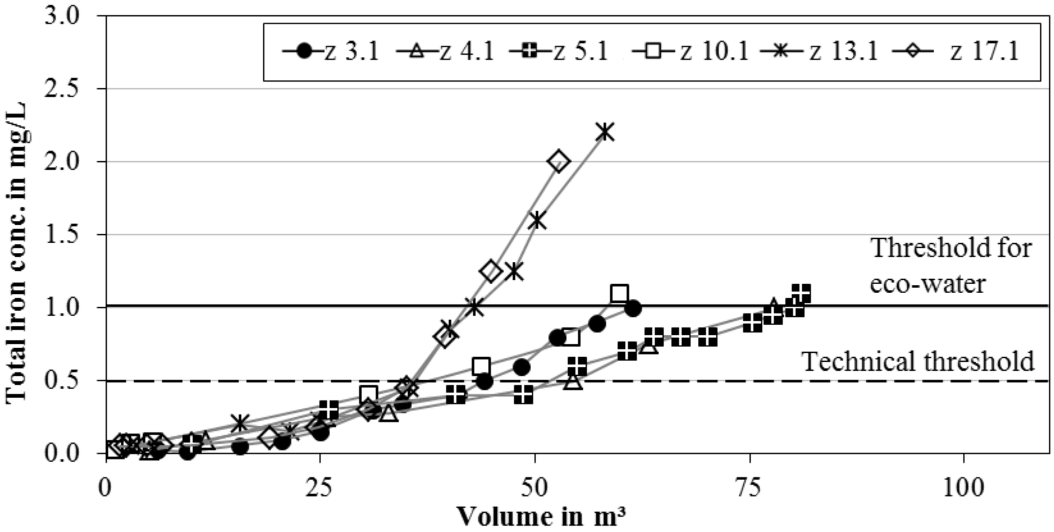

Figure 3 *Iron concentrations in extracted water from OW 2 in cycles with technical oxygen.*

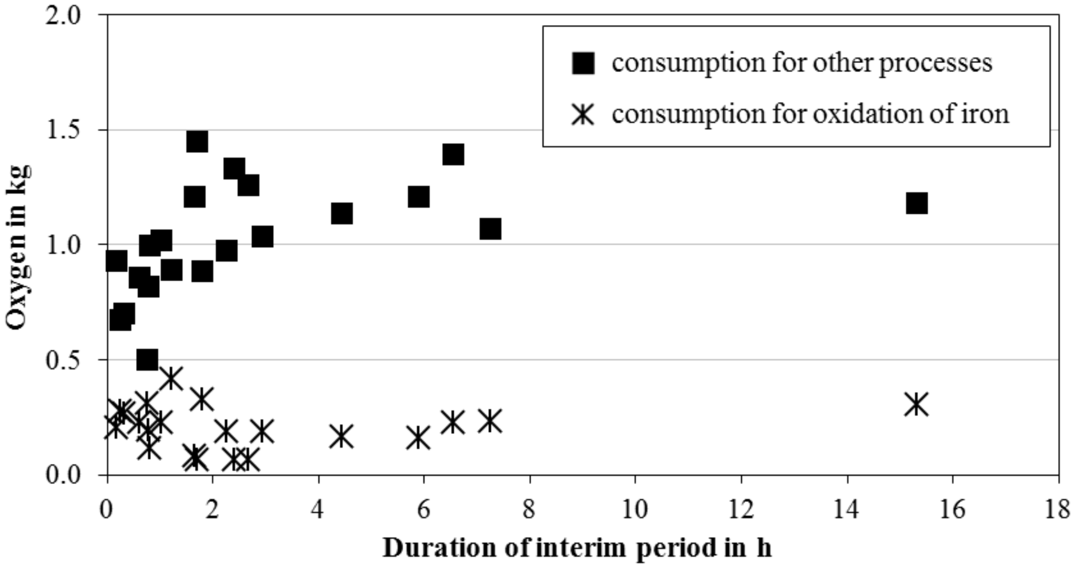

Figure 4 *Dependence of oxygen consumption for iron oxidation and other processes from duration of interim period at OW 1.*

In Spreewitz, where $Ca(OH)_2$ was added to the infiltrate to increase the buffering capacity, during all 10 cycles a high quantity of iron was removed in the subsurface. The iron concentration in the pumped groundwater was significantly reduced. After 10 cycles and a criterion of $Fe_{tot} < 1$ mg/L, the efficiency coefficient was still below 1. But there was a trend of a further decreasing iron concentration in the pumped water. A major portion of the infiltrated oxygen ($O_{2,\,pumped}/\ O_{2,\,infiltrated} = 44 – 80$ %) was pumped back, indicating that sufficient oxygen was available. There was no limitation caused by oxygen consumption for pyrite oxidation or other processes. As the CO_2 concentration in the infiltrate was low, no significant increase in alkalinity could be achieved by just adding $Ca(OH)_2$. Thus, the formation of a reaction zone around the well was limited due to low pH and low buffering capacity of the infiltrate. At the same time addition of $Ca(OH)_2$ increases the risk of calcite precipitation in the well or its vicinity.

Conclusions

The results of the described and other field experiments prove that subsurface iron removal can be applied even under critical boundary conditions such as iron concentrations > 10 mg/L, pH < 6 and alkalinity $K_{S4.3}$ <1 mmol/L. But such application requires additional treatment of the infiltrating water to increase its alkalinity, thus causing additional costs (Musche et al. 2015). Further research is required to increase alkalinity and prevent well clogging especially during infiltration.

Acknowledgements

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CHAPTER 5

Mine Water Geochemistry

Effects of pH on the Arrhenius Paradigm

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Abstract

Kinetic weathering reactions are temperature sensitive, and most industry standard kinetic tests are conducted at room temperature. The temperature effect on sulphide oxidation rates measured in room temperature experiments is generally scaled using the Arrhenius equation. Activation energies are only available for a limited number of mineral phases, therefore, temperature scaling is generally done by assuming metal leaching rates are controlled by oxidation of the dominant sulphide mineral, which is often pyrite. In order to evaluate this approach, 12 humidity cell tests were operated at room temperature until geochemical loading rates stabilized. The tests were then moved to a cold room at 4°C where the tests were continued. This temperature change would theoretically result in pyrite oxidation rates decreasing by a factor of 0.37 to 0.11 based on activation energies available in the literature. The decrease in sulphate loading rates generally fell within this range. However, distinct differences are observed in metal loading rates depending on the pH of the kinetic test. In acidic samples, most metal loading rates decreased to a similar degree as sulphate. Conversely, in pH-neutral tests declines in metal cation loading rates showed little change, or in some instances produced higher loading rates at colder temperatures. While temperature effects on individual elements may vary depending on the activation energy of the host mineral, increases in metal loading rates at lower temperatures is not consistent with the Arrhenius equation. These results demonstrate that under acidic conditions the Arrhenius relationship accurately predicts temperature effects on rates of metal cation release, however, this equation cannot accurately predict metal cation loading behavior in pH-neutral kinetic tests. The inability to accurately predict metal cation behavior in pH-neutral kinetic tests is interpreted to result from metal cation release being more closely tied to pH related solubility constraints than to weathering rates of primary sulphides.

Key words: Scaling Factors, Temperature Effects, Cold Climate

Introduction

A growing proportion of new mines and mineral prospects are located in arctic and sub-arctic environments where mean annual temperatures are near or below 0°C. These cold weather environments present challenges for water quality predictions. Kinetic weathering reactions (e.g., sulphide oxidation) are temperature sensitive, and most industry standard kinetic tests are conducted at room temperature. The temperature effect on sulphide oxidation is generally estimated using the Arrhenius equation of the form:

$$k = Ae^{-Ea/RT}$$

where k is the reaction rate, A is the pre-exponential factor, R is the noble gas constant, T is the temperature in Kelvin, and Ea is the activation energy. The activation energy must be experimentally derived for a mineral phase. Estimates of Ea values for pyrite range from 39 kJ mol^{-1} to 88.0 kJ mol^{-1} (Lowson, 1982; Nicholson, 1989; and, Kamai and Ohmoto, 1999). Data for other sulphide minerals is more limited, however, available data indicates activation energies are generally similar to the range observed for pyrite. For instance, activation energies for chalcopyrite, sphalerite and pyrrhotite have been estimated by Ahonen and Tuovinen (1991) as 77 kJ mol^{-1}, 45 kJ mol^{-1} and 40 kJ mol^{-1}, respectively.

The effect of temperature on sulphide oxidation rates can be estimated with the above equation and the range of Ea values observed for pyrite. The Arrhenius relationship normalized to the temperature of laboratory kinetic experiments is graphed in Figure 1. This relationship shows that pyrite oxidation rates at concentrations just above the freezing point of water (0.1°C) are 28% to 6 % of loading rates at room temperature (22°C).

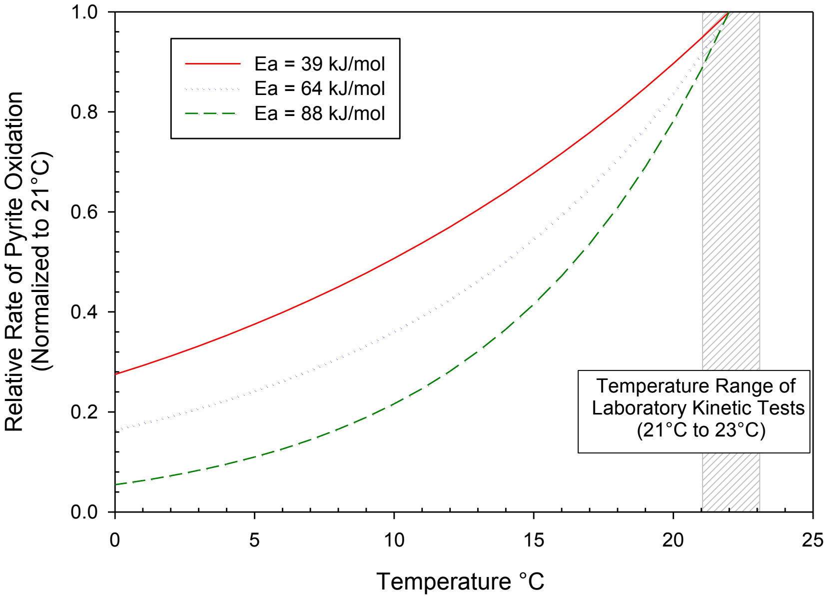

Figure 1*: Influence of temperature on pyrite oxidation rate normalized to 22°C.*

In scaling kinetic tests to field conditions, it is often assumed that temperature effects of mine waste can be described by an Arrhenius equation using the activation energy of the dominant sulphide mineral. This approach is predicated on the assumption that sulphide mineral oxidation rates are the primary control on metal release. The appropriateness of this assumption likely varies from site to site. In general, metal loading rates can be expected to be more closely linked to the oxidation rate of primary sulphide minerals in acidic mine waste environments where there are few secondary controls on metal mobility. Whereas in neutral pH environments, secondary mineral solubility and carbonate equilibrium will present a significant control on metal release and must also be considered when predicting temperature effects on metal release.

The temperature effects on kinetic test loading rates were investigated as part of a geochemical characterization program conducted to support source term predictions for the Casino project, which is a proposed copper porphyry mine in Yukon, Canada. This was done by operating 12 kinetic tests at room temperature until geochemical loading rates stabilized. The tests were then moved to a cold room at 4°C where the tests were continued. The difference in individual metal loading rates are then compared against predictions produced by the Arrheniums equation using a range of Ea values. The purpose of this comparison is to determine whether an Arrhenius relationship defined by the dominant sulphide mineral can accurately predict temperature affects on laboratory kinetic experiments.

Site Background

The Casino deposit is a gold-copper-molybdenum (Au-Cu-Mo) porphyry deposit that occurs in the Yukon Crystalline Terrane. The Terrane is dominated by the Yukon Group Metamorphics which are intruded by the Dawson Range Batholith. The project site is in a sub-arctic climate where mean monthly temperatures range from -18.1°C in January to 11.1°C in July.

The mineralization zones identified in the core of the Casino deposit include: an oxide cap (CAP) zone where sulphide and carbonate minerals have been leached; a supergene (SUP) zone where copper and sulphates leached from the CAP zone re-precipitated; and, a hypogene (HYP) zone which is unweathered and contains hydrothermal mineralization.

Methods

Kinetic test samples representing waste rock were obtained from drill core and samples representing tailings were obtained from metallurgical testing. The samples were characterized by acid base accounting (ABA) and quantitative X-ray diffraction (XRD) analysis prior to testing. Acid base accounting is used to measure sulphur speciation (total S, sulphate S and sulphide S) and various forms of neutralization potential. Acid base accounting parameters were measured following the procedures described in Price (2009). The mineralogical makeup of kinetic test samples was determined using XRD analysis with a Rietveld refinement as described in Raudsepp and Pani (2003).

Metal loading and acid generation rates were investigated using humidity cell and unsaturated column kinetic tests. Humidity cells consisted of Plexiglas cylinders (10.2 cm inner diameter, 25.5 cm length) filled with 1 kg of sample. Unsaturated columns were constructed using Plexiglas cylinders (21.0 cm inner diameter, 20.5 cm length) and a 5 kg crushed rock sample. Drill core samples of waste rock were crushed to approximately minus 6 mm while the grain size of metallurgical tailings were not modified.

The effect of temperature on metal release rates was evaluated on waste rock and tailings by operating 11 humidity cell and 1 column experiments at room temperature (22°C) until geochemical loading rates had stabilized, which required anywhere from 39 to 215 cycles. The kinetic tests were then moved into a cold room kept at 4°C where the experiments were continued. The temperature effects were then assessed by comparing the loading rates in the five cycles before and after the temperature change.

Results and Discussion

Sample Characterization

The results for sulphur speciation and inorganic carbon (i.e., carbonate) content for kinetic test samples are provided in Table 1 below. This analysis shows that sulphide-S is the dominant form of sulphur in HYP and SUP samples, while sulphate-S is dominant in the single CAP sample (Col 2A). X-ray diffraction results identified pyrite in all HYP and SUP samples, with the only other sulphide mineral identified being molybdenite in HC5. Other sulphur bearing minerals identified by XRD are K-jarosite in Col2A and gypsum in HC5 and T4. Inorganic carbon content is present in most HYP and SUP samples, the dominant carbonate mineral being calcite which is identified by XRD in all samples where inorganic carbon is detected. Calcite is also detected at a low concentration (0.3%) in HC9 by XRD where ABA analysis found inorganic C to be below detection limits. Samples lacking carbonate mineralization had a circumneutral to mildly acidic paste pH, indicating that non-carbonate buffering minerals are generally ineffective at maintaining a neutral pH.

***Table 1** Select Acid Base Accounting Results of Kinetic Test Sample*

Test ID	Mineralization Zone	Sample Type	Paste pH s.u.	Inorganic-C wt.%	Total-S wt.%	Sulphide-S wt.%	Sulphate-S wt.%
Col 2A	CAP	Waste Rock	5.3	<0.01	0.32	0.02	0.31
HC3	HYP	Waste Rock	8.4	0.27	4.23	2.04	0.03
HC4	HYP	Waste Rock	8.3	0.69	4.29	4.22	0.03
HC5	HYP	Waste Rock	8.1	0.21	2.21	1.07	0.07
HC6	HYP	Waste Rock	8.1	0.19	1.81	1.65	0.02
HC7	HYP	Waste Rock	7.1	0.29	3.26	3.16	0.08
HC8	HYP	Waste Rock	5.1	<0.01	4.28	4.13	0.03
HC9	HYP	Waste Rock	7.9	<0.01	0.92	0.86	0.02
HC10	HYP	Waste Rock	5.1	<0.01	3.56	2.97	0.05
HC11	SUP	Waste Rock	8.2	0.22	2.27	1.95	0.03
HC12	SUP	Waste Rock	5.4	<0.01	3.11	2.94	0.04
T1	HYP/SUP	Tailings	8.7	0.27	1.18	1.13	0.05
T4	HYP/SUP	Tailings	8.6	0.19	1.49	1.36	0.04

Temperature Effects on Acid Generation and pH

The change in pH and sulphate loading rates measured in the 12 kinetic tests in the 5 cycles before and after the temperature change are presented in Table 2. The decline in acid generation rates, as measured by sulphate, is used to calculate activation energies by assuming an Arrhenius relationship. These activation energy calculations are not produced with the intention of confirming or replacing literature values, rather, they are brought forward in the context of determining the effectiveness of using the Arrhenius equation to scale kinetic test results to colder temperatures.

Most of the derived activation energies in samples where pyrite is the dominant form of sulphur fall within the range of literature values (39 kJ mol^{-1} to 88 kJ mol^{-1} from Lowson, 1982; Nicholson, 1989; and, Kamai and Ohmoto, 1999). Two tests (HC6 and HC11) have calculated activation energies that are notably lower than this range. It appears that HC6 and HC11 had not reached steady-state sulphate loading rates before the temperature was decreased.

The unsaturated column Col2A, where K-jarosite is the dominant sulphate mineral, produced a relatively low activation energy for sulphate (21 kJ mol^{-1}). This calculated value is notably lower than literature values of activation energy for K-Jarosite which range from 51.6 kJ mol^{-1} to 63.8 kJ mol^{-1} (Zahria et al., 2010; Mireles et al., 2016). The cause of this discrepancy may be related to the relatively large increase in pH that occurred in this sample when moved to the cold room (+0.39 pH units). The rate of K-jarosite dissolution increases with pH (Elwood Madden, et a., 2012), hence, the increase in pH would have counteracted the temperature effects, leading to an underestimation of activation energy. These results indicate that the Arrhenius relationship provides a reasonably good approximation of the effects on sulphide oxidation in neutral and acidic pH kinetic tests where pyrite is the dominant sulphur mineral, but may not accurately describe dissolution rates of sulphate minerals such as K-jarosite if a decline in temperature is accompanied by a change in pH.

The effect of temperature on pH is variable. Kinetic test samples containing calcite mineralization showed only a small change in pH, ranging from -0.08 to +0.06 pH units. This is somewhat surprising, as the solubility of calcite increases at lower temperatures, which is expected to lead to an increase in pH. Samples that lacked carbonate content all produced acidic leachate and showed a more significant shift in pH, ranging from +0.21 to +0.65 pH units when moved from 22°C to 4°C conditions. This result indicates that the pH of carbonate buffered kinetic tests is relatively insensitive to temperature, while the pH of acidic samples is more responsive to changes in the rate of acid generation.

Table 2 *Sulphate loading and pH at 21°C and 4°C and calculated activation energies (Ea).*

	21°C		4°C		Ea
Test ID	pH	SO_4	pH	SO_4	kJ mol^{-1}
Col 2A	5.92	0.41	6.31	0.25	21
HC3	7.58	7.40	7.56	2.82	38
HC4	7.55	10.23	7.57	2.91	50
HC5	7.56	6.08	7.58	2.94	29
HC6	7.51	2.73	7.45	1.88	15
HC7	7.4	11.70	7.3	4.75	36
HC8	2.91	80.84	3.56	12.48	74
HC10	3.21	73.14	3.56	12.48	70
HC11	6.81	4.50	6.87	2.45	24
HC12	3.29	18.68	3.49	7.13	38
T1	7.75	18.05	7.69	5.53	47
T4	7.76	25.20	7.68	4.70	72

Notes: Sulphate loadings in mg/kg/week; pH in s.u.

Temperature Effects on Metal Loading Rates

The temperature effect on metal loading rates are examined by comparing loading rates observed in kinetic tests immediately before and after the tests were moved from room temperature (22°C) to a cold room (4°C). The factors by which loading rates change are presented in Table 3.

The contrasting behavior of oxyanions with divalent metal cations can be related to solubility constraints that effect mobility. Under pH neutral conditions metal cation solubility is limited by sorption and/or secondary mineral precipitation, while oxyanion forming metals are relatively soluble. Conversely, under acidic conditions the solubility of metal cations increases while sorption of metal oxyanions becomes more significant. The contrasting behavior of the oxyanions with divalent metal cations shows that aqueous speciation and related solubility constraints may play a role in determining temperature effects on metal loading rates.

The change in temperature that the kinetic tests experienced would theoretically result in a decline in pyrite oxidation rate by a factor of 0.11 to 0.37 assuming an Arrhenius relationship and the range of activation energies available in the literature for pyrite (39 kJ mol^{-1} to 88 kJ mol^{-1} from Lowson, 1982; Nicholson, 1989; and, Kamai and Ohmoto, 1999). Temperature effects on sulphate loading rates typically fall within this range (Table 3). Conversely, there is considerable variability in the temperature effects on metal loading rates which can be attributed to the additional influences of pH and the chemistry of individual elements.

Temperature effects on metal cation loading rates show a strong dependence on pH. For example, the measured loading rates of Cu, Mn, Ni and Zn change by a factor ranging from 0.15 to 0.41 in acidic kinetic tests (HC8, HC10, HC12), which is consistent with the theoretical range of 0.11 to 0.37. However, pH-neutral carbonate buffered kinetic tests (HC3, HC4, HC5, HC6, HC7, T1 and T4) loading rates change by a factor of 0.52 to 1.7, which consistently fall outside the theoretical range. In fact, the metal cations Co, Mn, Ni and Zn produce higher loading rates at cold temperatures in a number of the pH-neutral kinetic tests as shown by ratios > 1.0. Although this result is inconsistent with behaviour predicted by the Arrhenius equation that assumes reaction rates decline with temperature, previous studies have reported increases in Zn loading rates by factors of of 1.4 to 2.1 where pH-neutral kinetic tests were moved from room temperature to a refrigerated environment (SRK, 2006).

Table 3 *Ratio of humidity cell loading rates observed before and after temperature change.*

Element	HC3	HC4	HC5	HC6	HC7	T1	T4	HC11	HC8	HC10	HC12	Col 2A
pH	7.58	7.55	7.56	7.51	7.4	7.75	7.76	6.81	2.91	3.21	3.29	5.92
Alkalinity	0.89	1.26	1.13	1.08	0.95	0.94	0.94	0.92	NS	NS	NS	1.82
Sulphate	0.38	0.28	0.48	0.69	0.41	0.31	0.19	0.54	0.17	0.17	0.38	0.59
As	NS	NS	NS	NS	0.55	0.64	0.66	0.40	0.28	0.28	NS	NS
Ba	0.72	0.97	0.80	0.91	0.85	1.01	0.94	1.44	1.07	1.07	1.42	0.67
Cd	0.35	NS	NS	NS	1.23	0.64	NS	NS	0.14	0.14	0.21	0.56
Ca	0.57	0.84	0.91	0.94	0.62	0.71	0.48	0.82	0.39	0.39	0.23	0.66
Co	1.15	1.09	1.46	1.10	1.16	1.01	0.49	0.21	0.16	0.16	0.33	0.62
Cu	0.87	0.98	NS	0.42	0.98	0.90	0.52	0.26	0.18	0.18	0.29	0.72
Mg	0.56	0.86	0.81	0.79	0.56	0.69	0.50	0.75	0.13	0.13	0.15	0.63
Mn	0.98	1.35	1.77	1.47	1.01	0.89	0.99	2.42	0.20	0.20	0.41	0.61
Mo	0.34	0.19	0.43	0.35	0.32	0.37	0.26	0.14	0.65	0.65	NS	0.81
Ni	1.06	NS	NS	NS	1.08	0.73	1.13	NS	0.15	0.15	0.22	0.59
K	0.52	0.67	0.51	0.72	0.53	0.52	0.50	0.60	0.48	0.48	0.26	0.48
Se	NS	0.41	NS	NS	0.38	0.31	0.33	0.46	0.31	0.31	0.34	0.68
Si	0.45	0.72	0.57	0.57	0.63	0.69	0.55	0.59	0.41	0.41	0.39	0.50
Na	0.43	0.58	0.37	0.86	0.42	0.42	NS	0.53	0.65	0.65	0.54	0.54
Sr	0.59	0.76	0.82	0.89	0.68	0.70	0.52	0.78	0.72	0.72	0.41	0.75
U	0.88	1.44	0.73	1.92	1.08	0.20	0.24	1.44	0.13	0.13	0.21	0.38
Zn	NS	NS	NS	NS	NS	0.68	1.06	1.07	0.15	0.15	0.27	0.64

Note: "NS" means difference is Not Significant because median values at reporting limit. Ratios reported as loading rate at 4°C divided by loading rate at 22°C.

A different pH dependent trend is observed for other elements when temperature is decreased. Unlike metal cations, temperature effects on Se and Mo in pH-neutral kinetic tests show a decline in loading rates by a factor of 0.19 to 0.41. This decline is similar to behavior predicted by the Arrhenius relationship for pyrite of 0.11 to 0.37. Selenium and Mo speciate as negatively charged oxyanions that are relatively soluble at a neutral pH but are effecting by sorption to mineral surfaces under acidic conditions. Molybdenum exhibits a smaller decline in acidic samples (0.65 in HC8 and HC10) than in pH-neutral samples, which is the opposite behavior exhibited by metal cations such as Cu, Co, Mn, Ni and Zn.

These results show that the temperature effects on metal loading rates are determined, in part, by solubility constraints specific to the element in question. The mobility of metal cations in neutral pH environments is often limited by pH related solubility constraints, such as sorption and secondary mineral precipitation. In acidic samples secondary mineral formation and sorption of metal cations is less effective at controlling metal cation solubility than in neutral pH samples. The Arrhenius equation can provide a reasonable prediction of temperature effects on loading rates when metal release is governed by the primary mineral weathering rates. However, the Arrhenius equation generally over predicts temperature effects on metal loading rates when secondary solubility constraints are present.

Conclusions

This investigation examined the temperature effects on geochemical loading rates of 12 laboratory kinetic tests representing mine waste rock and tailings. The results were compared against the Arrhenius equation using the activation energy of the dominant sulphur mineral. The primary observations are as follows:

- Pyrite oxidation as measured by sulphate follows behaviour predicted by the Arhenius equation;
- K-jarosite dissolution does not follow the Arrhenius relationship due to a rise in pH at colder temperatures;
- Metal cations follow the Arrhenius relationship at acidic pH but not at neutral pH; and
- Metal oxyanions follow the Arrhenius relationship at neutral pH but not at acidic pH.

This study shows that an Arrhenius equation can accurately predict sulphide oxidation rates while loading rates of other elements do not always conform to expected behaviour. The ability of the Arrhenius equation to predict temperature effects on laboratory kinetic test can be related to the pH and aqueous speciation of the element in question. That is, elements that are relatively soluble (*e.g.,* metal cations at acidic pH) generally conform to predicted behavior while elements effected by solubility constraints do not. These results show that an Arrhenius equation can provide a reasonable prediction of temperature effects on loading rates when metal release is governed by the primary mineral weathering rates. However, the Arrhenius equation provides a poor prediction of temperature effects when geochemical loading rates are effected by secondary solubility constraints.

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Characterization of Acid Producing Potential of Spent Ore from Heap Leach Plant

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Abstract

Heap leach method is a method to process ore in a gold mine where the ore is heaped on open-air impermeable lined leach pads and irrigated with alkaline cyanide solution that percolates through the heap and leaches the gold. There are two types of heap, namely permanent or static and on-off or dynamic heap. In the static heap, the new heap cycle gold ore are placed on top of the older heap to form multiple stacking. Whereas at the end of heap cycle the spent ore in the dynamic heap will be removed from the pads and disposed in the waste dump.

Hydrothermal, in particular high sulfidation epithermal, gold ore deposit has generally been strongly overprinted by surface weathering (oxidation) mechanisms near-surface. This type of deposit is characterized by the abundance of sulfide minerals especially in the transition and fresh zones which lead to the forming of acid mine/rock drainage (AMD) both from waste rock and ore. As one of the important environmental issues in the mining operation AMD potential should be managed properly and it requires the good understanding the geochemical characterization of waste rock.

In a static heap leach operation it is also important to understand the geochemical characteristics of spent ore because it should be dumped in the waste dump after cyanide irrigation process. The results show that there is only very slight change in geochemical characterization of PAF ore after being irrigated with cyanide solutions. This finding is important in the development of AMD management measures in waste rock and spent ore dumps. Potentially acid forming spent ore should be encapsulated to prevent the formation of AMD while non-acid forming spent ore could be used as capping material in the PAF encapsulation system.

Key words: Spent ore, heap leach, acid mine drainage

Introduction

In the last 15 years several new gold mines have been developed in various part of Indonesian archipelago extracting hydrothermal type of gold deposit. Hydrothermal deposits are formed by the concentration of some elements as the product of reaction between ore-bearing hydrothermal fluid and wall-rocks. This ore systems can be found in various geological settings and are hosted in different type of wall-rocks (Zhu et al, 2011). Epithermal deposit is hydrothermal deposit formed at shallow depth and can be distinguished into two principle styles of mineralization, namely low and high sulfidation (White & Hedenquist, 1995). The shallow epithermal environment in mining areas is dominated by intensely hydrothermally altered (silica-clay-alunite-pyrite) volcanoclastic and intrusive rocks. This broader intermediate argillic alteration envelope in some areas is cross-cut by localized structures that facilitated advanced argillic alteration. Advanced argillic alteration is characterized by extreme acid leaching of the volcanic host-rock and the resulting removal of mobile cations to leave only the most acid-resistant elements in the form of stable secondary minerals (vuggy silica, silica-alunite, silica-alunite-clay, silica-clay-alunite and silica-clay). This study is related to the high sulfidation epithermal gold deposits in Indonesia that are characterized by the abundance of sulfide minerals, therefore, acid mine/rock drainage (AMD) becomes one of the important environmental issues in the mining operation as geochemical characterization has indicated the potential of AMD generation both in the ore and waste rock.

In some mines, heap leach method has been implemented to process the ore and produce dore bullion for further refining process. Heap leaching is a technique where run-of-mine or crushed and/or agglomerated gold ores are stacked over an engineered impermeable pad, irrigated with alkaline cyanide solution that percolated through the heap under atmospheric conditions. The leachates or metal loaded solutions are collected for metal recovery processes. This method is selected primarily to take advantage of its low capital cost relative to other methods although the recovery is generally lower than agitated leach plant. There are two common types of pads used in gold heap leaching, namely permanent heap construction on a pad with multiple stacking and on-off pads or single stacking (US EPA, 1994). Permanent heaps are typically built in lift where the leached ore is not removed and the new ore will be stacked on top of it. This method is sometimes defined as static heap leach. In single stacking method the spent ore will be removed from the pad and new fresh ore will be placed on the pad. This method is sometimes referred as dynamic heap method.

In the dynamic heap method, spent ore is usually placed in the waste dump. Since some of the ore is classified as potentially acid forming material, it is important to understand whether the spent ore has the potential to generate AMD, in particular when the ore before leaching is classified as potentially acid forming. Accordingly, a proper management method could be developed to mitigate the AMD problem.

Samples and Methods

The samples were taken from the dump of single stacking or dynamic heap leach spent ore after being irrigated with cyanide solution for more than 60 days. For comparison, spent ore samples were also taken from a multi-stacking heap leach which is already in operation for almost 10 years. Respective ore samples were collected from both mine sites.

All rock samples underwent static test comprising total sulfur, acid neutralization capacity (ANC), paste pH and net acid generation (NAG) tests. Column leach kinetic tests were also conducted to all samples for weeks.

Static testing allows for the direct comparison of the amounts of acidity, expressed in maximum potential of acidity (MPA) assuming it is the function of total sulfur only, and acid neutralization capacity (ANC) present in each sample. The positive value of net acid producing potential (NAPP) indicates that the sample has an excess of acid-generating minerals and classified as potentially acid forming (PAF).Conversely, excess neutralization potential is expressed by a negative value of NAPP and this sample is deemed non-acid forming (NAF). For acid generation test, the sample is mixed with a strongly oxidizing solution which is intended to rapidly dissolve all acid-forming phases. If sufficient neutralization capacity is present the NAGpH will exceed a value of 4.5 in the final solution and the sample is classified as NAF. PAF sample is defined if the produced acid outweighs the neutralization capacity indicated by NAGpH value of less than 4.5.

While static testing could not determine the kinetics of AMD generation process, kinetic testing, in this case column leach test, will give the timing of AMD onset and could be used to predict the mine drainage water quality as well.

Results & Discussion

a. Dynamic heap leach (DHL) spent ore

The results of static test for spent ore samples representing a dynamic heap leach is shown in Table 1. According to standard screening criteria both for acid-base accounting and net acid generation test the samples are classified as PAF and DHL spent ore 1 sample shows more acid potential than DHL spent ore 2.

Table 1 *Static Test Results of DHL Spent Ore Samples*

Sample Code	TS [%]	MPA*)	ANC*)	NAPP*)	NAG pH	NAG pH = 4.5*)	NAG pH = 7*)
DHL spent ore 1	2,26	69,00	0,0	69,20	2,49	50,30	57,20
DHL spent ore 2	0,45	13,78	0,0	13,78	2,94	6,70	8,30

Remarks: *) = in kg H_2SO_4/ton of rock; TS = Total Sulfur [%], MPA = Maximum Potential of Acidity, ANC = Acid Neutralizing Capacity, NAPP = Net Acid Producing Potential, NAG = Net Acid Generation

Table 2 *Static Test Results of DHL Ore Samples (Praseto, 2015)*

Sample Code	TS [%]	MPA*)	ANC*)	NAPP*)	NAG pH	NAG pH = 4.5*)	NAG pH = 7*)
DHL ore 1	2,05	62,80	0,00	62,80	2,44	26,90	30,00
DHL ore 2	0,42	12,90	0,00	12,90	2,82	9,40	10,40

Remarks: *) = in kg H_2SO_4/ton of rock; TS = Total Sulfur [%], MPA = Maximum Potential of Acidity, ANC = Acid Neutralizing Capacity, NAPP = Net Acid Producing Potential, NAG = Net Acid Generation

The high-sulfidation mineralization has been strongly overprinted by surface weathering (oxidation) mechanisms near-surface. This weathering process has produced enrichment in gold and silver and depletion in copper and sulfides resulting in an ore type that is highly amenable to the heap leaching. However, economic-grade Au mineralization may still exist at depths that are only partly oxidized or unoxidized. Naturally, these transition and fresh zones contain higher abundances of sulfide minerals (predominantly pyrite). Typical characteristics of ore samples, predominantly oxidized ore, in AMD generation is shown in Table 2. Both ore samples are classified as PAF although from the NAPP value DHL ore 2 sample is less acid potential. However, column leach test results for both ore samples are quite similar with pH range between 2 and 4 (see fig. 1).

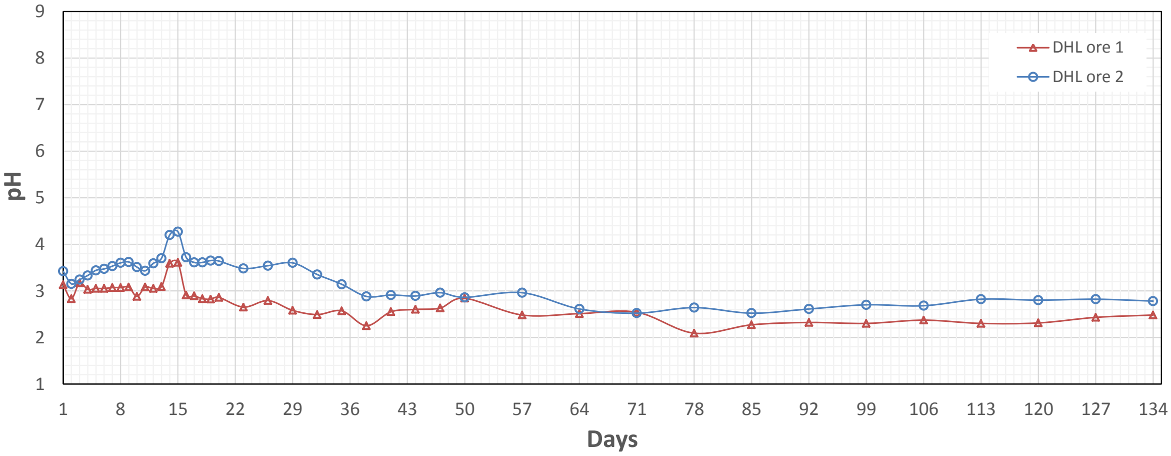

Figure 1 *Leachate pH of DHL Ore (Praseto, 2015)*

Kinetic testing for spent ore samples indicating residual alkalinity in the samples as shown in Figure 2. Lag time of approximately 29 days occurs for DHL spent ore 1 which is classified as high capacity PAF according to static test results. Different characteristics is shown for DHL spent ore 2 with more than three times longer lag time. Although it has low NAGpH this sample could be deemed as low capacity PAF due to small amount of Sulfur. Even during kinetic test it was previously predicted that this sample will not produce any acid leachates but after 92 days the leachate pH decreased drastically to 3. At the end (after 134 days) both spent ore samples produce similar leachates to the ore samples with pH values around 3.

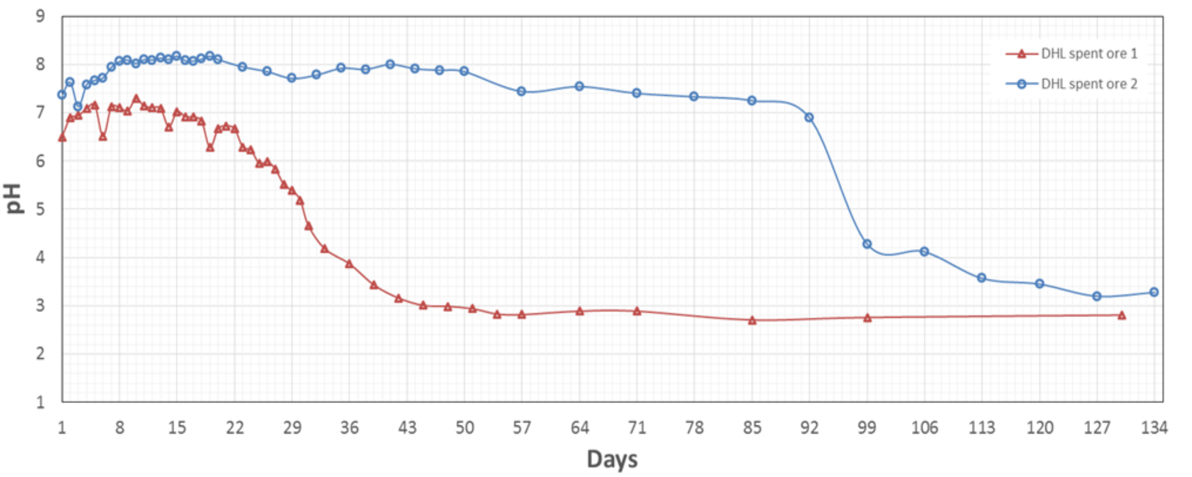

Figure 2 *Leachate pH of DHL Spent Ore*

According to Marsden & House (1992) iron sulfides could decompose in alkaline cyanide solutions to form iron cyanide complexes and various Sulfur species. However, the decomposition rate of pyrite in cyanide solutions is the lowest compare to arsenopyrite, marcasite and pyrrhotitte. It means that pyrite as the main source of AMD would not or only slightly change in the alkaline cyanide irrigation process It is confirmed with the results of spent ore characterization where both samples are still showing the potential to generate acid. The lag time in producing acid leachate during kinetic test could be interpreted as residual alkalinity in the spent ore fraction that is being washed by the time due to regular deionized water spraying.

This findings are important for the management of spent ore in the static heap leach plant. Ore characterization in AMD generation will not be changed after being irrigated by cyanide solution in the heaps meaning that PAF ore will still become PAF spent ore. Understanding the ore geochemical characteristics in AMD sensitive gold mine becomes important in developing proper spent ore management to minimize the environmental risk by preventing AMD generation.

b. Spent ore from multiple stacking heap leach

In multiple stacking heap leach, the ore for next leaching cycle will be stacked on the top of leached ore from previous cyanide irrigation and the leached ore will stay on the pad forever. During post closure the heap pad will be covered and rehabilitated. But we are fortunate because there is a plan to re-process the old heap since economic amount of gold is still be found in the spent ore. Re-excavation work of old heap provide the opportunity to take old spent ore samples that already in the leach pad for more than 10 years. Three spent ore samples (defined as SHL spent ore) were selected that represent the ore from oxidation zone.

The result of static tests for SHL spent ore is presented in Table 1. According to NAPP criteria, all samples are classified as PAF with high capacity (>100 kg H_2SO_4/ton of rock). This classification is also confirmed with NAG test results with NAGpH below 4.5.

Table 3 *Static Test Results of SHL Spent Ore Samples*

Sample Code	TS[%]	MPA$^{*)}$	ANC$^{*)}$	NAPP$^{*)}$	NAG pH	NAG pH = 4.5$^{*)}$	NAG pH = 7$^{*)}$
SHL Spent Ore 1	7.39	226	<0.50	226	3.98	0.80	2.80
SHL Spent Ore 2	6.83	209	<0.50	209	2.71	34.30	41.10
SHL Spent Ore 3	6.23	191	2.70	188	2.80	20.70	29.40

Remarks: *) = in kg H_2SO_4/ton of rock; TS = Total Sulfur [%], MPA = Maximum Potential of Acidity, ANC = Acid Neutralizing Capacity, NAPP = Net Acid Producing Potential, NAG = Net Acid Generation

Respective ore samples were selected from core of oxidized zone in the mining area. They have quite similar characteristics to the spent ore and are deemed as PAF with high capacity (NAPP > 100 kg H_2SO_4/ton of rock and NAGpH < 3).

***Table 4** Static Test Results of SHL Ore Samples*

Sample Code	TS[%]	MPA*)	ANC*)	NAPP*)	NAG pH	NAG pH = 4.5*)	NAG pH = 7*)
SHL Ore 1	4.78	146	0	146.00	2.53	39.30	47.00
SHL Ore 2	11.60	355	0	354.96	2.32	79.50	91.10
SHL Ore 3	8.09	248	0	248.00	2.47	52.30	62.50

Remarks: *) = in kg H_2SO_4/ton of rock; TS = Total Sulfur [%], MPA = Maximum Potential of Acidity, ANC = Acid Neutralizing Capacity, NAPP = Net Acid Producing Potential, NAG = Net Acid Generation

Kinetic tests for both ore and spent ore samples were conducted for more than 55 days and the results are shown in Figure 3 and 4. While the ores are showing similar trend in leachates quality (pH value 1.5 to 3.4) which are in line with the static test results (PAF high capacity), the results for spent ore samples are showing different values, in particular spent ore 3 that is defined as high capacity PAF with NAPP = 288 kg H_2SO_4/ton of rock and NAGpH < 3.

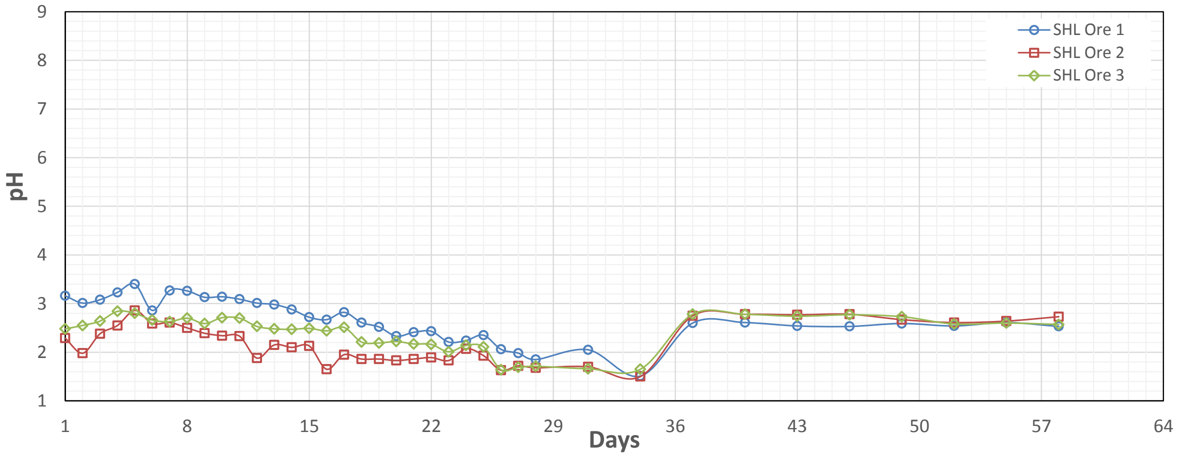

***Figure 3** Leachate pH of SHL ore*

Leachate pH values for SHL spent ore 3 are in the range of 6.8 to 8.1 compare to the acidic leachate values of other spent ore samples (see fig 4). Since the static testing result showing high capacity PAF, spent ore 3 sample seems to contain residual alkalinity from cyanide irrigation process similar to trend in dynamic heap leach. Longer kinetic testing up to 20 weeks would explain whether the alkaline characteristic is permanent or it is only residual alkalinity from the irrigation process.

There is similarity between SHL and DHL spent ores characteristics from AMD perspectives. Final leachates in kinetic testing indicated acid producing capacity of samples that confirmed with the results of static testing. Cyanide irrigation process would not change or, if any, only very small change, the geochemical characteristics in AMD generation of the ore in the leach pad.

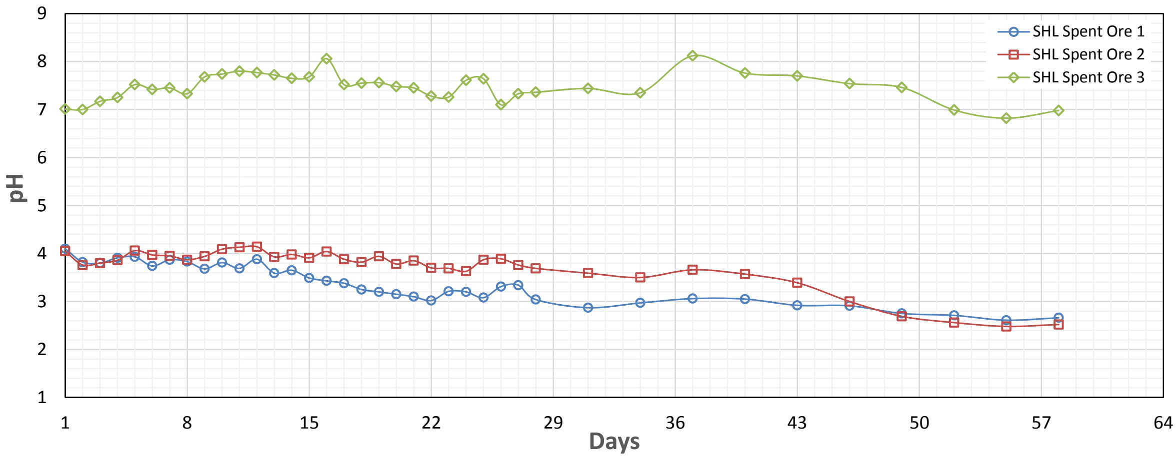

Figure 4 *Leachate pH of SHL spent ore.*

Conclusions

High sulfidation epithermal gold deposit is characterized by ore which is suitable for heap leaching process. Having abundance of sulfide minerals particularly in from weathering transition and fresh zones, acid mine/rock drainage is one of the important environmental issues in the mining operation of such deposit generated both by waste rock and ore. In an on-off or single stacking heap leach operation, the leached ore, defined as spent ore, will be removed from the pad and dumped together with waste rock and should be treated accordingly.

From the static testing criteria spent ore samples from dynamic or single stacking heap leach plant were classified as PAF, however, they have shown lag time in producing acid leachates during kinetic testing. There were indications of residual alkalinity from cyanide solution irrigation process which occurred in alkaline environment to optimize gold leaching process. It also could be concluded that only very small amount of pyrite have been decomposed during the cyanide irrigation process in the heap as shown in the final leachate pH of 3 after almost 20 weeks of column spraying which is similar to the leachate pH of ore columns. Similar results have been observed for spent ore samples from permanent or static heap leach operation.

The characterization of spent ore in dynamic heap leach operation is important in the AMD management of the mine. PAF spent ore should be placed accordingly to prevent the AMD generation. Encapsulation of PAF spent ore and PAF waste rock will be the best option in securing the long term reliability.

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Acid- and base-neutralization capacity in mine water and brines

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Extended Abstract

Acidimetric and alkalimetric titration to the endpoint of pH 4.2 and 8.3 is commonly used in water chemistry to determine the amount of inorganic carbon species in water [1]. However, in mine water and brines the determination of inorganic carbon species should not be based on this method because buffering components such as polyvalent metals (e.g. iron, copper, manganese), non-carbonic acids (hydrogen sulfide, sulfuric acid, phosphoric acid, boric acid, silicic acid, organic acids, etc.), and the acid-base behavior of metals (aluminum, manganese, zinc, nickel, etc.) may be dominant and lead to completely wrong results with respect to the carbon species. As a kind of go around the hot peroxide acidity procedure is widely used for measuring the acidity of mine drainage. In this context, the poorly defined terms "net alkalinity" and "net acidity" are commonly used in particular in the mine-water community [2].

However, a better defined and more reliable approach is to determine the total inorganic carbon (TIC) by means of TIC analysis using NDIR (non-dispersive infrared) spectroscopy and then calculating the carbon species in the water based on the pH of the investigated water by using a thermodynamic speciation code like PHREEQC. Additionally, the acidimetric or alkalimetric titration curve provides hints on the buffer capacity of the water while the endpoint values are only of minor or no interest. The other elements can be determined by ion chromatography, ICP-MS or other modern technologies. Species distribution calculation will then be done with the help of chemical thermodynamic modeling, using e.g. PHREEQC, proving additional information such as saturation indices for certain minerals.

Two examples are presented: The first is the brine from the lithium-rich Salar der Uyuni, Bolivia, where boric acid dominates both alkalinity and acidity, which leads to completely wrong results for the carbon species if this is not considered. The second example presented is acid water from the pit mine lake Burghammer, Germany. For this water with a pH of 2.9 the titration curve and endpoints show that carbonic acid only plays a minor role for the buffer capacity of the water. Even after liming of the water to maintain neutral pH values, the alkalinity and acidity end-points do not reflect the carbonic acid species. They are overestimated by one order of magnitude by using the endpoints of titration in comparison to the TIC analysis readings.

Key words: alkalinity, acidity, silicate, borate, sulfide, metal, TIC, titration, thermodynamic model, PHREEQC

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Geochemical trends in evaporative tailings ponds – an experimental study

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Abstract

Environmental best practices and practical considerations commonly require mines to store process water in large reservoirs such as tailings ponds. In many jurisdictions, mining companies need to demonstrate an understanding of the geochemical evolution and environmental impact of such reservoirs. The development of predictive mine drainage chemistry models is commonly complicated by the highly variable geochemical behaviour of the different dissolved constituents in contact with exposed mine materials. In dry environments, the geochemistry of tailings ponds may be driven by evapo-concentration where certain dissolved species become more strongly enriched than others. This discrepancy is especially evident in neutral environments where the concentrations of many species are solubility-controlled.

To better understand the relative attenuation mechanisms occurring in an evaporative tailings pond, a small-scale (30L) laboratory pond was subjected to approximately 96% evaporation where seven water samples were collected and analyzed at different evaporation steps over a time period of 21 days. The experimental pond water was in contact with a layer of non-acid generating tailings to provide nucleation and adsorption sites. Measured and theoretical concentration factors for several species were calculated and compared at each evaporation step to put the brine evolution into context.

The pH remained circum-neutral and increased slightly from 7.7 to 8.2 over the course of the experiment. Decreasing redox conditions were indicated by an increasing NO_2/NO_3 ratio. Other geochemical trends with degree of evaporation suggested that Ca and alkalinity were limited by calcite precipitation early on, while Ca and sulphate precipitated as gypsum during slightly more evolved stages of the test. Visible gypsum did in fact form on the pond surface, consistent with the timing of the geochemical signature. Other major cations (K, Na, Mg) behaved conservatively. The geochemical behaviour of dissolved trace metals and metalloids was variable. Base metals Cu, Co, N, and Zn were effectively scavenged by co-precipitation and/or adsorption onto secondary phases, most likely Fe-hydroxides. Metalloids that form oxy-anionic complexes were attenuated (As, Sb) or behaved conservatively (Mo, Se) becoming progressively enriched in the evolving brine. For Mo in particular, the dissolved geochemical load increased as the pond water became more brine-like. This is interpreted to be a result of desorption or other mobilizing processes releasing Mo from the material in response to the slight increase in pH. Comparison of the apparent mass loadings removed from solution with the elemental budget in the secondary precipitate indicates that, especially for strongly solubility-controlled species, ion exchange between tailings and water occurs to attain or approach geochemical equilibrium. These results give new insight into the relative solubilities of various species in neutral evaporative tailings ponds, highlighting the effect of minor changes in the ambient regime (e.g., pH, Eh) on the aqueous geochemical composition.

Evapo-concentration, tailings pond, mine drainage, aqueous geochemistry, adsorption

Introduction

Tailings storage facilities (TSFs) are integral components of many mining operations and can cover many square kilometers of land, causing these facilities to have a major impact on the local water balance. Various types of tailings disposal strategies exist (e.g., tailings slurry deposition, dry stack, etc.) where TSF designs are commonly governed by site geographical constraints, climate, and environmental considerations. Where tailings are deposited in the form of a slurry, tailings ponds commonly form and inundate portions of the settled tailings. The surface area of such tailings ponds can vary significantly seasonally as new tailings are added and as a result of precipitation and evaporation. Environmentally, establishing a pond in the TSF can be advantageous as it increases the proportion of wetted tailings, which inhibits the oxidation of pyrite and, therefore, acid production. However, tailings ponds may serve as a water source for mining or other (e.g., agricultural irrigation) purposes and become part of the local ecosystem long-term. Therefore, the prediction of the geochemical and hydrogeological regime is crucial, and most commonly a regulatory requirement, to avoid contaminant transport into the receiving environment. Particularly in arid climates, evaporation will strongly affect the TSF pond water reservoir leading to the enrichment of dissolved geochemical species, sometimes to brine-like concentration levels. Due to the highly variable behavior and saturation indices of the various dissolved species, modelling the geochemistry of an evolving evaporative water body in contact with fine-grained tailings solids can be challenging. Previous studies investigating the effect of evapo-concentration on water chemistry have largely focused on major elemental trends in salt lakes (e.g., Deocampo & Jones 2013), however little is known about the geochemical evolution of minor and trace elements in such systems. To gain an understanding of the mechanisms controlling the geochemistry of evaporating tailings ponds for parameters that are commonly of concern in mine drainage, a small-scale experiment simulating an evaporating tailings pond was conducted. The results of this study are intended to help constrain solubility maxima, the relative timing of reaching the latter as well as mechanisms controlling tailings-water interactions.

Methods

The tailings pond was simulated by filling an acid-cleaned, chemically resistant polyethylene (49 L) tub with 7.1 kg of a dry tailings composite and 30.2 kg of tailings supernatant (fig. 1). Once the tailings material had completely settled, a water sample was collected to determine the initial pond-water chemistry.

In the initial stages of the experiment, three 100 watt lamps were installed facing the analogue pond to accelerate evaporation. For the final experiment configuration, a 900/1500 watt fan heater was used to accelerate evaporation.

Evaporation was monitored by weighing the container and calculating the mass lost by evaporation. Eight ~100 mL samples were collected from the pond at various evaporation stages of the experiment. The timing of sample collection was based on geochemical and practical constraints, where a geochemical speciation model (PHREEQC) was run to identify residual water volumes at which evaporation would have a relevant geochemical effect that can be used for TSF considerations. Sample volumes and corresponding evaporation stages are reported in Table 1.

The water samples were extracted from the top of the experimental pond using a clean syringe and filtered using a 45 µm syringe filter. Samples were tested at the Lorax lab for pH, alkalinity, and conductivity. A sample aliquot was also preserved in-house and sent to ALS Laboratories in Burnaby, BC for analysis of anions, total-phosphate, dissolved metals and acidity.

Between the second and third sampling event grains of light-coloured, flaky precipitates were observed on the water surface. These aggregates grew in diameter over the course of the experiment and eventually sank to the bottom of the experimental container. After the last water sample was collected, the tailings were allowed to air-dry completely. Precipitate flakes (19 g) were extracted from the top of the tailings using acid-cleaned plastic tweezers (fig. 1). The precipitate was sent to SGS Laboratories in Burnaby, BC for solid-phase analysis (aqua regia digest with ICP-MS finish).

Table 1 *Sampling schedule and volumes*

Sampling Step	Date Sampled	Total Mass Before Sample (kg)	Sample Taken (L)	Evaporated
0	March-04-15	38	0.11	0%
1	March-13-15	25	0.11	44%
2	March-18-15	19	0.11	68%
3	March-20-15	15	0.11	79%
4	March-23-15	14	0.11	85%
5	March-24-15	13	0.095	89%
6	March-24-15	11	0.10	93%
7	March-25-15	10	0.12	96%

Figure 1 *Bench-scale experimental tailings pond (left) and precipitate on top of dry pond (right)*

Results and Discussion

Ongoing evaporation of a standing water body will result in the oversaturation and attenuation of most, if not all species at different points in time and at different levels. Analytical results of the water chemistry at the various evaporation steps are provided in Table 2. The geochemical composition of the tailings material in contact with the experimental pond water is given in Table 3. To put the experimental results into context for each species, measured concentrations were compared to modelled values that would be expected if no solubility limits existed. These theoretical concentrations were calculated incrementally as a function of evaporation based on the assumption that all dissolved species accumulate linearly proportional to the amount of water being lost. For this, a concentration factor needs to be defined for each calculation step to account for the amount of geochemical load being lost during the water sampling events. In a very general sense, this can be written as

$$F_{tx} = C_{sx}/C_{s0} \qquad \text{(eq. 1)}$$

where F_{tx} is the theoretical concentration factor at evaporation step x, C_{sx} is the dissolved concentration of species s at the same evaporation step, and C_{s0} is the initial dissolved concentration of species s. Since water is being removed for sampling, the cumulative concentration factor is the product of the incremental concentration factors F_{ti} that have to be calculated for each evaporation step:

$$F_{tx} = \prod F_{ti} \qquad \text{(eq. 2)}$$

The theoretical incremental concentration factor F_{ti} can be calculated as a function of the evaporative water loss between each sampling cycle which, in turn, can be derived based on the water sample volumes extracted:

$$F_{ti} = 1/[1-(V_e/(V_r-V_s))] \qquad \text{(eq. 3)}$$

where V_e, V_r, and V_s are the water volumes evaporated, remaining in experiment, and sampled, respectively. The cumulative theoretical concentration factor F_{yx} can then be compared with the measured concentration factor F_{mx} at the same evaporation step x, calculated as

$$F_{mx}= C_{mx}/C_{m0} \qquad \text{(eq. 4)}$$

where C_{m0} and C_{mx} and are the measured initial and evolved concentrations at evaporations step x, respectively. In general, it can be expected that $F_{mx} < F_{tx}$, due to secondary mineral controls and/or adsorption mechanisms in the natural system. The closer F_{mx} approaches F_{tx}, the more conservative the according dissolved species behave.

Table 2 *Geochemical composition of water samples collected at different evaporation steps during the tailings pond experiment*

Evap. step	0	1	2	3	4	5	6	7
Water volume (L)	29	16	9.2	6.0	4.2	3.2	1.8	1.1
% evaporated	0%	44%	68%	79%	85%	89%	93%	96%
pH	7.73	7.88	7.97	7.96	8.04	N/A	8.09	8.21
Alkalinity	62	103	12	10	151	#N/A	234	283
SO_4	1750	3070	3110	3290	3270	3450	4320	5970
Cl	109	193	325	469	610	744	1010	2010
NO_3	1.2	1.9	3.1	4.4	6.2	7.7	10	21
NO_2	0.022	0.29	0.62	0.95	1.0	1.2	1.5	2.8
Al	0.0037	0.0032	0.0079	<0.0025	0.0053	0.0031	0.0040	0.0053
Sb	0.0037	0.0054	0.0071	0.0093	0.0093	0.0095	0.014	0.021
As	0.0024	0.0026	0.0033	0.0043	0.0044	0.0045	0.0064	0.0087
Cd	0.000022	<0.000025	0.000033	<0.000025	<0.000025	<0.000025	0.000044	0.000035
Ca	602	1090	905	859	724	656	841	653
Co	0.0014	0.0037	0.0057	0.0070	0.0074	0.0074	0.010	0.014
Cu	0.0069	0.014	0.021	0.021	0.022	0.023	0.031	0.042
Fe	<0.002	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.0090
Pb	0.000042	<0.000025	0.000032	<0.000025	0.000047	<0.000025	0.000029	0.000074
Mg	48	103	165	263	355	361	590	1080
Mo	0.047	0.17	0.33	0.52	0.69	0.80	1.3	2.7
Ni	0.0041	0.0066	0.0093	0.012	0.013	0.012	0.018	0.026
K	30	59	90	129	167	171	255	393
Se	0.0026	0.0059	0.0096	0.015	0.021	0.024	0.037	0.076
Na	58	106	161	258	345	376	563	1110
Zn	<0.001	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025

Notes: all concentrations are given in mg/L; alkalinity is reported in units of mg $CaCO_3$/L

A comparison of F_{mx} and F_{tx} is plotted for dissolved anions in Figure 2a with increasing values on the x-axis being equivalent to increasing water loss volumes where the circles on the curves represent evaporation steps x. The highest theoretical concentration factor has a value of 22.9, corresponding to an evaporative water loss of 96%. Sulphate becomes solubility-limited at relatively low evaporative water losses, Cl and NO_3 behave nearly conservatively. Alkalinity shows a decrease in the measured concentration factor which can be interpreted to be a result of both atmospheric equilibration and carbonate precipitation. In later stages of the experiment, this parameter closely follows the trend observed for sulphate. In this context, it should be noted, however, that pH systematically increases from 7.7 to 8.2 throughout the course of the experiment. Interestingly, measured NO_2 concentrations increase much more dramatically than predicted by the theoretical model suggesting that this anion becomes relatively enriched by other processes in addition to evapo-concentration. This is interpreted to be a result of the lower solubility of oxygen in highly saline water leading to more reducing conditions in the tailings contact water with water evaporation. The same effect would be caused by an increasing temperature which is to be expected in an evaporating water pool exposed to heat lamps. In natural systems, the decrease of redox potential may also be related to the metabolism of organic matter by heterotrophic bacteria which in turn drive oxygen consumption (Deocampo & Jones 2013). It should be noted that the loss of NO_3 strongly outweighs the increase of NO_2 concentrations, such that an overall loss of nitrogen load is observed, likely through denitrification or adsorption.

Previous studies have found that compositional trends in evaporative environments can be traced based on major anionic concentrations (e.g., Hutchinson 1957), where evolving brines tend to lose alkalinity and sulphate over time, as chloride is enriched. This trend is consistent with observations from the laboratory experiment, in which chloride behaves the most conservatively among these three anions (fig. 2a).

Major cation concentrations are generally controlled by the contact material (i.e., tailings) and mineral saturation indices in the evaporating waters. Due to its high solubility, Na is by far the most common cation in evolving brines of evaporative, natural salt lakes. Magnesium, Na, and K, all follow relatively similar concentration trajectories, where Mg falls closest to the 1:1 line (fig. 2b), suggesting that this species is evapo-concentrated conservatively with little or no mass loss to mineral precipitates or adsorption. Evidently, the major cation removal mechanism is that of calcite and gypsum precipitation as Ca increases only slightly in the first sampling cycle after which it is being removed from solution as solubility limits are reached. This is consistent with both sulphate and alkalinity following similar trends (fig. 2b). The dip in the alkalinity curve relatively early on in the experiment can therefore be explained by the rapid crystallization of calcite, directly followed by gypsum/anhydrite saturation and re-equilibration of alkalinity with the atmosphere. This is consistent with the theoretical mineral precipitation sequence observed in most saline lake regimes (e.g., Deocampo & Jones 2013) and the first visible occurrence of flaky mineral precipitates at the water surface between evaporation steps 2 and 3 (fig. 1). Commonly, in natural brines Mg-rich calcite and dolomite is precipitated before gypsum saturation is attained, however, this depends on the Mg/Ca ratio as well as the availability of CO_3 in solution. The supernatant water used for the experiment has a relatively high initial concentration of both Ca and SO_4, likely causing an earlier onset of gypsum precipitation than would be expected in natural waters and therefore suppressing Mg saturation. The concurrent 'kink' in Mg, Na, and K concentration factors between evaporation steps 4 and 5 may be an analytical artifact or the co-precipitation of these species in a pulse of a Ca-phase crystallization, but the trajectory of the trend line suggests it is unlikely to be caused by the precipitation of discrete Mg-, Na-, K-bearing minerals.

It is known that many dissolved trace metals that may be of environmental concern in neutral mine drainage are strongly attenuated through adsorption and co-precipitation while others remain in solution over a relatively wide range of pH and redox conditions (Chapman et al. 1983; Cravotta & Trahan 1999). Hydrous ferric oxides (HFO) and Al-hydroxides are highly insoluble under oxidizing, circum-neutral conditions and, especially the former, have been shown to represent a major sink for dissolved trace metals, mostly due to their amorphous nature and large surface area. Both Al and Fe are actively being removed from solution as indicated by the consistently low concentrations below detection limit (Fe) or within a factor of two of their initial concentration (Al) in the most concentrated solution. Only after the last evaporation step does Fe have a detectable concentration of 0.009 mg/L, possibly a result of the increasingly reducing conditions and the higher relative proportion of the more soluble Fe^{2+} versus Fe^{3+}. A F_{mx}-over-F_{tx} plot for Co, Cu, and Ni is shown in Figure 2c, and illustrates that attenuation mechanisms are efficiently scavenging these metals after evaporation step 3 (79% water loss) leading to a flattening of the curves. A slight increase in concentration is nevertheless observable as water continues to be evaporated.

Metalloids such as As, Mo, Se, and Sb are commonly the most problematic parameters in neutral mine drainage as they form anionic complexes in solution which are not easily adsorbed at low H^+-activities. A bimodal trend is evident for measured concentration factors of these species in Figure 2d, where As and Sb become attenuated, while Se and Mo are slightly to moderately enriched in the evaporating solution. The latter process is only possible if a geochemical load from the tailings material is in fact added to the aqueous phase. This indicates that, in response to changing geochemical conditions in the evolving brine, Mo and to a lesser degree Se loads, are not only kept in solution but have increased solubility as the tailings contact water undergoes evapo-concentration. The most plausible explanation for this trend is the slight increase in pH over the course of the experiment leading to a suppression of selenate and molybdate adsorption capacities and therefore, leading to the solubilization of these species from the tailings material. The sensitivity of Se and Mo solubility to pH in a circum-neutral regime is well-documented by several adsorption studies (e.g., Balistrieri & Chao 1990).

As the evaporating tailings contact water evolves into a progressively more saline brine, it becomes supersaturated with respect to certain species. As shown in Figure 1, a flaky, colourless precipitate formed at the water surface between evaporation steps 2 and 3. These crystals grew in diameter over the course of the experiment and eventually sank to the tailings-water interface. After termination of the experiment, this phase was sampled and submitted for solid-phase (aqua regia digest) analysis. One way

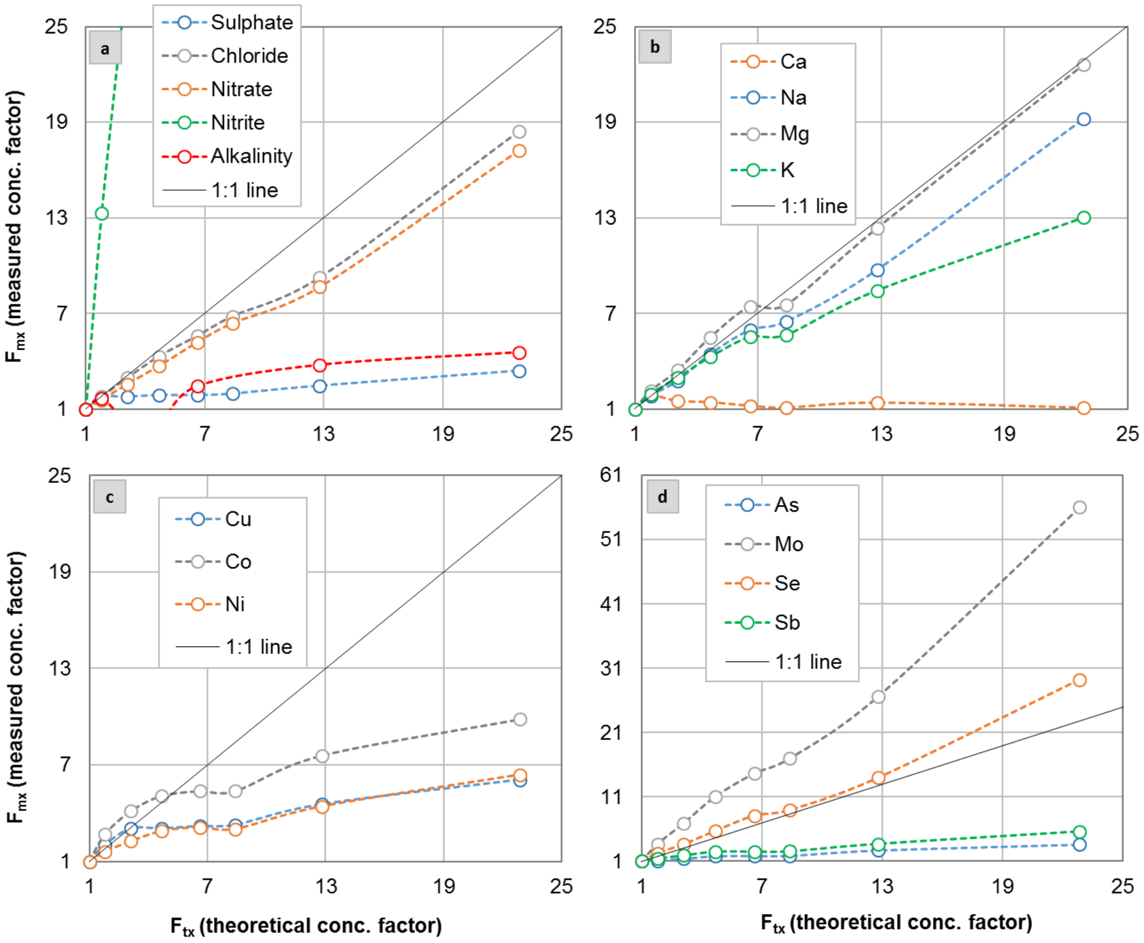

Figure 2 *Theoretical versus measured concentration factors for selected dissolved species in water samples from the bench-scale tailings pond evaporation experiment*

to assess the solid-phase secondary phase data is by comparison with the mass balance budget (i.e., geochemical loads) in the evolving brine and the total mass lost from solution for each species through attenuation mechanisms. The total mass lost from solution due to geochemical processes can be calculated as the sum of geochemical loads lost during all evaporation increments accounting for the dissolved mass lost as a result of sample collection. A geochemical load L is hereby defined as:

$$L = C \times V \qquad \text{(eq. 5)}$$

Theoretically, using this approach the relative impact of secondary mineral precipitation and adsorption on the individual dissolved species can be constrained. Furthermore, comparison of the total mass lost throughout the experiment with the mass budget of the secondary precipitates provides insight into partitioning elemental behaviour into this phase and the impact of its formation on the water chemistry. However, it was observed that the collected secondary precipitate contained impurities of tailings likely causing contamination in the solid-phase analysis. To assess the magnitude of contamination, the aqua regia digestible solid-phase composition of the secondary precipitate (tab. 3) was compared with that of the tailings material. Assuming that the tailings material is homogeneous and that certain elements will have a negligible concentration in the experimental pond water (and therefore in the pure secondary precipitate phase), the lowest ratio of a precipitate constituent relative to its content in the tailings phase should give an approximation of the degree of tailings contamination in the precipitate phase. Applying this approach to the entire suite of measured elements yielded that tailings impurities make up around 20% of the secondary precipitate mass. A corrected solid-phase composition can hence be calculated as:

$$S_{PC} = S_{P0} - 0.2 \times S_T \qquad \text{(eq. 6)}$$

where S_{PC} and S_{P0} are the corrected and measured solid-phase content for a given species, while S_T is the solid-phase content for the same species in the tailings.

Due to analytical constraints, the precise solid-phase contents of Ca and S in the secondary precipitate are reported as overlimit results (tab. 3), which in consideration of the other analyzed constituents suggests that the predominant secondary mineral phase is gypsum. For the remaining species, the corrected precipitate composition was converted into absolute mass loads (by normalization to an adjusted precipitate mass of 14.4 g) and contrasted with the calculated mass lost from solution during the experiment if the dissolved concentration was consistently above the detection limit (tab. 3). Absolute mass loads of Al, Co, and Ni were found to be greater than those that are apparently attenuated during the evaporation experiment. Notwithstanding analytical limitations and uncertainties related to the total mass of the precipitate, this indicates that the tailings material may selectively act as a source for dissolved constituents as the brine evolves. For Al in particular, the mass contained in the collected precipitated phase by far exceeds the dissolved Al budget in the experimental pond. Since this species is strongly solubility-controlled under neutral conditions and is expected to form a discrete phase rather than partition into gypsum, it is inferred that ionic exchange between the tailings and the pond-water may occur for selected constituents to attain geochemical equilibrium. As such, the low apparent mass load removed from solution for some species should not be considered absolute values but rather represents an overall net budget with a geochemical exchange between the different media constantly occurring (Eugster 1980), depending on the changing geochemical regime. The net addition of Mo loads from the tailings material to the evolving brine supports this finding.

The mass of many other species detected in the precipitate only constitutes a small fraction of the attenuation budget (tab. 3). Notably, the major ions Mg, K, and Na account for less than 10% their respective loads lost during the evaporation experiment indicating that (i) these species are being attenuated by different a means such as physically separated discrete phases and/or adsorption and (ii) the gypsum phase is relatively pure with little fractionation of major cations, other than Ca, occurring.

Table 3 *Composition of solid-phase materials and mass balance of evaporation experiment*

	Tailings	Secondary Precipitate			Total Load removed	Precipitate impact
		Measured	Corrected	Absolute mass		
	ppm/%	*ppm/%*	*ppm/%*	*mg*	*mg*	
Al*	1.8	0.42	0.06	8.84	0.10	8749%
As	5.3	3	1.93	0.03	0.060	46%
Ba	145	31	1.62	0.02	0.56	4%
Ca*	3.9	>15	*N/A*	*N/A*	16649	*AL*
Cd	0.034	0.04	0.03	0.00048	0.00060	80%
Co	27	7.7	2.27	0.033	0.026	124%
Cu	475	104	7.90	0.11	0.16	72%
Fe*	3.4	0.73	0.04	5.75	0.049	*AL*
K*	0.16	0.08	0.05	6.80	488	1%
Mg*	1.7	0.55	0.20	28.87	331	9%
Mn	290	97	38.35	0.55	1.7	32%
Mo	35	10.7	3.53	0.05	-1.2	-4%
Na*	0.050	0.11	0.10	14.38	589	2%
Ni	81	23.8	7.42	0.11	0.093	115%
S*	0.23	>5	*N/A*	*N/A*	44472	*AL*
Sb	0.17	0.11	0.08	0.0011	0.086	1%
Se	<1	<1	*N/A*	*N/A*	0.0013	*AL*
Sr	74	662	647	9.32	88	11%
Zn	23	9	4.42	0.06	0.026	*AL*

Notes: *species reported in % unless otherwise stated; AL = not reported due to analytical limitations; Precipitate impact is calculated as the absolute mass over the load removed per species.

Conclusions

A bench-scale experiment was conducted simulating the evaporating environment of a tailings pond in an arid climate. The key geochemical findings from this experiment are:

- The pH remains circum-neutral and increases slightly from 7.7 to 8.2 over the course of the experiment;
- As to be expected for neutral waters, dissolved Fe and Al concentrations remain low, likely as a result of Fe- and Al-hydroxide precipitation;
- Ca and alkalinity are limited by calcite precipitation early on, where Ca and SO_4 precipitate as visible gypsum shortly after. Other major cations (K, Na, Mg) behave relatively conservatively at the concentrations attained in the experiment but would likely precipitate as distinct phases if the concentration of these species was greater in the initial solution;
- The geochemical behaviour of dissolved trace metals and metalloids is variable in the tailings contact water as evaporation proceeds:
    - Base metals Cu, Co, and Zn are effectively scavenged through co-precipitation with and/or adsorption on secondary phases, most likely Fe-hydroxides;
    - Nitrate is transformed into nitrite and likely removed from solution via denitrification;
    - Metalloids that form oxy-anionic complexes may be attenuated (As, Sb), or behave conservatively (Mo, Se) becoming progressively enriched in the evolving brine. For Mo in particular, a geochemical load may even be added from the solid tailings material. This is interpreted to be a result of desorption or other mobilizing processes related to the slight increase in pH;
- Comparison of the apparent mass loadings removed from solution with the elemental budget in the secondary precipitate indicated that, especially for strongly solubility-controlled species, the ion exchange between tailings and water is required to attain the observed equilibrium concentrations in the final evaporative solution and to account for the calculated mass balance. This shows that the evolving brine chemistry is not solely driven by “one-way” attenuation mechanisms, but adapts to the changing geochemical conditions.

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Advanced Customisable Leach Columns (ACLC) – A New Kinetic Testing Method to Predict AMD risks by Simulating Site-specific Conditions

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Abstract

One of the most significant issues in the prediction of how waste materials will evolve geochemically within waste storage facilities is the applicability of scaling laboratory test results to field conditions. This is an important aspect laboratory data is primarily used for predictive calculations to determine geochemical evolution of waste materials in the field. This issue has arisen predominantly as a result of the relative paucity of field monitoring data from waste rock storage facilities (WRSFs) and the fact that laboratory test methods are not typically linked to specific field conditions rather are based on generic standardised methods. This issue is compounded by the fact that the majority of the test methods used are based on technology now over ten years old.

To address the limitations of current laboratory kinetic testing methods a new method has been developed by OKC that can accommodate and replicate site specific conditions. This method is termed the advanced customisable leach column (ACLC). The highly engineered columns have allowed for field conditions to be simulated in a laboratory setting.

OKC has utilised site data from instrumentation placed in multiple waste rock dumps as the basis of design and field calibration of the method. Key features of the columns include both their capacity, size and technical specification. The inclusion of fully programmable solenoid controlled air supply, ability to operate under very low liquid solid ratios, and in line heating options allow for variable water flux, airflow and pressure as well as temperature control. Columns can therefore be adapted for different conditions depending on site specific conditions and variability. Ongoing monitoring of the column conditions by automated temperature control and monitoring, automated oxygen consumption and carbon dioxide production monitoring, and soil moisture/matric suction monitoring enable rapid and reliable data collection for interpretation.

Key words: Pyrite oxidation rate, kinetic testing, liquid solid ratio

Introduction

The prediction of how waste materials will evolve geochemically within waste rock storage facilities (WRSFs) has been the subject of many hundreds of thousands of hours of research by geoscientists globally. Despite the quantity of research there are two significant areas of uncertainty that remain as partially resolved issues: (a) the majority of the research carried out has been at the laboratory not site scale leading to uncertainty over the applicability of scaling laboratory test results to field conditions (b) many predictions made using computer modelling have not, or are not normally able to be, validated from site data.

These areas of uncertainty have arisen predominantly as a result of the relative paucity of relevant field monitoring data from WRSFs and the fact that laboratory test methods are not typically linked to specific field conditions. They are more commonly based on generic standardised methods and are designed primarily to simulate accelerated weathering conditions that do not relate to field conditions in a linear manner.

To address these specific issues the authors have over the last three years made significant progress in the gathering of field data to determine internal WRSF geochemical and hydrological conditions. This has been achieved as a result of the development and deployment of advanced field monitoring equipment within numerous WRSFs. The findings from data collected from these monitoring installations have previously been reported in a number of papers presented through 2013-2014 (Pearce and Barteaux, 2014a; Pearce and Barteaux, 2014b). A range of WRSFs were investigated to include both active facilities and historical closed facilities of around 10-30 years in age. These investigations included approximately 2,000 m of sonic drilling, the recovery and detailed analysis of over 2,000 samples of core material and the installation of over 200 sensors at depths between 5 and 140 m within the waste which have provided over 5 million points of monitoring data to date and are still actively generating data.

The quantity and quality of materials testing and in situ monitoring data collected has provided OKC the opportunity to assess and evaluate the comparability of laboratory testing methods to the macro scale. In addition these data have allowed OKC to determine the specific factors related to in situ field conditions that act as the main controls on geochemical evolution of waste materials in field conditions

OKC has used this data to develop a new test method termed the advanced customisable leach column (ACLC).

Methods

Scalability of testing methods

Laboratory testing methods have been developed and refined over many years for geochemistry assessment and acid and metalliferous drainage (AMD) predictions, which has resulted in a broad set of standardised testing methods being generally accepted internationally by the mine-geochemistry industry. This has been possible by and large because laboratory experiments are completed in a controlled environment with high degree of precision and accuracy. However common factors, and consequently the limitations, to all laboratory assessments is the scale at which these experiments are carried out, and the conditions under which they are carried out.

Indeed, it is the rational for the design of these laboratory tests that presents possibly the most significant challenge. The primary rationale for these tests has been, in general to create a low cost, bench top scale test, using existing technology, to simulate an environment of ‘accelerated weathering’ so that oxidation rates can be studied in short timeframes of 6 to 12 months, at the bench top scale, at a cost that is scalable at the commercial level, and using existing technology. A key assumption behind these accelerated weathering tests therefore is that the results provide useful data that can be extrapolated to field scale to make predictions about field conditions and to make planning decisions. It should be noted that this assumption is not based on proven field calibration exercises and conclusive research, but is rather an artifact of ‘reverse’ engineering. In other words, the tests were created to provide a solution to a time, cost and technology constraint, not designed to provide an answer to the question about predicting field geochemical conditions.

Commonly used kinetic testing methods offer a good example of the challenges when attempting to determine how laboratory data should be used to extrapolate from the laboratory (micro) to site (macro) scale. Tests such as humidity cells (ASTM, 2012) and leach columns (AMIRA 2002) utilise a few kilograms of material that has been crushed to a few millimetres in size and then exposed to wetting and drying cycles with very high leaching rates. The concept of these kinetic tests is that by using small grain sizes and high leaching ratios the weathering processes (sulfide oxidation rates and carbonate dissolution) can be accelerated allowing the assessment of sulfide oxidation rates, acidity generation, neutralisation reactions, and leachate geochemistry within a reasonable and practicable timeframe in regards to mine planning.

Because of the large amount of published data from these tests it can be stated with reasonable confidence that it is beyond doubt that these tests achieve the aim of simulating accelerated weathering. However, the precise method, and value of how to apply these results in a scaled up situation, for example in the extrapolation of data to predictions of field conditions, such as oxidation rates or seepage quality, has not yet been conclusively determined.

Table 1 outlines some scale factors that require consideration when using kinetic test data for ‘predictions’ of field conditions, which will have a significant influence on the ability to predict field geochemical conditions and processes from laboratory data.

Table 1 *Laboratory to field scale factors*

Scale parameter	**Industry standard Laboratory test conditions**	**Typical field conditions**	**Challenges extrapolating from lab to field**
Grain size	<6mm	60% >6mm	Oxidation rates faster and dissolution of silicates/carbonates higher for smaller grain sizes. Lab tests may over estimate both sulfide oxidation rates and acidity buffering processes
Geochemical system	Open	Variable from open to closed	Open systems discharge acidity closed systems store acidity, lab tests are not reflective of field drainage geochemistry
Mass of material	1-2 kg	>1 Mt	Heterogeneity effects not accounted for in lab tests, bulk geochemistry of material in the field may not be well represented by material tested in the lab
Airflow (Oxygen supply)	Diffusion dominated potentially restricted	Advection dominated potentially restricted	Lab tests assumed unlimited oxygen supply, field conditions may vary, generally significantly lower than lab conditions
Temperature	20-30 degrees	0-100+ degrees	Due to effect of thermal properties by total mass of material, field temperatures may be significantly higher than lab, this can effect geochemical reaction rates
Liquid : solid ratio	8:1 per year	0.001: 1 per year	Lab leachate is order of magnitude dilute then field conditions due to high L:S ratio. No restriction on sulfide oxidation rates based on H2O supply in lab, field reaction rates may be H2O supply limited.

Because of the significant differences between laboratory and field conditions the relative effects of the listed scale parameters (Table 1) are inherently site specific. Therefore to scale up results from the laboratory to the field initially requires the generation of a detailed set of calibration functions to derive a scale up factor. It is outside the scope of this paper to provide detail on all of these factors, however one of these factors, the L:S ratio, is described in more detail as this is probably the most significant factor that is overlooked when laboratory results are interpreted and applied to field conditions.

Liquid Solid (L:S) ratio

Since it is the relative rate of supply of oxygen and/or water to a system that will be the primary control on the intrinsic oxidation rate (IOR), and seepage quality (due to solubility controls) it is necessary to establish what field and laboratory conditions and how they are inter related (or not).

The liquid to solid ratio (L:S) is a convenient way to express the relative supply of H_2O into the system, this simply reflects the weight for weight balance of water against the mass of the porous solid through which the liquid is passing. Free draining leach columns have very high L:S ratios in general, an AMIRA (IWRI and EGi, 2002) column has an annual L:S ratio of approximately 8:1 for example. In contrast

WRSFs typically have low L:S ratios and annual ratios in semi arid environments like the Pilbara of Western Australia are estimated to be around 0.001:1 (assuming a 40 m high WRSF has 400 mm of net percolation per annum). The difference between field and laboratory L:S ratios is therefore many orders of magnitude. Given the L:S ratio is 8:1 in free draining leach column tests then there is a significant excess of H_2O for pyrite oxidation not to be rate limited, based on stoichiometry there is approximately 300 times excess H_2O. As a result of this significant 'over supply' the conditions set up in the laboratory are not as controlled as would be envisaged as the effect of the supply rate of oxygen and water are not studied. That is, it is not an outcome of the testing to determine what effects the test conditions (over supply of oxygen and water) has on reaction rates, or leachate quality.

It should also be noted that the use of such excess H_2O in these tests will inevitably result in significant dilution of leachates. Therefore, leachate strengths are very unlikely to be representative of field conditions, and are in most cases likely to underestimate concentrations by a significant margin. For materials with low sulfide contents this is likely to be of particular concern as these tests will tend to significantly underestimate the concentration of contaminants of AMD leachates in the field as implied dilution factors are many times what may occur in the field.

Industry methods

Oxidation rates and long term predictions for mine drainage quality have typically been estimated through the application of humidity cell and leach column methodologies. The humidity cell (ASTM, 2012) and free draining leach columns (AMIRA, 2002) are two industry accepted kinetic testing methods that expose samples of mine waste rock and tailings materials to wetting and drying cycles to primarily accelerate the oxidation of sulfidic materials. The oxygen-gradient and oxygen consumption methods have been developed as alternatives to laboratory humidity cell and column leach tests and have also been applied in the field (Elberling, 1993; Kempton and Atkins, 2009).

A key feature of all of these tests is that they only allow estimation of the pyrite oxidation rate (POR) or the intrinsic oxidation rate (IOR). In reality oxygen consumption will be influenced by the pyrite oxidation rate (POR) and other oxygen consuming reactions such as carbon oxidation rate (COR).

Humidity cells and free draining leach columns

Samples are typically exposed to wetting and drying cycles to accelerate the oxidation of sulfidic materials. Although these cycles can be modified in an attempt to replicate climatic site conditions, they typically involve wetting cycles that result in significantly greater liquid to solid ratios than may actually be experienced within a waste rock storage facility. Oxidation rates are estimated by the sulfate release method through the stoichiometric relationship between the mass of sulfate released over time to the quantity of pyrite oxidized (AMIRA, 2002; ASTM, 2012; Elberling et al., 1994).

Using analytically determined sulfate concentrations in humidity cell or column leachates to estimate oxidation of sulfide can be difficult due to the tendency for secondary sulfate salts to precipitate before being released in the leachate (Hammarstrom et al.). This highlights an important distinction between the sulfate release rate and the sulfate production rate with the latter representing the weathering rate of pyrite (Sapsford et al., 2009). If all generated sulfate is not released the weathering rate will be underestimated assuming the release of sulfate is representative of pyrite oxidation. Conversely, the weathering rate may then be overestimated if at a later date, the stored secondary salts are dissolved and released into the leachate (Sapsford et al., 2009).

Oxygen-gradient and oxygen consumption methods

The oxygen-gradient method, otherwise known as the oxygen diffusion method, relates the flux of oxygen through a material to the rate of sulfide oxidation (Elberling et al., 1994). As oxygen is consumed by pyrite, a gradient forms in the profile which drives the diffusive transport of oxygen (Elberling et al., 1994). This method assumes that the main process controlling oxygen transport is diffusion and the amount of oxygen consumed by oxidative reactions is equal to the oxygen flux at steady-state conditions (Elberling et al., 1994).

The oxygen consumption method, which is becoming more prevalent in industry, measures oxygen consumption in a fixed chamber by monitoring changes in pressure or changes in oxygen concentration (Hollings et al., 2001). The consumption of oxygen is assumed to be proportional to pyrite oxidation enabling the calculation of a pyrite oxidation rate (kg pyrite/kg material/year) (Elberling et al., 1994; Schmieder et al., 2012).

One significant advantage of these two methods is the short testing period and therefore they are very useful in providing quick and inexpensive estimations of oxidation rates. However, these methods do not provide information on potential saline and metalliferous drainage quality with time as provided by humidity cell and column leach tests. Another uncertainty is how these methods account for pyrite oxidation by ferric iron or any other oxidation processes consuming oxygen in the subsurface. The oxidation of pyrite by ferric iron does not consume oxygen and therefore the oxidation rate estimated by the oxygen-gradient or oxygen consumption method may be underestimated if conditions conducive for ferric iron exist. Although the oxidation of ferrous to ferric iron does use oxygen, the stoichiometric relationship is different to that of pyrite oxidation.

Advanced customisable leach columns (ACLC)

Given the identified limitations associated with industry standard testing methods, and OKCs extensive database of in situ site monitoring data from WRSFs, OKC has sought to develop an alternative laboratory method to understand the kinetics of geochemical reactions. This method is termed advanced customisable leach column (ACLC). To date, laboratory methods have been designed on a reverse engineering principal as field conditions are not applicable to the design and conditions of the test. OKC has taken the opposite approach to design of ACLCs to enable field conditions to be replicated in the ACLC test or to be adjusted on a site specific and scaled basis. An important consideration of a site specific and scaled basis is the flexibility in design to allow the direct replication of field conditions and potential changes to conditions in future scenarios such as rehabilitation.

Establishing field conditions based on site data

Prior to designing the ACLC tests OKC completed a number of field investigations to determine in situ field conditions within a number of WRSFs. During 2013 and 2014 OKC completed drill programs that resulted in 2,000 m of sonic drilling, the recovery and detailed analysis of over 2,000 samples of core material and the installation of over 150 instruments within 12 WRSFs up to a depth of 100 m. The WRSF monitoring systems were equipped with instrumentation to measure in situ moisture, oxygen pore-gas concentrations, pore-water pressure and in situ temperature within the WRSFs. OKC has published a number of papers (Pearce, S. and Barteaux, M. 2014a, 2014b) describing the results of these large scale intrusive investigations of WRSFs in Western Australia. The principal finding from the study are that:

- L:S ratios are very low in the WRSFs due to the semi arid climate and the process of advective drying where by advective gas flux through the waste actively removes pore water. Geochemical analysis of drill core from this study indicates significant presence of secondary sulfate minerals which are indicative of precipitation of sulfate bearing minerals as a result of stationary pore fluids (and therefore a very low L:S ratios). The geochemical system can therefore be best thought of as semi closed in that oxygen and H_2O (possibly supplied from internal evaporation rather than matrix pore water flow) can enter the waste but very limited leachate leaves the system. This results in a buildup of secondary sulfate minerals.
- Data from oxygen and temperature probes installed within WRSFs along with analysis of sulfate:sulfide ratio of pyrite containing material were used to determine field gas flux rates within the WRSF using analytical calculations and field based IOR. This analysis indicates that gas flux may vary by an order of magnitude based on the internal structure of the waste and particle sizing. Oxygen ingress rates within the WRSF were found to range from locations with surplus to those with deficit required to support the theoretical POR derived from industry standard kinetic testing methods (AMIRA columns). It is noted that measured POR field rates range from 10% to approximately 80% of the laboratory rate. The supply of oxygen (gas flux)

is therefore likely an important control on field PORs, and importantly the data indicates that in some areas of the WRSF oxygen supply may not be a rate limiting factor to field POR.

Design and Construction

The ACLCs are engineered to closely simulate in situ WRSF conditions in the field, thereby replicating them in a laboratory environment. Specific field conditions that were included in design considerations comprise airflow rates, ambient temperature, and water dynamics (water application rates and drying). Components of the ACLC that support the control of these field parameters in the laboratory include the large capacity (25kg) and diameter (100mm) of the columns, a dedicated temperature controlled room, variable air flow gauges for each ACLC, automated air flow solenoids, and automated sprinkler heads. A fully automated monitoring system provides the ability to customise each ACLC to a specific set of controls, i.e. reduced or increased air flow rates.

Each ACLC is fitted with a material supporting layer at the base consisting of nylon balls, and geofabric to allow for leachate collection and to maintain air flow from the base of the column. At the top of the column custom sprinkler heads for the even distribution of water to the material surface. Whilst not necessary to replicate field conditions, these features improve the overall functionality of the system. Leachate samples are collected at the base of the columns by gravity drainage into large glass flasks. An engineered exhaust and watering system allow for each ACLC to be isolated from external pressure and air influences, meanwhile allowing for potentially low oxygen and hazardous gas to be extracted from the laboratory safely and efficiently.

Installation of Monitoring Equipment

The ACLCs are equipped with a fully automated monitoring system designed to monitor temperature, matric potential (wetting and drying), and oxygen and carbon dioxide concentration of exhaust gas. The system is controlled by programmable dataloggers, which can be customised to dictate measurement frequency, control air flow and water into the system, and are expandable to accommodate various sensor types and sensor numbers depending on research objectives. Sensors currently employed in the ACLC monitoring system include Apogee galvanic oxygen probes, Decagon MPS2 matric potential sensors, and non-dispersive infrared Co_2 instruments.

The MPS2 is utilised to monitor the suction (negative pressure) of the column material, providing information on wetting and drying processes occurring within the material following wetting events and during drying phases. The MPS2 also measures temperature which allows for monitoring potential exothermic oxidation reactions occurring in the ACLCs. Oxygen and Co_2 is monitored at the exhaust, located at the top of the ACLCs allowing direct measurement of oxygen consumption and thus determination of IOR but also allows estimation of COR and POR as Co_2 is measured as well as oxygen. Sensors are installed in-line with the exhaust system so that gas exiting the column will pass over the sensors, providing readings of composition.

Summary of method

Table 4 presents the key parameters for the humidity cell and free draining leach columns methods. For comparison, Table 4 also presents the potential ranges for key parameters for the ACLCs.

Table 4 *Laboratory to field scale factors*

Method	Sample Mass (kg)	Grain Size (mm)	Air Temp (°C)	Air Flow (L/m)	Annual Liquid to Solid Ratio
ACLC	10–25	<50	20–45	<0.1–1	>0.1
Humidity Cell (ASTM, 2012)	1–2	<6.3	23–31	1–10	13-26
Free Draining Leach Columns (AMIRA 2002)	2–2.5	<4	30–35	-	10-13

Comparison of leachate quality from lab to field

Figure 1 shows the results from analysis of field seepage data, leachate from the ACLC column constructed for the site, and AMIRA column testing data used for previous predictions of seepage water quality. As is clear from the results the higher L:S ratio of the AMIRA column significantly impacts the ability to make informed use of this data to predict field seepage conditions as concentrations of key metals like aluminum are significantly underestimated. In comparison the low L:S ratio of the ACLC test produces seepage quality results that are much closer to field conditions and therefore offer a much more direct means to assess and predict field seepage quality.

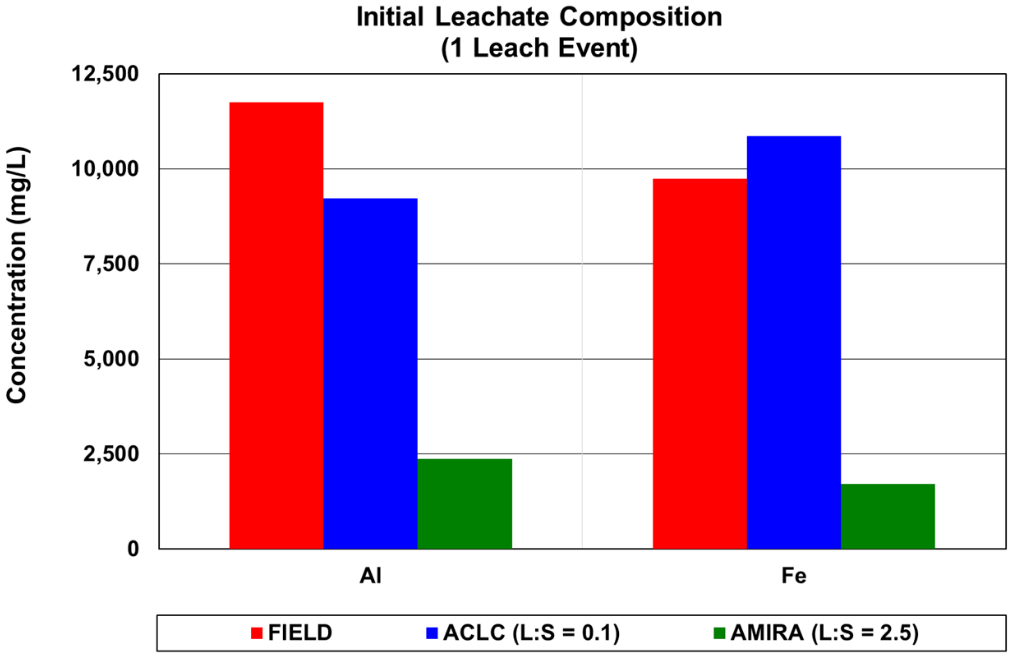

Figure 1 *Leachate quality based on field seepage, ACLC and AMIRA leach columns*

Conclusions

A number of key issues have been identified with using industry standard kinetic testing for predictions of geochemical evolution of waste materials containing sulfides in the field due to significant uncertainty with how to apply scale up factors for the extrapolation of laboratory data to the field. In an attempt to resolve this challenge of scaling up laboratory results, a new laboratory testing method has been derived that can accommodate and replicate site specific conditions. This method is termed the advanced customisable leach column (ACLC). The highly engineered columns have allowed for field conditions to be simulated in a laboratory setting while automated monitoring systems providing flexibility in controlling research variables.

Extensive field data collected as part of extensive intrusive WRSF drilling projects has been used as a basis for the design of the ACLC to allow laboratory conditions to closely replicate in situ field conditions thereby reducing the difficulty in scaling laboratory leach experiments to field scale. Reducing uncertainty about scaling factors will allow for more accurate estimates of field POR.

Key features of the columns include both their capacity, size and technical specification. Columns can be adapted for different conditions depending on site specific conditions and variability. Ongoing monitoring of the column conditions by automated temperature control and monitoring, automated oxygen consumption and carbon dioxide production monitoring, and soil moisture/matric suction monitoring enable rapid and reliable data collection for interpretation.

The flexibility of the design allows for more accurate field based assessment of POR, COR and IOR rates, through increased controls on temperature, water and oxygen availability. As such, by completing concurrent assessments of the same material type under different conditions the ACLC system allows the assessment of the potential effectiveness of waste management options, such as deposition within a reduced oxygen environment, as simulations of reduced net percolation rates or oxygen ingress rates can be accommodated.

Low L:S ratios that are common to WRSF during the periods during and shortly after construction, and over longer time frames in semi arid environments have been identified as a particular challenge for industry standard methods to replicate. These conditions can be better represented by the ACLC as leaching is not required to generate a POR, COR or IOR as inline oxygen and carbon dioxide monitoring allows direct measurement of these rates. This means that leaching rates at L:S <0.5 can be simulated which allows more representative estimation of seepage quality as the effects of solubility controls are directly studied.

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Estimation of pyrite weathering in Lusatian lignite open cast mines using geochemical investigation methods

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Abstract

In this paper the procedure of geochemical investigations in Lusatian lignite open cast mines is described. It is distinguished between geochemical investigations in the forefront of the mine and in dumps. Geochemical investigations in the forefront focus on the sediments above the lignite seam. Investigations in the dumps determine the geochemistry in the complete overburden of the open cast mine. Investigations in the forefront serve two purposes: 1) to predict the geochemical composition of the dumps in the lignite open cast mines and 2) to estimate hydrogeochemical processes in drained aquifers surrounding the mines.

Based on the investigations in the forefront the mean content of pyrite, calcite and other geochemical parameters in the future dump is estimated. Furthermore the acidification potential may be predicted. These data are used in models of different spatial discretisation to estimate the pyrite weathering. These estimations are verified by geochemical investigations in the dump. In already existing dumps the effective pyrite weathering rate is estimated using the analysed sulphur species. Often the zones of primary and secondary pyrite weathering may be defined. For this case the rate of pyrite weathering can be quantified separately.

In dumps in the Lusatian lignite mines the mean pyrite content is between 0.05 and 0.5 mass-%. Recent investigations estimate a profile-averaged pyrite weathering rate between 6 % and 18 %. The pyrite weathering rate is about 5 % in the zone of primary weathering and mostly above 25 % in the zone of secondary weathering. The thickness of the zone of secondary weathering is between 5 and 40 meter.

Key words: acid-base-accounting, rate of pyrite weathering, lignite mining, geochemical investigation

1 Introduction

Lignite is a main primary energy source in Germany and from the recent point of view of energy still necessary. Mineable lignite seams can be found in Germany only in unconsolidated rocks of tertiary age between 50 and 400 meter below the terrain. The lignite is mined in open cast mines using excavators. Therefore it is necessary to dewater the open cast mine. Dewatering of the open cast mines is often realised by screen wells.

In the Lusatian lignite mining area the Tertiary is between 150 and 200 meter thick. In the tertiary profile terrestrial and marine sediments alternates (Nowel et al. 1994). It consists of a series of fine sands, silt, clay and lignite seams. Altogether there are five important lignite seams in the tertiary profile in Lusatia. Mainly the 2nd Lusatian lignite seam (2. LFH) is mined.

In Quaternary there were three important glacial periods: the Elster, Saale and Weichsel glacial period. Typical sediments of the Quaternary are glacial till, glacial-limnic fine-sands, silt and clay as well as glacial-fluvial melt water sand and gravel. In the interglacial periods fluvial sand and gravel as well as peats and muds were deposited. The sandy-gravelly sediments are main aquifers. The thickness of the quaternary sediments ranges between a few meters at tertiary plateaus and more than 100 meters in Pleistocene channels. Deep channels intersect the 2. LFH and form the mosaic texture of the lignite mining area.

In the Lusatian open cast mines the lignite seams are excavated by conveyor bridges. Mostly, they consist of two chain-and-bucket excavators and a conveyor bridge. The conveyor bridge transports the overburden to the dump. In the open cast mine the disposal of the overburden is carried out in the open pit as inner dump. Due to the conveyor bridge technology the dumps have a three layered structure (fig. 1). At the base a dump consisting of non-cohesive material is prepared (base dump). Hereon the railway track of the conveyor bridge is located. The thickness of the base dump is between 10 and 20 meter. Above the main dump with a thickness between 40 and 65 meter follows, consisting of tertiary and quaternary material excavated by the conveyor bridge. It is a typical mixed soil dump. At the top a stacker dump is deposited to form the post-mining topography. Normally it consists of quaternary material free of pyrite or tertiary material with low pyrite get in the pre-cut of the mine. The stacker dump is usually between 10 and 30 meter thick.

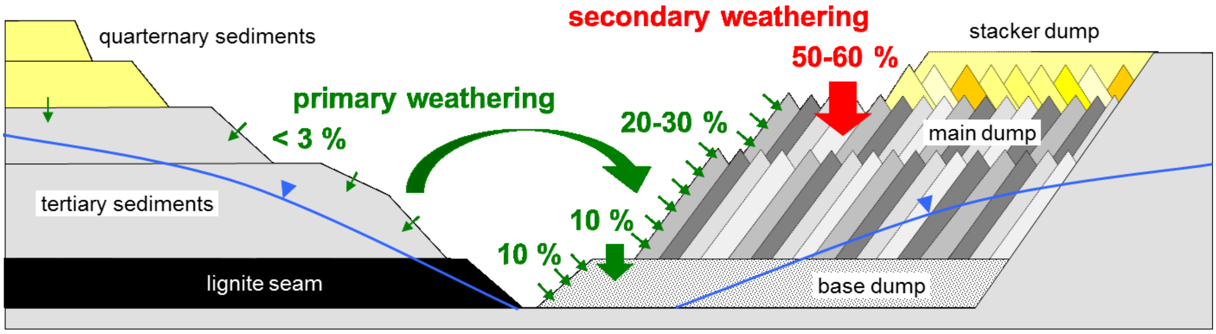

__Figure 1__ Scheme of mining technology and dump structure in the Lusatian open cast mines and detailed information to rates of pyrite weathering

Tertiary and quaternary overburden contains pyrite, which is mainly associated with organic and silty sediments. Low Pyrite is also contained in non-cohesive sediments. In contact with oxygen pyrite weathering occurs. This is the case during groundwater lowering as well as during exposure of the overburden in the open cast and in the dump. Depending on the geological and geochemical conditions groundwater chemistry is influenced by pyrite weathering e.g. by sulphate, metals and acidification.

Pyrite weathering can be distinguished into primary and secondary weathering. Primary weathering already begins during dewatering in the forefront of the mine. Furthermore primary weathering takes place at the temporary exposed work surfaces and slopes in mine and in dumps. At the dumps it ends by covering with new deposited overburden (fig. 1).

However, secondary weathering is more important. It takes place at long-term exposed surfaces at the top of the main dump and slopes. The depth as well as the rate of pyrite weathering is mainly determined by pyrite content and diffusion of oxygen. The latter one depends on time of exposure and on air permeability in the dump deposits. Secondary weathering normally ends by covering the main dump with a stacker dump, consisting of material free of pyrite or by groundwater rise. It is necessary to know specific rates of pyrite weathering to predict groundwater chemistry in dumps and to assess chemical balancing measures.

2 Methods

2.1 Geochemical investigations

Geochemical investigations in the forefront focus on the sediments above the lignite seam. Investigations in the dumps determine the geochemistry in the complete overburden of the open cast mine. Both investigations are realised by core drilling with liners DN80 to DN100. Liners studied geologically and geochemically. Laboratory investigations including determination of dry residue, loss on ignition as well as iron, carbon and sulphur content. Furthermore carbon and sulphur species are identified. Effective cation exchange capacity is determined at selected samples from the surrounding of the mines to estimate parameters for transport modelling. At samples from dump investigations the soluble substances are identified by water leaching tests. At the end of the year 2015 in total 35 drillings in the forefront and in the surrounding of Lusatian lignite mines as well as 25 drillings in dumps are geochemically investigated (fig. 2, tab. 1).

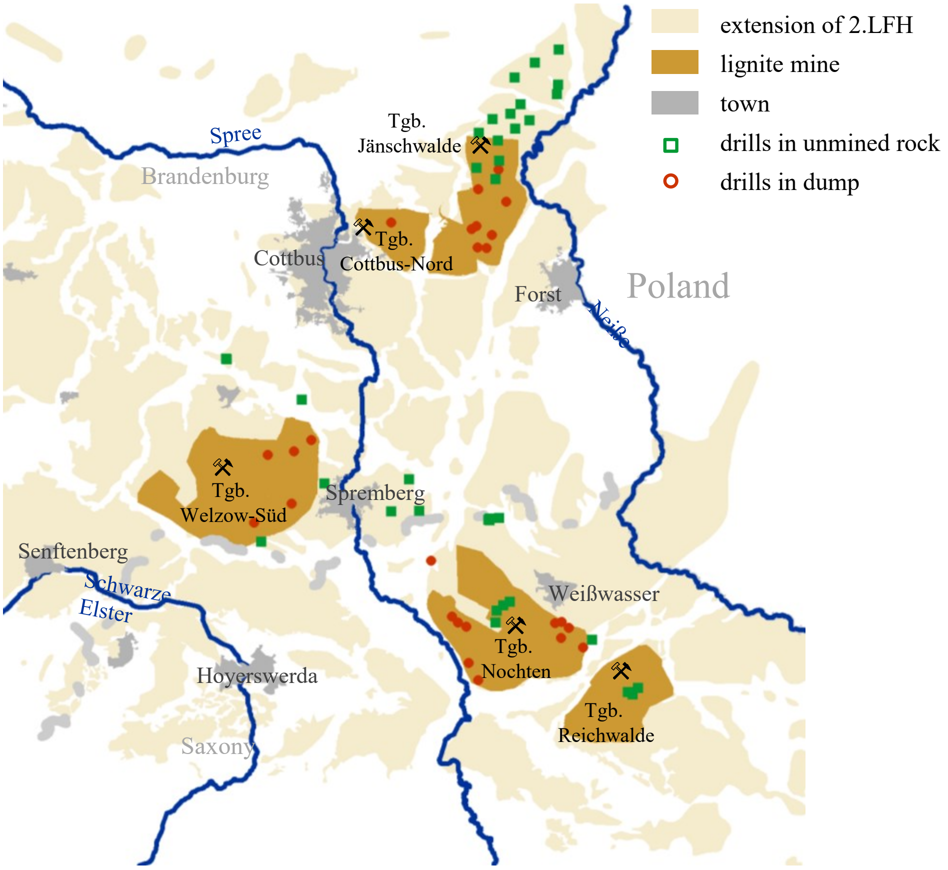

Figure 2 *Lusatian lignite open cast mines of the Vattenfall Europe Mining AG*

Table 1 *Number of geochemical investigations in Lusatian lignite mines*

Open cast mine	forefront and surrounding	Inner dump	Outer dump
Reichwalde	3	-	-
Nochten	12	10	1
Welzow-Süd	5	5	-
Cottbus-Nord	-	1	-
Jänschwalde	15	9	-

2.2 Acid-Base-Balancing

Balancing pyrite and calcite content may estimate the acidification potential as a worst case scenario, if the complete pyrite is weathered. At aerobic conditions 4 mole calcite per mole pyrite are necessary to buffer acids delivered by complete pyrite weathering at pH ≥ 7 (tab. 2). Anaerobic conditions requires half of calcite, however, ferrous iron remains in the groundwater. Discharge into surface water may oxidise ferrous iron and causes acidification of open pit lakes as well as sedimentation of iron ochre in water courses. The acid-base-balancing of the sediments is evaluated as follows (tab. 3).

Table 2 *Pyrite weathering and calcite buffering depending on oxygen conditions*

Pyrite weathering	Calcite buffering
anaerobic conditions	
$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$	$2H^+ + Fe^{2+} + 2CaCO_3 \rightarrow 2HCO_3^- + 2Ca^{2+} + Fe^{2+}$
Aerobic conditions	
$FeS_2 + \frac{7}{2}O_2 + \frac{1}{2}H_2O \rightarrow Fe^{3+} + 2SO_4^{2-} + H^+$	
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$	$4H^+ + 4CaCO_3 \rightarrow 4HCO_3^- + 4Ca^{2+}$

Table 3 *Classification of acid-base-balancing*

Molar ratio of calcite to pyrite	class
≥ 4	buffered
$2 \ldots 4$	partially buffered
≤ 2	potentially acidic

2.3 Rates of pyrite weathering

The rate of pyrite weathering may be estimated on the basis of the ratio of sulphate-sulphur and the sum of inorganic sulphur:

$$r_{\frac{\text{sulf}}{\text{sulf+dis}}} = \frac{\sum_{i=1}^{n}\left(m(i)\cdot\rho_{tr}(i)\cdot\left(M_{sulf}(i)-\overline{M}_{sulf}^{0}\right)\right)}{\sum_{i=1}^{n}\left(m(i)\cdot\rho_{tr}(i)\cdot\left(M_{sulf}(i)-\overline{M}_{sulf}^{0}+M_{dis}(i)\right)\right)}$$

$r_{\frac{\text{sulf}}{\text{sulf+dis}}}$	Profile-averaged rate of pyrite weathering	[%]
$m(i)$	Thickness of layer i	[m]
M_{sulf}	Content of sulphate sulphur in layer i	[mass-%]
$\overline{M}_{sulf}^{0}$	Background of sulphate sulphur	[mass-%]
M_{dis}	Content of disulphide sulphur in layer i	[mass-%]
$\rho_{tr}(i)$	Dry bulk density of layer i	[g/m³]

The equation takes the background of sulphate sulphur ($\overline{M}_{sulf}^{0}$) into account, e.g. as gypsum or barite. In fact, investigations in the forefront show low content of sulphate sulphur in Pleistocene and Tertiary sediments. Normally dry bulk density is not determined. It is assumed that dry bulk density does not depend on sulphur content. Therefore dry bulk density may be cancelled in the equation. The thickness-averaged rate of pyrite weathering provides a sufficient estimation at the specific drilling location. Besides this, the rates of pyrite weathering for several layers may be falsified by mass transport (leaching). Normally in the upper part of the profile (releasing area) the rate is under-estimated, whereas in the lower part of the profile (input area) the rate is overestimated.

2.4 Groundwater chemistry

Mineralisation and especially concentrations of sulphate are increased in groundwater of dump aquifers caused by pyrite weathering. Normally the groundwater is anaerobic, consists of varying portions of calcium, magnesium and ferrous iron and is slightly acidic. In case of a complete oxidation the acidity of the groundwater in the dumps is evaluated regarding to the effects on surface waters. This may be done by simple molar equivalent balancing of bicarbonate and iron concentrations:

$$\text{Aci} \approx K_{B8,2}^{ox} \approx [HCO_3^-] - 2\cdot[Fe^{2+}]$$

or by hydrogeochemical modelling. In the former case only acidity is determined, which correspond to $K_{B8,2}^{ox}$. In the second case pH-value (pH_{ox}) and further values of acidity e.g. $K_{B4.3}^{ox}$ and $K_{B8,2}^{ox}$, are represented.

3 Results

Results are presented for the lignite mines Nochten in the south and Jänschwalde in the north of the Lusatian lignite mining area.

3.1 Investigations in the forefront area and acid-base-balance of the sediments

Stratigraphic-geochemical profiles are constructed as a result of the investigations in the forefront (fig. 3 and fig. 4). On the basis of the results in different drillings a statistical data pool is generated for specific stratigraphic layers.

Generally the highest pyrite content is found in cohesive tertiary sediments (silt above and below the lignite seam). These sediments contain between 0.6 and 2.9 mass-% pyrite. Elevated pyrite content may also be found in transported tertiary material and in quaternary limnic sediments. For example limnic sediments deposited during the glacial period Elster in the open cast mine Jänschwalde contains between 0.6 and 2.3 mass-% pyrite.

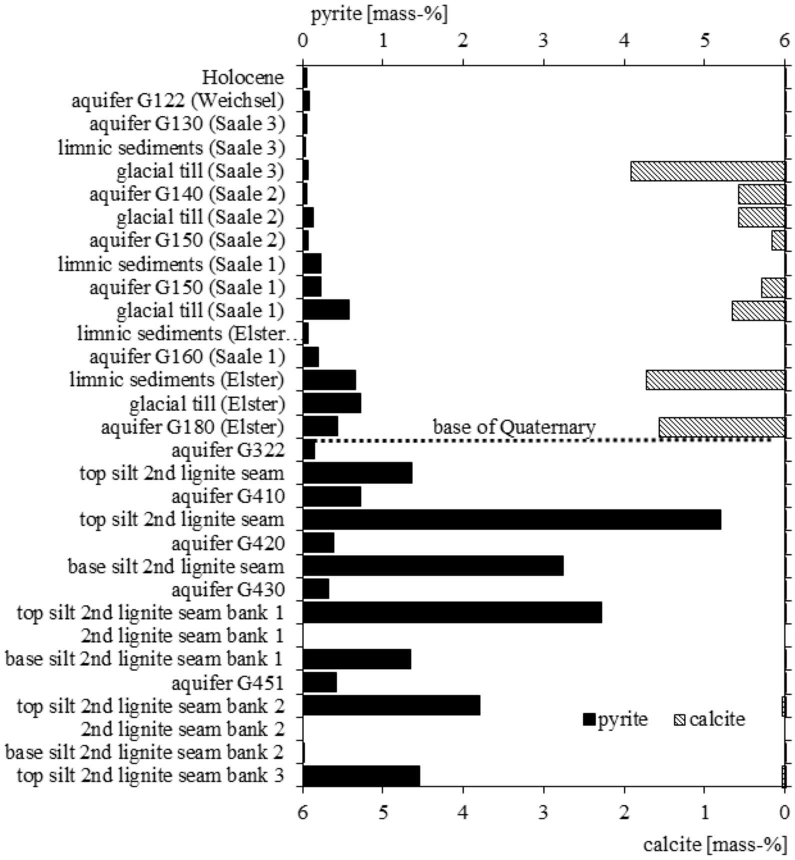

Figure 3 *Stratigraphic-geochemical profile in the forefront area of the lignite mine Jänschwalde*

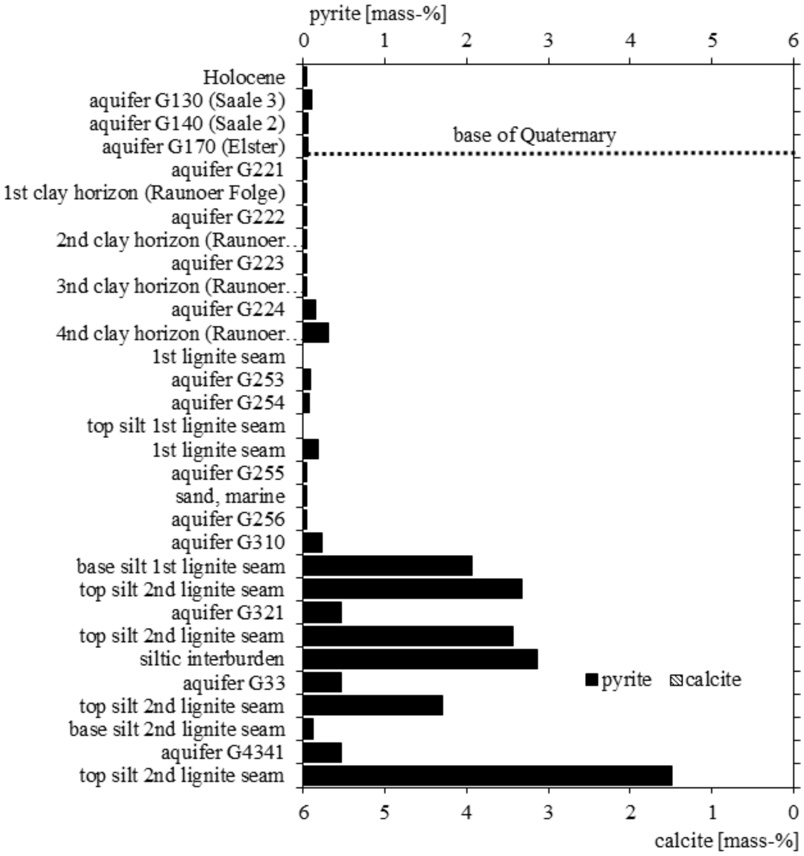

Figure 4 *Stratigraphic-geochemical profile in the forefront area of the lignite mine Nochten*

Appreciable contents of calcite can be found only in quaternary sediments. Glacial till and glacial-limnic sediments contain up to 5 mass-% calcite. These sediments are mainly common in the northern part of the Lusatian lignite mining area, for example open cast Jänschwalde (fig. 3, tab. 4). The calcite content in the open cast Nochten is very low caused by the thin quaternary overburden (fig. 4, tab. 5).

On average the overburden in the lignite mine Jänschwalde contains between 0.2 and 1.0 mass-% pyrite (fig. 3, tab. 4). Calcite typically is between 0.2 and 1.6 mass-%. In the lignite mine Nochten pyrite content is comparable to Jänschwalde. Due to the thin quaternary overburden calcite is often below the limit of determination (0.01 mass-%) and therefore negligible (fig. 4, tab. 5). Contents of disulphide sulphur, total sulphur, calcite, and iron as well as the distribution of each stratigraphic layer are stored in a digital stratigraphic model of the mine.

Table 4 *Averaged contents of sulphur, pyrite, and calcite and molar ratio of calcite to pyrite in the overburden of the lignite mine Jänschwalde*

location	drill hole	thick-ness	number of samples	sulphate as sulphur	disulphide as sulphur	pyrite FeS_2	calcite $CaCO_3$	molar ratio calcite to pyrite
		m	-	mass-%	mass-%	mass-%	mass-%	-
forefront Jänsch-walde	9323	77	35	<0,01	0,34	0,63	0,61	9,7
	10759	54	17	<0,01	0,51	0,96	0,27	2,8
	11651	100	68	<0,01	0,17	0,32	0,53	16,7
	11676	90	68	<0,01	0,24	0,45	0,39	8,8
	11703	77	86	<0,01	0,20	0,37	0,25	6,7
	12074	99	67	<0,01	0,14	0,27	0,31	11,5
	13211	103	74	<0,01	0,19	0,35	1,22	4,2
	14041	87	77	<0,01	0,46	0,86	1,58	2,2
	15217	104	92	0,02	0,12	0,23	0,75	4,0
forefront Jänsch-walde-Nord	14807	91	74	0,02	0,33	0,61	3,34	6,5
	14808	79	44	0,02	0,36	0,67	0,66	1,2
	14811	88	64	<0,01	0,29	0,54	1,55	3,5
	14813	75	53	<0,01	0,42	0,79	0,02	<0,1
	14814	65	46	<0,01	0,33	0,62	1,43	2,8

Table 5 *Averaged contents of sulphur, pyrite, and calcite and molar ratio of calcite to pyrite in the overburden of the lignite mine Nochten*

location	drill hole	thick-ness	number of samples	sulphate as sulphur	disulphide as sulphur	Pyrite FeS_2	calcite $CaCO_3$	molar ratio calcite to pyrite
		m	-	mass-%	mass-%	mass-%	mass-%	-
forefront Nochten	13165	93	100	<0,01	0,27	0,50	<0,01	<0,5
	13167	96	113	0,02	0,18	0,33	<0,01	<0,5
	13558	82	126	<0,01	0,33	0,62	<0,01	<0,5
	13561A	97	116	<0,01	0,25	0,47	<0,01	<0,5

The averaged acid-base-balancing is about 6 mole calcite per mole pyrite in lignite mine Jänschwalde (tab. 4). Mostly the overburden is well buffered. In contrast the molar ratio in overburden of the lignite mine Nochten is below 0.5 mole calcite per mole pyrite (tab. 5). Therefore the sediments are potentially acidic. Groundwater chemistry in the dump of the lignite mine Nochten verifies this.

Based on the molar ratio of calcite to pyrite the geochemical disposition of the overburden can be estimated. Mostly calcite is well available in the dumps. There is no calcite containing dump material which is acidic. Besides this rate of pyrite weathering largely depends on physical and geochemical soil properties as well as on exposure time. Therefore the evaluation of the geochemical disposition of dump material requires an estimation of the rate of pyrite weathering. These objectives are derived from the geochemical investigations in dumps.

3.2 Geochemical investigations in dumps and rate of pyrite weathering

In the Lusatian lignite mines the mean pyrite content is between 0.05 and 0.80 mass-% in dumps (tab. 6 to tab. 7). In the lignite mine Jänschwalde the mean calcite content is between 0.10 and 1.6 mass-% (tab. 6). Dumps in the lignite mine Nochten are nearly free of calcite (tab. 7).

***Table 6** Averaged contents of sulphur, pyrite, and calcite in the dump of lignite mine Jänschwalde*

location	drill hole	thickness	number of samples	sulphate sulphur	disulphide sulphur	pyrite FeS_2	calcite $CaCO_3$	profile-averaged rate of weathering
		m		mass-%	mass-%	mass-%	mass-%	-
inner dump	16412	73	24	0,03	0,40	0,75	0,65	6 %
	15483	80	63	0,03	0,16	0,30	0,38	16 %
	15484	66	37	0,04	0,38	0,71	0,13	8 %
	14430	50	18	0,02	0,22	0,40	0,31	6 %
	14431	57	17	0,01	0,17	0,32	0,94	6 %
	14432	68	16	0,06	0,11	0,20	0,14	35 %
	14433	61	39	0,04	0,17	0,32	0,29	20 %
	14434	51	28	0,03	0,30	0,55	1,62	7 %

***Table 7** Averaged contents of sulphur, pyrite, and calcite profile-averaged rates of pyrite weathering in outer and inner dumps of lignite mine Nochten*

location	drill hole	thickness	number of samples	sulphate sulphur	disulphide sulphur	pyrite FeS_2	calcite $CaCO_3$	profile-averaged rate of weathering
		m		mass-%	mass-%	mass-%	mass-%	-
outer dump	13587	26	14	0,10	0,26	0,48	0,02	28 %
inner dump	13638	70	21	0,02	0,09	0,17	0,02	18 %
	13352	130	81	0,01	0,03	0,06	0,01	18 %
	13353Z	97	68	0,01	0,08	0,15	0,03	12 %
	14541	94	55	0,02	0,14	0,27	0,03	9 %
	14542Z	100	51	0,02	0,18	0,33	0,02	8 %
	13420Z	91	38	0,03	0,21	0,39	0,03	12 %
	13422Z2	83	46	0,02	0,24	0,45	0,02	6 %

The effective rates of pyrite weathering, calculated by the ratio of sulphate sulphur and the sum of inorganic sulphur, is mainly between 6 % and 18 % in the lignite dumps (tab. 6 to tab. 7). The rates of pyrite weathering are comparable in the various open cast mines. Lower rates can be found at locations which are covered immediately. Higher rates can be found at locations which are uncovered over a long time.

The effective pyrite weathering rate is about 5 % in the zone of primary weathering. Often the zone of secondary pyrite weathering can be defined on the basis of contents of sulphate and disulphide sulphur as well as their ratio. In the zone of secondary weathering the rate exceeds 25 % and is therefore considerably higher than in the zone of primary weathering. The thickness of the zone of secondary weathering is between 5 and 40 meter. In the outer dump of the lignite mine Nochten rate of pyrite weathering is about 50 %. Recently the thickness of the secondary weathering zone is about 10 meter. Due to the missing cover of the outer dump and the location above the groundwater table the zone of secondary weathering extends over time. In contrast pyrite weathering stops in inner dumps by covering them with a stacker dump or by rising of the groundwater.

3.3 Groundwater chemistry

Hydrochemical analyses of the groundwater in dumps confirm geochemical estimations (tab. 8). The dump groundwater in the lignite mines Nochten and Jänschwalde have comparable sulphate concentrations and weathering rates but differ significantly in alkalinity, iron concentration and therefore in the acid-base-impact in case of oxidation. The groundwater in dumps remains buffered at oxidation in lignite mine Jänschwalde. In contrast the groundwater reacts acidic in the dump of the lignite mine Nochten due to the missing calcite content.

Table 8 *Range of hydrochemical parameters in groundwater in dumps of the lignite mines Nochten and Jänschwalde (mean values and standard deviation)*

parameter	unit	lignite mine Nochten	lignite mine Jänschwalde
number of wells	-	12	19
pH-value	-	5,3 ± 0,5	6,3 ± 0,6
electrical conductivity	µS/cm	2.300 ± 900	2.400 ± 1.000
DOC	mg/L	7 ± 5	9 ± 6
TIC	mg/L	80 ± 50	120 ± 60
alkalinity $K_{S4,3}$	mmol/L	1,3 ± 1,0	7,5 ± 5,2
acidity $K_{B8,2}$	mmol/L	11,7 ± 5,6	7,7 ± 6,0
calcium	mg/L	260 ± 120	430 ± 210
magnesium	mg/L	100 ± 50	90 ±70
sulphate	mg/L	1.500 ± 700	1.200 ± 800
ammonium-nitrogen	mg/L	2,2 ± 1,1	2,7 ± 1,9
iron	mg/L	260 ± 160	90 ± 130
manganese	mg/L	6 ± 5	3 ± 3
aluminium	mg/L	0,5 ± 0,4	1,6 ± 3,1
arsenic	mg/L	60 ± 50	30 ± 50
cobalt	mg/L	50 ± 60	40 ± 40
nickel	mg/L	80 ± 80	180 ± 170
zinc	mg/L	270 ± 330	220 ± 260
calculated values for the acid-base-impact in case of oxidation			
pH_{ox}	-	3,4 ± 0,5	6,2 ± 1,9
$K_{S4.3}^{ox}$	mmol/L	-	4,8 ± 7,2
$K_{B4.3}^{ox}$	mmol/L	4,9 ± 3,7	-

4 Conclusions

Based on the geochemical investigations of the overburden in open cast mines the geochemical disposition of future dumps may be estimated. Pyrite weathering in lignite dumps is not complete, thus a simple acid-base-balancing overestimates the effective acidification. Geochemical investigations of inner dumps estimate the rate of pyrite weathering more reasonable. Thus appropriate estimations of the acidification potential of dumps are possible.

Results of the geochemical investigations in the various open cast mines correspond to hydrochemical analysis of the groundwater in dumps. Thus, geochemical investigations are suitable for assessing chemical balancing measures.

Acknowledgements

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Effects of scale of kinetic tests on leachate chemistry prediction

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Abstract

Kinetic tests, performed at varying scales under either ambient field or controlled laboratory conditions, form the most commonly used method within the mining industry for predictive assessment of the chemical quality of 'contact water' which may be generated through interaction of runoff or seepage with exposed mine wall rock, waste rock or tailings. At the laboratory scale, such tests are generally performed in accredited installations which deploy industry-standard protocols such as those established by MEND, ASTM and AMIRA. In contrast, field-scale tests are subject to no standardized protocols and tend to be undertaken on a bespoke basis, often dictated by sample material availability, climate and cost.

Given the high reliance placed on kinetic tests for long-term mine water quality prediction, an understanding of the extent to which such tests may be subject to bias through variations of test design or ambient conditions is extremely important. This paper demonstrates the variance observed between tests performed at both laboratory and field scales for a range of mining operations or new development projects across Australia and Latin America. In all cases, the sample materials subject to testing at these contrasting scales were either identical or closely analogous. Differences in water quality evolution trends are regarded as indicative of the effects of test scale, mode of operation and ambient conditions with respect to factors such as sample granulometry, homogeneity and ambient temperature, humidity or redox regime.

Key words: Kinetic testing, ARD, Scaling

Introduction

Accurate prediction of mine water quality prior to the initiation of new mining operations, or forecasting long-term evolution of mine water quality throughout the life of a mine is recognized in the minerals industry as critical for the assessment of project impacts and the pro-active design (and cost-estimation) of mitigation measures, including water treatment. Most commonly, prediction of future acid rock drainage (ARD) and/or metal leaching (ML) risks is undertaken through 'kinetic testing' of samples considered representative of material to be exposed as mine wall rock, or to be stored as waste rock or tailings throughout mine life, with subsequent extrapolation of test results to the mine facility scale, often performed through numerical geochemical modelling.

Kinetic tests are routinely performed at a range of scales and may be conducted under either laboratory or field conditions. All such tests involve the generation of leachate over a sustained period of time (ranging from months to years) through the interaction of infiltrating water with rock or tailings placed in a column or on a test pad. The majority of laboratory scale tests are performed using a relatively small sample mass, ranging from 1 to 10 kg. Most are performed in accredited laboratories in accordance with prescribed protocols established by bodies such as MEND (Canada; MEND 2009), ASTM (USA; ASTM 2013) and AMIRA (Australia; AMIRA International Ltd 2002). Each of these protocols is subject to some degree of idiosyncrasy. As a consequence, variations of weathering reaction rates and attendant solution chemistry may arise in response to differing conditions with respect to factors such as sample granulometry, temperature, solution irrigation rate and moisture content.

Field-scale tests are typically performed at a larger scale than those undertaken in the laboratory, with sample masses commonly ranging from 100 kg to several tons. Test design is generally bespoke and may involve the construction of large columns, barrels, cribs or leach pads. Irrigation may be undertaken artificially (to provide some level of temporal continuity of leachate production) or subject to natural irrigation by precipitation.

Given the reliance on kinetic tests as an industry-standard tool for the prediction of contact water quality, an understanding of the extent to which the results of such tests may be influenced by scale, design or mode of operation is fundamental for successful data extrapolation and, ultimately, quantitative hazard characterization. This paper provides insight into the nature and magnitude of bias which may be introduced to kinetic tests as a result of variations of scale and design, founded on numerous instances in which tests involving identical or closely analogous sample materials have been executed in parallel. These examples collectively encompass a wide spectrum of geological settings, ore/waste mineralogical compositions and climatic regimes across Latin America and Australia.

Sites and data

Case study settings

A comparative analysis of kinetic test datasets generated from laboratory and field-scale tests of essentially identical sample materials from five locations, as summarized in Table 1, was undertaken to elucidate potential effects of kinetic test design and scale on leachate evolution. The selected sites differ markedly in terms of geological setting, ore/waste mineralogy and climatic regime, thus providing a broad basis for assessment.

Table 1 *Summary of test settings and methods*

Site	Country	Metallogenic setting	Climate
Boddington	Australia	Archean shear-zone hosted Au	Sub-tropical, temperate
Pascua Lama	Chile / Argentina	High sulphidation epithermal system	Cool, arid
Alumbrera	Argentina	Cu porphyry	Cool, arid
Agua Rica	Argentina	Cu porphyry	Cool, temperate
Gaby	Ecuador	Au porphyry	Tropical, humid

Boddington, Western Australia

Boddington mine is operated by Newmont Boddington Gold (NBG). Gold is exploited from two orebodies, Wandoo North and South, hosted in the Saddleback Greenstone Belt (SGB) of Archean age. Gold mineralization is largely contained within diorite stocks emplaced in a sequence of volcanics ranging in composition from andesite to dacite. Mineralization is typical of Archean shear-zone hosted vein and stockwork systems, with Au occurring in association with minor chalcopyrite, phyrrotite and pyrite. Wandoo North is characterized by relatively intense chlorite/clinozoisite alteration plus minor epidote and trace calcite. Wandoo South is virtually devoid of calcite, with actinolite and albite pervasive.

The environmental geochemistry of Boddington arguably renders kinetic tests of waste rock more susceptible to the influence of subtle variations of test design or operating condition than is the case for other localities listed in Table 1. This reflects the presence of sulphides at trace abundances (70% of run-of-mine waste rock holds total S at <0.2%) in conjunction with effectively zero carbonate neutralization capacity (calcite abundances are routinely <0.01%). This has resulted in poor success throughout historical mine operations in the deployment of ABA and NAG test indices as a basis for differentiating potentially acid forming (PAF) and non-acid forming (NAF) rock in the run-of-mine waste stream. The former approach has been found to be uninformative as net-neutralization potential (NNP) values are virtually always in the range classifiable as ‘uncertain’ (between -20 and +20 kg/T $CaCO_3$). NAG tests have been found to be of equally limited value as virtually all samples yield pH values of <4.5 (conventionally classifiable as PAF) while NAG acidity values fall below <1 kg/T $CaCO_3$ (conventionally classifiable as NAF or indeterminate).

Column and humidity cell testing performed on Boddington waste rock by numerous consultants over a period spanning more than a decade to 2010 produced results which appeared inconsistent with rock classifications founded on static test indices. Extremely low (<0.2%) S content samples variably produced leachates ranging in pH between 3.2 and 7.5. Explanation for this highly variable weathering behaviour was first elucidated by Graeme Campbell and Associates Pty Ltd (GCA) through controlled laboratory tests performed using a modified AMIRA format (Campbell et al. 2012). In the trace sulphide, zero carbonate buffering system, maintenance of a near-neutral pH in GCA test columns was shown to be dependent on an aluminosilicate buffering reaction, functional at the inter-granular scale. This buffering mechanism was inferred from the GCA columns to sustain near-neutral pH conditions subject to a proton flux threshold equivalent, in terms of a sulphide oxidation rate, to around 5 mg/kg/day SO_4 yield. At higher rates of sulphide oxidation, the kinetics of alumino-silicate buffering are overwhelmed, resulting in depression of pH.

Pascua Lama, Chile/Argentina

Pascua-Lama lies at an altitude ranging from 4000 to 5300 m a.s.l. in the northern sector of the El Indio Belt, a regional metallogenic province which transgresses the central Chilean and Argentinian Andes. It is potentially a world class Au-Ag-Cu deposit hosted in intrusive, sub-volcanic and volcanic rocks of Late Paleozoic to Late Tertiary age. Hydrothermal activity and mineralization at ca. 8–9 Ma was largely associated with breccia emplacement at the intersections of a series of high angle faults. These are interpreted as the product of explosive phreatomagmatic activity during the waning stages of Miocene volcanism.

Pascua-Lama is in most respects a classic high-sulfidation epithermal system, characterized by a hypogene suite of sulphides and sulphates. Up to 50% of the sulphide assemblage is composed of pyrite and tetrahedrite-tennantite. The deposit shows evidence of successive phases of alteration, both with and without precious metal deposition. Early advanced argillic alteration was predominantly characterized by quartz-alunite-pyrite. This was followed by brecciation, and subsequently a second stage of advanced argillic alteration characterized by alunite-pyrite-enargite. Much of the zone of advanced argillic alteration is overlain by a silica cap, varying in thickness from 100–300 m.

Pascua Lama is distinguished from most other high sulfidation epithermal systems by an unusually high abundance of hypogene sulphate minerals (coquimbite, volteite, alunite and jarosite), a component of which is of high solubility. This has important implications for the environmental geology of the deposit. Both field and laboratory investigations suggest that contact water evolution is controlled by a complex range of processes involving both sulphide oxidation and sulphate dissolution. While both of these groups of processes constitute proton generating reactions, the dissolution of alunite and attendant precipitation of gibbsite induces buffering at around pH 3.5, subject to suitably constrained rates of proton flux from the oxidation of pyrite or other sulphides. In analogous fashion to the silicate buffering mechanisms described for Boddington (above), the ultimate pH and wider chemical composition of Pascua Lama contact-water may therefore be equally influenced by rates of oxidation as by sulphide abundance or mineralogy.

Alumbrera, Argentina

Alumbrera is a Cu-Au porphyry deposit which has been exploited via a single open pit since the 1990s. Its surface expression was originally that of a large bowl located at around 2600 m a.s.l. The deposit consists of several dacite-porphyry plugs which were intruded at around 8 Ma beneath the Farallon Negro volcano. Syn-intrusive hydrothermal fluid circulation resulted in pervasive alteration and mineralization of the porphyritic plugs and their volcanic host rocks. Subsequent erosion exposed the upper part of the volcano and its underlying porphyry system.

Stocks forming the Alumbrera deposit are compositionally similar, with phenocrysts of plagioclase, hornblende, biotite and quartz in a matrix of fine-grained quartz, K-feldspar, and minor plagioclase, biotite, and magnetite. High Cu-Au grades are associated with the zone of potassic alteration, surrounded by a larger zone of secondary biotite. The biotite zone is surrounded by epidote-chlorite alteration, lacking significant sulfides. Weaker, post-mineralization feldspar destructive alteration occurs both inside and outside this shell. Deposition of Cu-Au occurred within an assemblage comprising bornite-chalcopyrite-magnetite. Later pyrite veins cross-cut the zone of primary mineralization.

In some respects a classically zoned porphyry system, the environmental geochemistry of Alumbrera is distinguished by a high frequency of post-mineralization gypsum veining. This is pervasive throughout the deposit with the exception of a thin blanket of oxidation and secondary Cu enrichment in which the gypsum veins have been removed. The presence of this source of soluble sulphate is significant to the interpretation of kinetic tests as SO_4 yields appear poorly correlated to rates of sulphide oxidation.

Agua Rica, Argentina

Agua Rica is located in the Province of Catamarca, Argentina. It is a classical porphyry Cu system of late-Tertiary age, with some evidence of epithermal overprinting. The deposit is differentiated from Alumbrera (located only 60 km to the north of Agua Rica) by a significantly more extensive zone of secondary mineralization, dominated by chalcocite and covellite.

Primary mineralization was developed along the contact between early Paleozoic meta-sediments of the Sierra Anconquija Complex and a series of intrusions dominated by the Capillitas Granite. The intrusive rocks include multiple quartz-feldspar porphyries in association with which several phases of hydrothermal breccia emplacement occurred. The Melcho Intrusive Complex is an early multiphase porphyritic unit which is weakly mineralized and occupies the southern third of the project area. The main mineralized intrusions are centrally located and consist of the Seca and Trampeadero stocks. These are cross-cut by a large breccia pipe. In the northern third of the project area, a weakly mineralized igneous breccia occurs along with a biotite porphyry and a diatreme breccia which appears largely barren. The metasedimentary host rock exhibits mineralized contact zones.

Both the primary and secondary zones of mineralization at Agua Rica are predominantly net-acid forming. In the primary zone, this reflects the presence of assemblages of pyrite, bornite and chalcopyrite (with minor Zn sulphides) at up to 15% abundance. In the secondary blanket, bi-metal sulphides dominate the copper inventory. These are acid generating exclusively on oxidation by ferric Fe.

Gaby, Ecuador

Gaby is a large, low grade Au porphyry system located in the coastal lowland of the Province of Azuay, Ecuador. It occupies a humid tropical setting with annual rainfall ranging from 2000 to 4000 mm. It is, to date, unexploited with the exception of a number of small-scale underground workings which have advanced along the trace of a number of post-pophryry gold-bearing veins (the Tama Vein system).

The Gaby porphyry was emplaced into a sequence of Cretaceous volcanic host rocks during the Late Tertiary period. It comprises a tonalite intrusion, plus a series of breccias. These display pervasive argillic, potassic and propyllitic alteration with the associated development of veins and stockworks of quartz plus chalcopyrite, bornite, pyrite, pyrrhotite and gold. A zone of oxidation extends to depths of up to 50 m at the centre of the deposit. Secondary Au/Cu enrichment is otherwise absent.

The environmental geochemistry of Gaby is uncomplex. With the exception of a relatively small component of the mineralized zone which extends into basaltic host-rocks of the Pallatanga Unit, virtually all potential ore and waste grade material is devoid of carbonate neutralization capacity, with high abundances of pyrite (of the order of 3 to 6%). An extensive static testing program performed in 2005 resulted in the classification of >80% of the rock mass within a feasibility level open pit design developed by former concession holder, International Minerals Corporation, as PAF.

Test data sources

Table 2 provides a summary of the kinetic tests from which leachate data were compiled for use in comparative analysis of the effects of scale on rock weathering behaviour and associated contact water chemistry evolution. For each study location, sub-samples from a single stock of material were typically generated for use in the laboratory and field scale tests. The respective sub-samples were subject to bulk geochemical and/or mineralogical characterization to confirm consistency of composition of the laboratory and field scale test materials. Table 3 provides a summary of the characteristics of each pair of samples.

Table 2 *Summary of laboratory and field scale tests of rock materials applied for assessment of scale effects.*

Site	Boddington		Pascua Lama		Gaby		Alumbrera		Agua Rica	
	Lab	Field	Lab	Field	Lab	Field	Lab	Field	Lab	Field
Design	AMIRA column	PVC tank	MEND HCT	Field crib	MEND HCT	Field barrel	MEND HCT	Field pad	MEND HCT	Field pad
Sample wt (kg)	1	15000	1	2600 – 3000	1	200	1	500	1	500
Duration (weeks)	128	128	33	12	36	26	40	30	24	162
Irrigation	Weekly irrigation	Natural precipitation	Weekly irrigation	Irrigated based on annual average precipitation	Weekly irrigation	Natural precipitation	Weekly irrigation	Monthly cycle, 2000 litres in 28 days	Weekly irrigation	Natural precipitation
Total sample numbers	10	6	5	5	10	7	7	8	12	5
Comparison samples	C1	B1	HCT1	MCRIB1	HCT2	T1	HCT1	P5	HCT-11	Pad C
	C2	B2	HCT5	MCRIB4	HCT3	T3	HCT5	P8		
	C4	B5								

Table 3 *Acid base accounting and basic mineralogical characteristics of samples used for assessment of kinetic test scale effects.*

Site	Samples		LAM description	Total S (%)	Sulphate S (%)	AP (kg CaCO$_3$/t)*	Carbonate NP (kg CaCO$_3$/t)	Principal mineralogical components (from XRD) (%)
	Lab	Field						
Boddington	C1	B1	Diorite - actinolite	0.2	<0.01	6.3	1.8	Biotite (9%), Chlorite (2%), Hornblende (2%)
	C2	B2	Diorite - Clinozoisite	0.2	<0.01	6.3	2.0	Pyrite (0.3%), Chalcopyrite 0.1%), Biotite (18%)
	C4	B5	Diorite - Silica-biotite / actinolite	0.35	<0.01	10.9	1.5	Pyrrhotite (0.3%), Chalcopyrite (0.1%), Sericite (13%)
Pascua Lama	HCT1	MCRIB1	Steam heated granites	0.9	3.6	28.1	0.8	Alunite (4.5%), K-feldspar (3%), Gypsum (0.5%)
	HCT5	MCRIB4	Alunite altered granites	2.1	1.2	65.6	1.2	Alunite (14%), Gypsum (2.2%), Jarosite (1.1%), Pyrite (0.5%)
Gaby	HCT2	T1	Hornblende porphyry	0.9	0.02	27	8	Pyrite (1%), Actinolite (12%)
	HCT3	T3	Avila Breccia	2.2	0.02	69	5.3	Actinolite (47%), Pyrite (2.6%), Pyrrhotite (1.5%), Chalcopyrite (0.4%)
Alumbrera	HCT1	P5	Andesite - K alteration	6	3	94	6	contains Gypsum**
	HCT5	P8	Andesite - epidote chlorite alteration	0.02	<0.01	0.6	97	
Agua Rica	HC11	Pileta C	Trampeadero porphyry	2.0	<0.01	63		Pyrite (2%), Bornite (0.2%), Chalcopyrite (0.2%)

*Calculated from sulphide S

**Indicated by bulk geochemistry and geological description

Results and discussion

Leachate pH and solute concentration trends

Median values of pH, plus the SO_4 and Cu concentrations in leachates from both laboratory and field scale kinetic tests from each selected location are shown in Table 4. The evolution of pH and sulphate concentration in leachates from both types of test are shown in Figure 1. Values of pH in the field tests are routinely lower than in the corresponding laboratory test. Solute concentrations are generally higher.

The nature and magnitude of observed differences in pH evolution in leachates from the laboratory and field scale test pairs (Figure 1) contrasts significantly between sites. In samples characterized by high acid production potentials (with sulphide abundances in excess of 2% or, in the case of one of the two Pascua Lama samples, a significant hypogene sulphate presence), comparably rapid rates of sulphide oxidation are evident in the field tests from their initiation. This results in a more rapid rate of leachate pH depression throughout all phases of the tests. In contrast, two of the Boddington sample pairs (C1-B1, C2-B2) display pH levels which are closely comparable through the first 20 or more weeks of weathering. Thereafter, the field columns are subject to significantly accelerated acidification, with pH values after ca. 140 weeks in the order of 4 compared with laboratory column leachate levels in the pH 5 to 6 range. This differential pH evolution is inferred to arise from the periodic accumulation and subsequent flushing of sulphide oxidation products in the field tests in response to natural (climatic) variations of irrigation regime. These periodic ‘pulses’ of acidity overwhelm the weak, kinetically-constrained, silicate buffering system characteristic of Boddington rock. This effect does not occur in the laboratory due to the more limited ‘storage’ of acidity arising from weekly irrigation.

Table 4 *Median values of pH, concentrations of sulphate and copper in laboratory and field scale tests of analogous materials.*

Site	Laboratory test	Field test	pH (pH units)		SO_4 (mg/l)		Cu (mg/l)	
			Laboratory	Field	Laboratory	Field	Laboratory	Field
Boddington	C1	B1	6.1	4.6	29.5	720	0.004	1.266
	C2	B2	5.5	3.7	7.0	745	0.1	31
	C4	B5	5.9	3.1	63.0	3900	0.002	14
Pascua Lama	HCT1	MCRIB1	3.8	3.0	47	2528	0.069	1.5
	HCT5	MCRIB4	3.9	3.0	668	4040	0.230	5.2
Gaby	HCT2	T1	6.2	3.3	26	827	0.119	25.4
	HCT3	T3	5.3	2.6	46	3030	0.175	22.9
Alumbrera	HCT1	P5	6.9	7.2	1037	1463	0.100	0.60
	HCT5	P8	8.6	7.7	0.04	1185	0.020	0.025
Agua Rica	HC11	Pileta C	5.1	2.5	15	ND	5.21	17.20

Role of sulphide oxidation rates

Further elucidation of the causes of differential pH (and solute concentration) evolution in the pairs of field and column tests for which results are presented in Figure 1 is provided from analysis of the estimated sulphide oxidation rates (SOR) characteristic of each test. Table 5 shows the rate of sulphate yield from each test on a mass specific basis, with values shown to represent the average and maximum levels recorded in each case. Sulphate yield may in the majority of the tests be regarded as a reasonable proxy of sulphide oxidation rate. The principal exceptions to this include the HCT1 - P5 sample pair from Alumbrera in which sulphate concentrations in both laboratory and field test leachates are predominantly controlled by gypsum dissolution, and the Pascua Lama sample pairs in which dissolution of alunite, jarosite and other hypogene sulphates is the dominant influence.

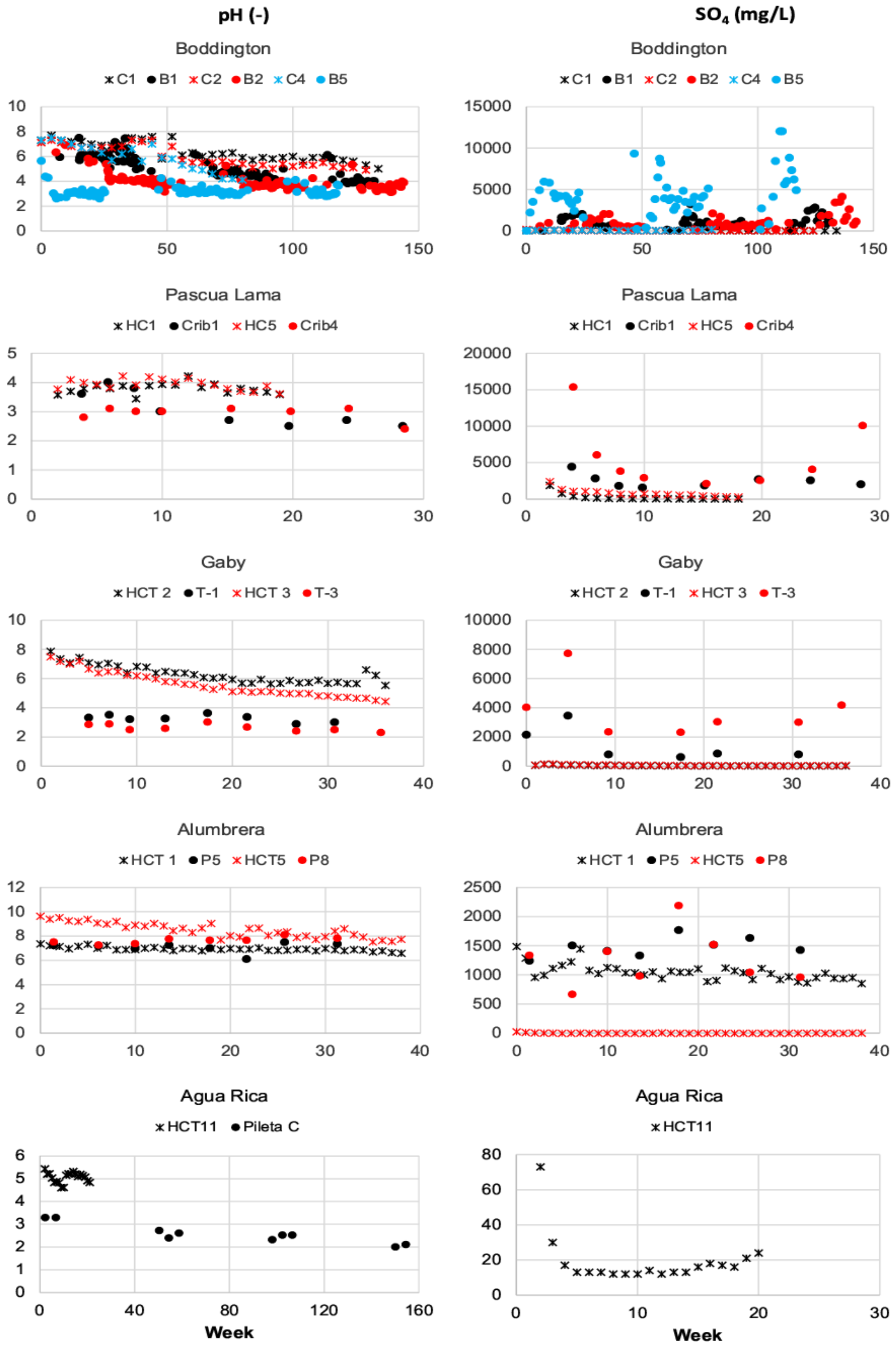

Figure 1 *Evolution of pH and sulphate concentrations in laboratory and field scale tests*

In several test pairs the more rapid depression of leachate pH level over time, with associated increase of solute load, can be equated to a systematically higher level of sulphide oxidation from an early stage in the test period. Typically this is seen in samples where significant net acid production potential is indicated by ABA analyses, with AP >20 kg/T $CaCO_3$ equivalent, with low, but some carbonate buffering capacity present (Table 3). The Gaby pair HCT3 - T3 reflects this condition. In the laboratory test, an average SOR of around 9 mg/kg/wk appears initially to be countered by carbonate dissolution in the early stages of the test, and to some extent throughout. In contrast a much higher rate (in excess of 70 mg/kg/wk) in the field test consumes carbonate rapidly and permits an acute depression of pH.

In certain tests, the relationship between SOR and pH evolution in the paired laboratory and field tests is more complex. This is demonstrated by the Boddington sample pairs C1 – B1 and C2 – B2, characterized by trace sulphides (0.2%) in a matrix virtually devoid of carbonate. In these test pairs, the average SOR is actually greater in the laboratory environment than in the field test. However, the range of SORs recorded over time, and in particular the maxima recorded during the test period are greater in the field tests. In the laboratory tests, buffering by non-carbonate mechanisms appears adequate to counter the proton yields associated with a relatively constant SOR of around 5 mg/kg/wk with excursions of up to no more than around 14 mg/kg/wk. The buffering system is not able to react effectively to sporadic maxima of up to 20 mg/kg/wk or greater as observed in seasonal 'first-flush' events in the field setting.

Table 5 *Average and maximum mass-normalised sulphide oxidation rates (SOR) in laboratory and field scale tests of analogous materials.*

Site	Laboratory test	Field test	Average laboratory SOR (mg/kg/week)	Maximum laboratory SOR (mg/kg/week)	Average field SOR (mg/kg/week)	Maximum field SOR (mg/kg/week)
Boddington	C1	B1	5	14	3	19
	C2	B2	5	14	3	22
	C4	B5	10	25	13	72
Pascua Lama	HCT1	MCRIB1	10	46	97	231
	HCT5	MCRIB4	60	106	199	721
Gaby	HCT2	T1	17	66	19	148
	HCT3	T3	9	85	76	153
Alumbrera*	HCT1	P5	515	744	46	54
	HCT5	P8	1	12	226	265
Agua Rica	HC11	Pileta C	9	31	No SO_4 data	

*Assumes a volume of 500 ml discharging from the HCT

Causes of differential sulphide oxidation rate

Investigations performed for paired laboratory and field tests involving either (a) empirical correlation of variations of SOR with environmental factors such as temperature and precipitation or (b) experimental variation of specific factors such as temperature and moisture cycles in laboratory columns has provided strong evidence to explain the generally more aggressive oxidation regime created in field scale versus laboratory tests. The specific factors considered of importance in this context include the following:

1) Sample homogeneity. In virtually all laboratory scale tests, the preparation of samples involved crushing to a uniform sub-2 mm or finer grain size. This has the fundamental effect of creating a relatively homogeneous medium in terms of mineralogy. Under such conditions, sulphide oxidation throughout the test sample is likely to be uniformly equilibrated with buffering reactions, including carbonate dissolution. This stops the generation of localized zones within the sample matrix where disproportionately high abundances of sulphides may acutely depress the pH of interstitial water within the pore space, the related stabilization of ferric Fe and the resultant propagation of an enhanced sulphide oxidation rate through the sample matrix. In field

tests, the inherently greater degree of sample heterogeneity with respect to both mineralogy and hydraulic properties favours the induction of localized centres for acute ARD propagation.

2) Granulometry. A further consequence of the fine-grained nature of laboratory test samples is that sulphides, plus those phases which are instrumental in acid consumption are intimately mixed in a manner which facilitates reactions to occur at the granular scale in a manner which optimizes their respective kinetics. This contrasts significantly from conditions inferred to exist in several of the field tests for which data are presented.

3) Moisture content. Field columns or cribs show evidence that oxidation rates may rise to exceed buffering capacity sooner when permitted to dry to, or near, residual moisture. This is particularly evident in the Boddington field cribs. In Pascua Lama Crib 1, a sharp reduction in pH is also observed in conjunction with the first flushing event (snowmelt) following a prolonged period of zero water infiltration. Such conditions are specifically averted in laboratory humidity cells run in accordance with any of the MEND, AMIRA or ASTM protocols. For the Boddington laboratory columns, the significance of variation of the moisture content regime was assessed through advertent drying of the columns for several weeks with effect from week 109 (see Figure 1). After re-wetting, the pH decreased by 1.5 to 2.5 pH units and remained at these comparatively low levels until test completion.

4) Temperature. A further factor which has been confirmed experimentally to influence SOR rates within both field and laboratory test environments is temperature. In the field setting, this is inevitably a direct function of climate. For substantial periods the Pascua Lama crib tests were operated at close to 0 ºC, with oxidation kinetics inherently constrained. A more striking bias in the leachate chemistries from paired laboratory and field tests has been confirmed to occur in the case of the Boddington samples, where laboratory columns were operated at 20°C while field tests were subject to summer ambient temperatures of 30ºC. Following the induced elevation of temperature to around 30°C in a series of test columns performed on Boddington rock demonstrated significant increases of SOR to levels broadly comparable to those documented in Table 5 for the field crib tests (Campbell et al. 2012).

Conclusions

The results and interpretation presented in this paper of comparative leachate chemistry evolution trends in ‘paired’ kinetic tests performed at laboratory and field scales prompts the central conclusion that more ‘conservative’ test results are routinely derived from large scale tests performed under ambient field conditions. A critical implication of this is that the chemistry of kinetic test leachates is not exclusively a function of mineralogical properties of the sample medium. In making inter-site comparisons of kinetic test data, due regard must therefore be afforded to the specifics of test design and operation. Without the necessary understanding of the context or environmental conditions under which leachate data are generated, their value for extrapolation to ‘real world’ field conditions may be critically undermined.

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REE-Enriched Mn-Oxide Precipitates in Water-Bearing Fractures in the Ytterby Mine, Sweden

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Abstract

The Ytterby mine, Sweden, is known for the discovery of eight elements, including yttrium and five of the rare earth elements (REE). The mine was in operation from 1750 to 1933 and was after closure used as a storage depot for fuel from the 1950s to 1995. A tunnel was opened in the 1950s through the bedrock into the mine to allow access to the storage depot. Recent water monitoring campaigns (2012-2015) in the mine revealed a black substance (denoted YBS) in some fractures opening into the tunnel.

Analysis of the YBS (elemental analysis, phase analysis by XRD, SEM with energy dispersive X-ray spectrometry, IR- and EPR-spectroscopy, preferential leaching at pH 4) showed that the main mineral component of the YBS is the manganese oxide birnessite. Also minor quantities of other less well defined manganese oxides were found, as well as silicates (quartz grains, possibly feldspar grains) and calcite. Birnessite has typically the composition $M_x(Mn^{3+},Mn^{4+})_2O_4xAq$, with M=Na,Ca and x=0.5. The birnessite component in YBS had a Mn^{3+}/Mn^{4+} ratio of 1.04/0.96 with M = 0.42 Ca + 0.03 (REE+Y), 0.03 Mg and 0.03 other metals. All of these metals were firmly associated with the structure, since no release was observed at pH 4, except for significant fractions of the total Na, Mg, Ca-contents. Thus, REE+Y correspond to 1% of the total YBS mass and up to 3% of the metal content in the birnessite phase. This corresponds to an REE enrichment factor of the order 10^6 (YBS-birnessite/fracture water). Birnessite with a substantial fraction of REE in the lattice has not previously been reported.

The formation of birnessite is a microbial process. Identification of the microorganisms present in the Ytterby system is in progress.

Key words: Mine water geochemistry, manganese oxide precipitation, birnessite, rare earth elements

Introduction

The Ytterby mine located on Resarö in the Baltic Sea, Sweden, is known for the discovery of five of the rare earth elements (REE), as well as yttrium, scandium and tantalum (Enghag 1999). In the 1750s quartz and feldspars, were mined from Ytterby as raw materials used for the production of porcelain, and by 1933 the mine was closed. The mine, which is a single shaft with a depth of some 145 m, was used for storage of fuel from the early 1950s until 1995. A tunnel was opened through the bedrock into the upper part of the shaft, 29 m below ground surface but above the fuel storage level and 5 m above sea level.

A black soft precipitate with an oily appearance was observed, seeping from some of the fractures in the tunnel, during monitoring campaigns in 2012 and 2014, see Figure 1 (Sjöberg 2012; Sjöberg 2014). Analysis of this precipitate, which was also observed to occasionally produce gas bubbles, was the objective of the present study, focusing mainly on its mineralogical composition. Of particular interest was the investigation of associated trace elements and organics in this unusual environment with potential sources of REE as well as uranium and thorium in the bedrock.

A detailed description of the project is given by Sjöberg et al. 2016.

Figure 1 *Photo of the precipitate (YBS)*

Geology/hydrology

The bedrock in the Ytterby area is part of the crystalline basement of the Baltic Shield. Isotopic age determination of pegmatite from the region indicates an age of approximatively 1795 Ma (Romer and Smeds 1994). The pegmatite in the mine is bordered by amphibolites as well as gneiss. Some 50 minerals have been identified in the pegmatite, including 15 containing REE (Sundius 1948, Brotzen 1959).

The hydraulic conductivity in the bedrock in the mining area is of the order $3x10^{-8}$m/s, corresponding to an inflow of water to the shaft of some 9 m^3/day (Rydström 2001). The inflow comprises infiltrating precipitation, as well as intruding shallow groundwater, and deep groundwater to the lower parts of the mine shaft.

Methods

The black precipitate (denoted YBS) from the tunnel leading to the mine shaft was collected during water sampling campaigns in 2012-15 using sterile equipment and stored in glass bottles prior to analysis. Water was collected in polyethylene bottles from fractures, the mine shaft and shallow groundwaters from several sampling holes near-by the mine. Samples were filtered (0.2 μm) and pH, temperature and conductivity were measured in the field. Samples for element analysis were acidified and stored in a fridge prior to analysis.

Solid YBS characterization

Analysis by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry was carried out (Stockholm University) in order to get compositional information, as well as a visual picture of the YBS.

Mineralogic phases were determined by X-ray diffractometry (XRD) (Stockholm University and Swedish Museum of Natural History).

Structural information was also obtained from infrared and electron paramagnetic resonance spectroscopy (Örebro University and Linköping University).

The various procedures and analyses are described in detail in Sjöberg et al. 2016.

Element analysis of YBS and water

Solid samples of YBS were washed and dried and digested following different procedures. The digested YBS samples and the water samples collected in the field were analyzed at four different laboratories (by ICP-MS, ICP-OES; ALS Scandinavia, Sweden; Activation Laboratories Ltd, Canada; Örebro University, Sweden and Friedrich Schiller University, Germany).

YBS leaching

A leaching test was performed in order to establish how minor components of the YBS were associated with the major matrix:

Exchangeable, carbonates, fresh hydroxides - leaching at pH 4 with 0.11 M HAc

Results and discussion

The composition of the YBS (one of the four analyzed samples, also used in the leaching test) is given in Table 1.

Table 1 *Concentrations and leachable fractions at pH 4 of major components and trace elements above the 0.02%-level.*

	YBS mg/kg	Leachate pH4 %		YBS mg/kg	Leachate pH 4 %
Na	320	44	Al	750	0
K	411	4	Si	2480	0
Mg	3590	47	V	471	0
Ca	60750	22	Mn	354065	2
Sr	635	20	Fe	790	0
Ba	1860	<1	Cu	1310	0
Y+REE	11410	0	Zn	421	0

The leachable fraction at pH 4 corresponds to exchangeable and adsorbed metals, as well as carbonates. The major component in the remaining YBS is Mn with 83.5% of the total mass of metals plus Si, followed by Ca (11.2%), REE+Y (2.7%), Na+K+Mg+Sr+Ba (1.1%), Al+Si (0.8%) and V+Fe+Cu+Zn (0.7%). The Al+Si-fraction can be attributed to silicate and quartz grains in the precipitate that is largely an oxide of Mn(III) +Mn(IV).

Scanning electron microscopy images (SEM) of YBS, Figure 2, show dendritic shrub-like or microspherolitic botryoidal morphologies with concentrations of Mn of 82-86%, Ca 8-13% Mg <2% and all other elements (besides O) <1%. Mn/Fe-ratios are above 100, comparable with the analyses, Table 1, giving Mn/Fe = 448. Individual quartz grains can be seen in some images, as well as calcite particles, not part of the Mn-oxide matrix.

A biogenic origin is indicated from the electron paramagnetic resonance spectroscopy that confirms the presence of a biogenic MnO_2 component having a spectral width of 600 Gauss, and an abiotic component with a spectral width of 1800 Gauss (Sjöberg 2014).

The infrared spectrum only shows one weak absorbance peak at 1630 cm^{-1} (possibly C=O), as well as a pronounced absorbance below 800 cm^{-1}indicating a dominating metal oxide, but no distinct C-H peaks.

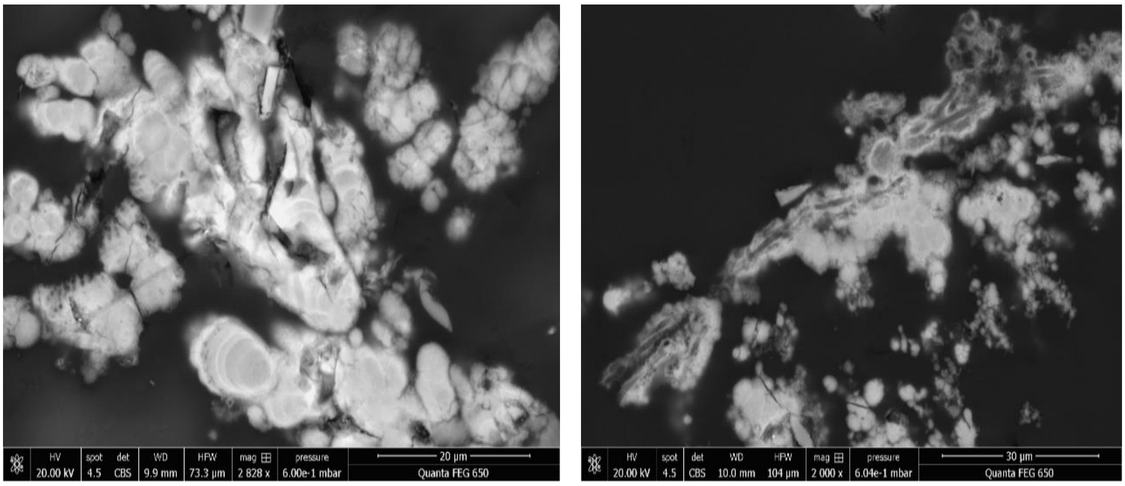

Figure 2 *SEM images of the YBS*

Carbon isotopic analysis has previously indicated that dried YBS contains about 1.8% carbon, including ca 0.6% that is organic (δ^{13} of -24,73; Sjöberg 2014). Leaching with an alkaline solution did not release the organic carbon (no humic acids), but solvent extraction and lipid extraction indicate that the organic carbon fraction contains a range of lipids which indicate that the YBS contains a biogenic fraction (work in progress).

X-ray diffractogram, Figure 3, confirms that YBS consists of some 80-90% of a manganese oxide of the birnessite type (typically $M_{0.5}[Mn(III),Mn(IV)]_2O_4$ xAq, where M usually is Na or Ca). There are also minor fractions of calcite, some other manganese oxides (manganates), as well as feldspars and quartz but no distinct iron oxide phase.

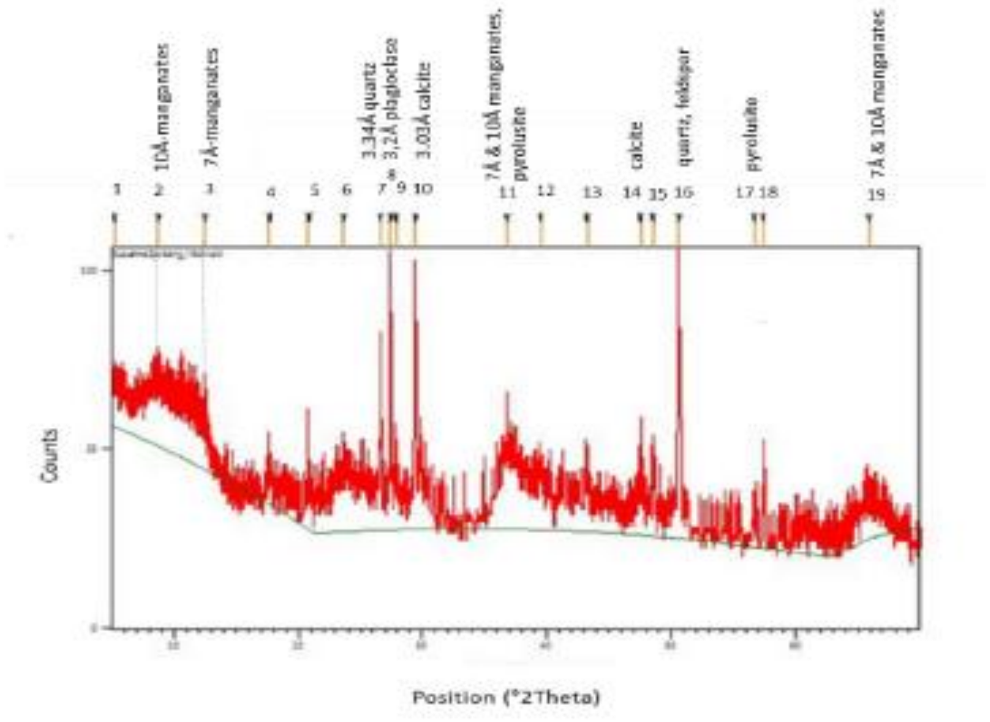

Figure 3 *X-ray diffractogram of the precipitate (Sjöberg 2014)*

Concentrations, with omission of the leachable fraction (pH 4), and corresponding number of atoms/mol, assuming 2 manganese atoms in the birnessite unit, are given in Table 2. Two different cases are compared:

I: All of the manganese (except the leachable fraction) constitutes the birnessite phase

II: Only 90% of the non-leachable manganese constitutes the birnessite phase, with 10% in other non-defined manganate phases.

Table 2 *Composition of the proposed birnessite phase calculated from the concentrations of non-leachable major components and trace elements above the 0.02%-level*

	YBS mg/kg	YBS mmol/kg	YBS atom/mol (I)	YBS atom/mol (II)
Mn	347560	6330	2	2
Ca	47380	1180	0.37	0.42
REE+Y	11410	85.5	0.025	0.030
Mg	1900	78.3	0.025	0.028
Na+K+Sr+Ba	2940	37.2	0.012	0.013
V+Fe+Cu+Zn	2990	50.4	0.016	0.016
Total			2.45	2.50

I: 98% of total manganese in birnessite
$M_{0.45}(Mn^{3+},Mn^{4+})_2O_4$ xAq with $Mn^{3+}/Mn^{4+}= 0.94/1.06$
M = 0.37 Ca + 0.025 (REE,Y) + 0.025 Mg + 0.028 other metals
REE+Y = 2.7% of the metals, 1.1% of the total mass

II: 88% of total manganese in birnessite
$M_{0\ 50}(Mn^{3+},Mn^{4+})_2O_4$ xAq with $Mn^{3+}/Mn^{4+}= 1.04/0.96$
M = 0.42 Ca + 0.030 (REE,Y) + 0.028 Mg + 0.029 other metals
REE+Y = 3.0% of the metals, 1.1% of the total mass

The composition according to assumption II is close to the ideal composition, however with 0.03 (REE+Y) in the structure.

The source of manganese is the groundwater; there are no accumulations of discrete manganese minerals in the bedrock surrounding the mine. The source of REE is obviously the REE-rich minerals in the pegmatite.

Some water data are given in Table 3, representing present oxic conditions with substantial in-flow of precipitation and shallow groundwater into the mine and the water-bearing fractures above the groundwater level (from the 2015 campaign, Förster 2015). All of GW 2, Shaft and Fracture waters have presently a Ca-carbonate signature and a high pH. Groundwater GW 1, from a sampling hole close to the Baltic Sea, has a Na-carbonate signature with a higher sulfate level. Considerably higher concentrations have been recorded of all the major species, including manganese, in deep groundwaters in the area (Augustsson et al. 2009) as well as in the shaft (anoxic conditions with little inflow of surface water). However, no older records showing past levels of REE in the mine or in the the groundwaters are availabe. Therefore, data in Table 3 may not be representative of the conditions during the early years of the tunnel, when precipitation of birnessite was initiated. However, an enrichement factor, defined as [Concentration in solid YBS]/[Concentration in solution], [Lit/kg] would be of the order 10^6 when calculated using present day concentrations.

Table 3 *Present water chemistry in shallow groundwaters and fracture water*

	GW 1 mg/l	GW 2 mg/l	Shaft mg/l	Fracture mg/l
pH	8.17	7.95	8.29	8.30
Cl^-	10.5	10.5	24.4	15.3
SO_4^{2-}	51.7	21.5	29.7	29.4
HCO_3^-	240	21.5	29.7	29.4
DOC	8.2	6.6	8.0	4.2
Na	102	34.2	19.3	28.4
K	3.08	1.75	4.83	1.54
Mg	3.81	5.51	7.99	7.71
Ca	13.4	51-0	59.7	53.4
Mn	1.31	1.09	1.80	2.77
REE+Y	0.0011	0.0018	0.0028	0.0068

GW 1, GW 2: Shallow groundwater within 50 m from the mine

Shaft: Surface water in the shaft

Fracture: Water in fracture with YBS precipitate

Conclusions

The black precipitate discovered in Ytterby mine tunnel fractures is mainly birnessite, together with other manganese oxide phases not yet specified. In addition minor fractions of quartz, feldspars and notably calcite, not associated with the birnessite were found. The birnessite appears to have a biogenic origin, as indicated by the morphology (SEM) and by the presence of some 0.6% organic carbon, containing lipids and no humic substances. An arbitrary composition can be assessed as $M_{0.5}(Mn^{3+},Mn^{4+})_2O_4$ xAq, where M = 0.42 Ca + 0.030 REE,Y + 0.028 Mg + 0.029 other metals, with a Mn^{3+}/Mn^{4+} - ratio of 1.04/0.96. The REE fraction appears to be a structural component in the birnessite and not only adsorbed and easily exchangable. What makes the YBS-birnessite unique is the REE-enrichment: Ca 3% of the metal content, corresponding to 1.1% of the total mass.

Work is in progress to assess the formation process, where REEs are replacing sodium and largely calcium in the lattice, and to identify if manganese oxidizing bacteria are involved in the formation of this REE enriched birnessite.

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Fine Ash Leaching in Tailings Dams – An Impact on the Underlying Aquifers?

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Abstract

Fine ash is a by-product generated during coal combustion and gasification at power stations around the world. The majority of fine ash is stored on tailings dams over decades where it is influenced by weathering processes. In the presence of water, weathering causes dissolution of fine ash components which may be transported along preferred pathways through the tailings dam or re-precipitate. This study aimed to investigate the leaching behavior of fine ash and to evaluate the impact of long-term leaching on the underlying aquifers. Fresh and weathered fine ash samples were collected from different depths of a tailings dam in Mpumalanga, South Africa. A kinetic leaching test was conducted to analyse the leachate composition, calculate the release rate of major ions and trace elements of environmental concern and to compare the leachate composition with the groundwater chemistry. Leaching results showed that the release rates of elements including Ca, B, Ba and Al decreased with depth and age of the fine ash while it increased for V, Mo, Cu, Mn, Si, Li, Cr and SO_4. A constant release rate was measured for Se, Fe, Na, Mg, K, NO_3 and Zn. The main components of the fine ash leachate (SO_4, Ca, Na, Cl, Mg and K) were found to influence the water composition of the underlying aquifers. Downstream of the tailings dam, the water type of the shallow aquifer changed from Ca/Mg/SO_4/Cl/NO_3 to $NaSO_4$/Cl with a significant increase in Na, K and decease in Ca and Mg over time. A reverse trend in water type alteration was observed in the deeper aquifer. This confirmed that the leachate plume moved laterally and vertically from the shallower to the deeper aquifer and that the underlying clay strata were insufficient in retaining the leachate from the tailings dam.

Key words: fine ash, leaching, tailings dam, aquifer

Introduction

South Africa is heavily dependent on its coal production to generate low cost electricity by coal-fired power stations to meet the growing energy demand. During coal combustion, high quantities of by-products are generated including fly, bottom and gasification ash (Mahlaba *et al*. 2011). South Africa produces approximately 30 Mt of fly ash annually, making it the fourth largest fly ash producer in the world (Furter 2011). For disposal purposes, the combustion by-products are mixed and screened into a particle size range between 0.01 µm and 250 µm and above 250 µm, forming fine and coarse ash respectively (Mahlaba *et al.* 2011). Approximately 5% of the generated fine and coarse ash is recycled; the remainder is disposed separately on tailings dams either hydraulically or via conveyor belts (Gitari *et al*. 2009).

The chemical composition of fine ash is influenced by the coal constituents, the materials added during combustion, the combustion process itself and on the pollution control technology applied (Neupane and Donahoe 2013). Major fine ash components include SiO_2, Al_2O_3, Fe_2O_3 and CaO (Gitari 2006; Mahlaba *et al*. 2012). Minor oxides are MgO, Na_2O, K_2O, P_2O_2, TiO_2, MnO and SO_3 (Mahlaba *et al*. 2012). A wide variety of trace elements may occur in fine ash which differs depending on the coal composition (Akynemi *et al*. 2012). In addition, the high specific surface area and small particle size of fine ash favours the accumulation of trace elements and results in a high chemical reactivity (Gitari 2006).

The disposal of fine ash on tailings dams over decades poses a potential threat to the environment if heavy metals leach into the surrounding area due to weathering. Weathering processes occur in physical, chemical and biological forms and are influenced by temperature changes, precipitation and pressure within the tailings dam (Selby 1993). Chemical weathering processes include dissolution and precipitation of minerals, cation exchange, reduction and oxidation as well as hydration and hydrolysis which may alter the composition of fine ash over time (Price 2009). Ingressing CO_2 from the atmosphere and the infiltration of rain water are the main causes for changes in pore water pH, which control the mobility of several elements and consequently the leachate composition of fine ash (Gitari *et al*. 2009).

The leaching capacity of fine ash and the extend of environmental pollution depends on the chemical composition of the ash, and the type of disposal, wet or dry, which may enhance or reduce the leaching of toxic elements into the environment. The literature has been controversial about the effects of fine ash disposal on the environment. Research conducted on the leaching potential of fine ash by Mahlaba *et al*. (2011) and Matjie *et al*. (2005) indicated that no significant leaching of toxic elements took place from fine ash tailings dams into the environment. Carlson and Adriano (1993) conversely observed that fine ash which was disposed in form of saline slurry in drying ponds showed enhanced leaching of toxic elements into the environment. Jones (1995) found that elements such as B, Cd, Cr, Co, Se and As leached from fine ash dams which are harmful to fauna and flora, even at low concentrations. In addition, leaching tests conducted on fine ash produced by Sasol and Eskom often revealed major soluble ions such as Ca^{2+}, Na^{+}, SO_4^{2-}, K^{+} and Cl^{-} (Gitari *et al*. 2009; Matjie *et al*. 2005). These ions can be problematic to the environment as their concentration in solution cannot be controlled (Matjie *et al*. 2005).

The purpose of this article is to describe the leaching chemistry of fresh and weathered fine ash and to assess the influence of fine ash leaching on the underlying shallow and deeper aquifer. Each tailings dam is a unique system due to its heterogeneity in chemical composition and layering of alternating grain sizes. Therefore, this research aimed to add to the understanding of fine ash leaching through a tailings dam profile to predict the impact of long-term ash storage on the environment.

Materials and Methods

Twenty-four weathered fine ash samples were collected from the terraces of a tailings dam and one fresh ash sample was collected from the surface of a tailings dam in Mpumalanga, South Africa. Three samples were collected per terrace, dried, well mixed and thereafter combined to one composite sample. X-ray fluorescence (XRF) was utilized to determine the chemical composition for each sample. Each composite sample was split with a riffle splitter to a sample size of 1 kg for kinetic leaching. In total, eight composite samples and one replicate were leached over a test period of 21 weeks by using humidity cells.

The humidity cells were constructed according to option B described in the ASTM D5744-13 (2013) guideline with several alterations. The cell height was changed to 12.5 cm and the outer and inner diameter was altered to 19.9 cm and 19.45 cm respectively due to the dimensions of the PVC pipe available. The filter medium was composed of 2 mm thick polyester felt positioned on top of the perforated plate. An inlet was added at the upper part of the humidity cell for the inflow of moist and dry air according to Price (2009). A drainage outlet was constructed at the bottom side of the humidity cell (fig. 1). The humidity cell test procedure was conducted according to the ASTM D5744-13 (2013) guideline.

Inductive coupled plasma/optical emission spectrometry (ICP/OES) with the aid of a Perkin Elmer Optima 3000 DV ICP system was applied to analyse the chemistry of the obtained leachate. For each humidity cell sample, the pore volume (V_p) was calculated with the following equation:

$V_p = \frac{weight\ of\ saturated\ sample - weight\ of\ dry\ sample}{\rho_w}$, where ρ_w is the density of water: $\rho_w = 1.01\,\frac{g}{cm^3}$.
The leachate chemistry results were normalised against the exchanged pore volume (EPV) of each fine ash sample and compared to the sample depth of the tailings dam. In addition, the leachate chemistry of the fine ash was compared to the groundwater chemistry of five boreholes obtained during 25 years of monitoring in the vicinity of a fine ash tailings dam. The boreholes were located downstream of the groundwater flow direction and included two shallow (BH1S, BH2S) and one deep aquifer intersecting boreholes (BH1).

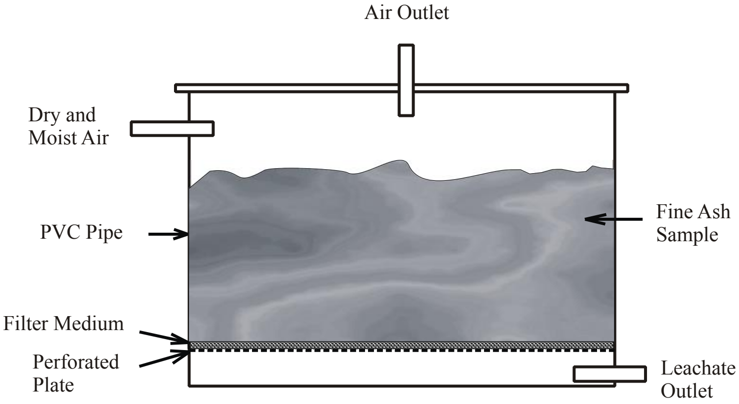

Figure 1 *Humidity cell design with alterations (modified from Price 2009).*

Results and Discussion

Chemical Composition of Fine Ash

An XRF analysis of the fresh and weathered fine ash samples indicated that the chemical composition contained major oxides SiO_2, Al_2O_3, CaO, Fe_2O_3, and minor oxides MgO, TiO_2, Na_2O, K_2O, P_2O_5 as well as MnO. A broad spectrum of trace elements were detected in both fresh and weathered fine ash which varied in concentration due to the alternating composition of the coal source. XRF-results indicated that the fresh fine ash was on average more enriched in trace elements As, Br, Co, Cr, Nb, Pb, Rb, V and Y. Most of these trace elements occurred as oxyanions and were therefore more readily leached from the negatively charged fine ash particle surface at a high pH (9.4). Consequently, weathered fine ash was more depleted in trace elements, as they were rinsed off from the particle surfaces during leaching.

Leachate Composition

The average concentrations of readily soluble components detected in the fine ash leachate after 21 weeks of induced weathering are indicated in Table 1. Sulfate, Ca, Na, Cl, Mg and K were highly soluble in fresh and weathered fine ash. This was mainly caused by the interaction of fine ash with brine during disposal that formed soluble salts on the particle surface. These salts were readily dissolved during leaching.

Table 1 *Average concentrations and standard deviation (±) of readily soluble fine ash components after kinetic leaching over 21 weeks.*

Soluble components	Concentration (kg/t)
SO_4	2.67 ± 1.13
Ca	0.74 ± 0.26
Na	0.56 ± 0.53
Cl	0.41 ± 0.47
Mg	0.10 ± 0.08
K	0.09 ± 0.04
B	0.027 ± 0.009
NO_3	0.022 ± 0.019
Si	0.007 ± 0.003
Li	0.004 ± 0.003
Al	0.003 ± 0.001
Cr	0.002 ± 0.001

Leaching Profiles of Major and Minor Elements

The average release rates of major (Si, Al, Fe, Ca and M-alkalinity) and minor (Mg, Na, K, Mn, NO_3 and SO_4) fine ash components as well as trace elements were compared to the depth of the tailings dam (fig. 2). It was found that most elements were released at a higher average rate from the fresh fine ash compared to weathered fine ash. This was caused by elements being concentrated on the relatively big surface area of the fine ash particles during cooling after combustion. Elements which did not show an increased release rate in fresh fine ash compared to weathered fine ash included K, Fe and Mo. This suggests that a large amount of these elements was locked in the ash matrix and was rather gradually released during weathering of the fine ash particles. Potassium is particularly known to be absorbed into the fine ash particle during amorphous clay formation, leading to a relative constant concentration in the leachate.

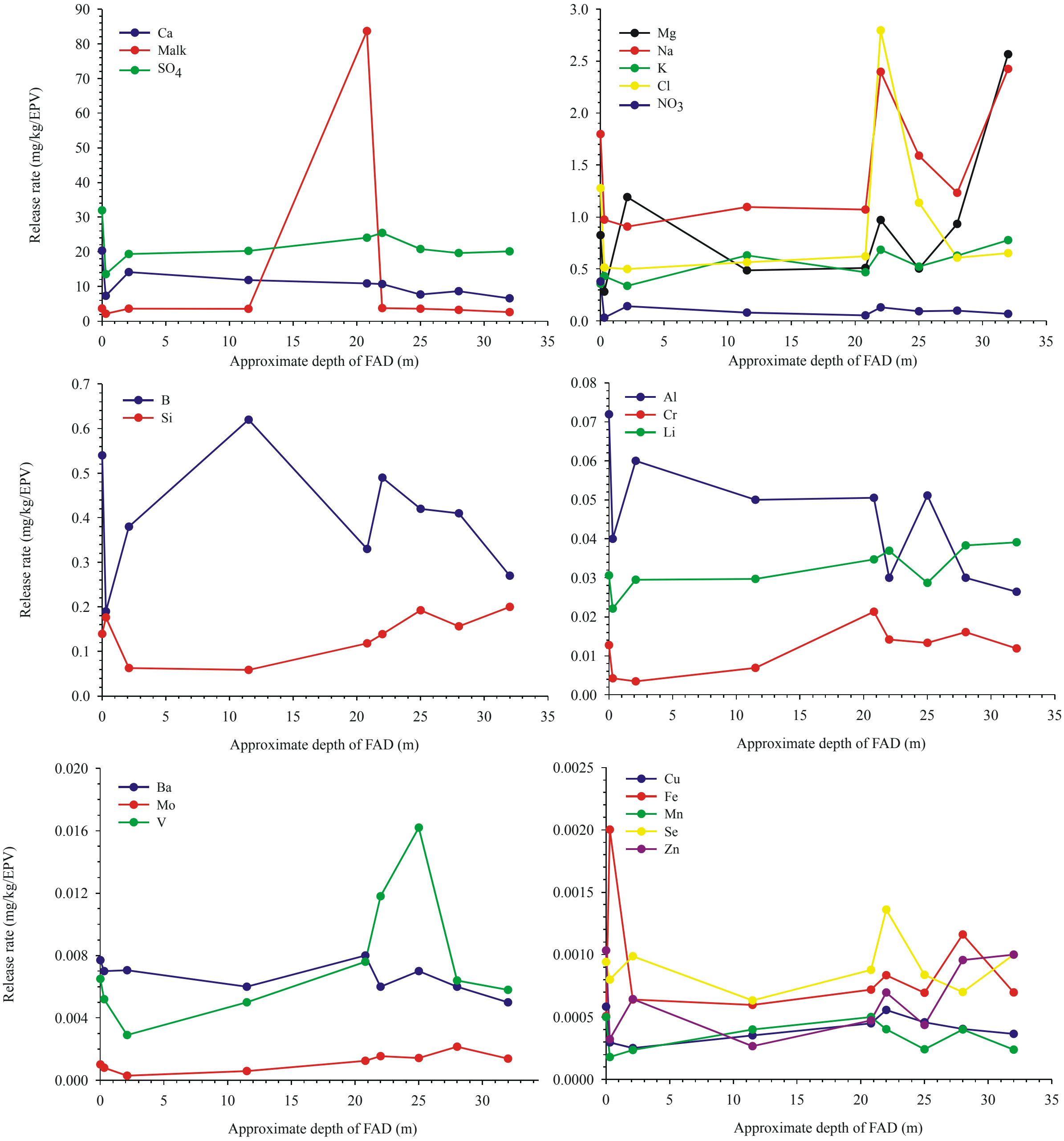

Figure 2 *Leaching rate profiles of major and minor components and trace elements in fine ash normalised to exchanged pore volume (EPV).*

At a depth of circa 0.3 m from the top of the tailings dam, the release rate of Ca, Mg, SO_4, NO_3, B, Al, Li, Se, Mn and Zn was substantially lower, whereas Fe and Si had an increased release rate (fig. 2). It is suggested that the low release rates were influenced by the precipitation of less soluble secondary mineral phases in the presence of atmospheric CO_2 and water reducing the release rates at shallow depth. The high release rate of Fe was attributed to the elevated Fe concentration in the fine ash collected at 0.3 m depth which was a result of the addition of Fe-rich catalysts during the combustion process.

At approximately 2.1 m depth, the release rate of Ca, Mg, NO_3, Al, Se and Zn was elevated compared to other major, minor and trace elements (fig. 2). This could be a result of ingressing atmospheric CO_2 at shallow depth forming carbonic acid which in turn dissolves carbonate minerals and glass particles. The formation of carbonic acid also led to higher concentrations of HCO_3^-, Ca^{2+}, Mg^{2+}, NO_3^- and associated trace elements Al, Se, and Zn ions in solution. During evapotranspiration near the surface, these ions then precipitated as carbonate and sulphate minerals as well as amorphous clay if oversaturated. Gitari *et al.* (2009) also noted that enhanced weathering took place at the upper layer of a tailings dam where carbonates formed in the presence of atmospheric CO_2 and water.

Except for the leaching rates varying at shallow depth, three general trends of release rates with increasing depth were observed in the unsaturated zone of the tailings dam:

- Elements which had a decreasing release rate with depth (Ca, B, Al and Ba);
- Elements which had an increase in release rate with depth (V, Mo, Cu, Mn, Si, Li, Cr and SO_4);and
- Elements which had a constant release rate throughout the depth of the tailings dam (Se, Fe, MAlk, Na, Mg, K, Cl, NO_3 and Zn).

The declining release rates of Ca, Al, B and Ba suggests that these elements are progressively leached over time and lower concentrations are therefore available to be leached from the deeper and older fine ash samples. In addition, during prolonged weathering, Ca and Al continuously precipitate to form an amorphous crust on the fine ash particles which alters into crystalline clays which are less soluble (Janssen-Jurkovicová *et al.* 1994). Barium and B could co-precipitate with amorphous clay and other secondary mineral phases which could decrease their solubility with depth and age of the tailings dam.

An increase in release rate observed with depth of most trace elements could be explained by their concentrations increasing relative to the other elements in the leachate solution which were more likely to precipitate or adsorb onto mineral surfaces in an alkaline environment. Oxyanions such as V, Mo, Cr (VI) and SO_4 are expected to be leached and transported from upper to lower fine ash layers as they are more soluble under alkaline conditions due to the increased negative charge of the fine ash particles (Jones 1995). An increase in the Si release rate with depth represents the gradual dissolution of primary silicate minerals present in the fine ash (Brubaker *et al.* 2013).

Elements which had a constant release rate throughout the unsaturated zone of the tailings dam suggested that their dissolution and precipitation had reached an apparent steady state in the system. The solubility of these elements was most probably controlled by the dissolution rate of major mineral phases containing these elements.

An elevated release rate of all major, minor and trace elements of interest was observed in the saturated zone at 22 m and 25 m. This could be a result of percolating rain water mobilising highly soluble elements over time. These elements may be transported through the tailings dam to lower layers where they accumulate and become supersaturated. A higher moisture content (57%) and lower pH (9.2), measured in the deeper layers towards the middle of the tailings dam, enhance the dissolution of soluble salts and the precipitation of less soluble hydroxide and carbonate minerals facilitated by a long interaction time between the pore water and ash.

Implications of Leaching on the Groundwater Chemistry

Long-term monitoring of boreholes downstream of the tailings dam over 25 years showed changes in groundwater over time. The shallow aquifer (BH1S) altered from a $Ca/Mg/SO_4/Cl/NO_3$ water type to a

NaSO$_4$/Cl water type over time (fig. 3). This was caused by increasing concentrations of Na, K and Cl and decreasing concentrations of Ca and Mg. Calcium and Mg were precipitated as oxides and/or exchanged with other ions in the rock matrix and were hence attenuated in the plume migration process. The low alkaline pH in the pore water also promoted the release of Na, K and Cl from the host rock due to a lower CEC.

An opposite trend in the water type alteration was observed in the deeper aquifer (BH1). The water type of the deeper aquifer changed from a NaSO$_4$/Cl to a Ca/Mg/SO$_4$/Cl/NO$_3$ water type (fig. 3). This indicates that movement of the fine ash leachate plume occurred from the upper to the deeper aquifer containing the most readily soluble ions Ca^{2+}, Mg^{2+} as well as Na^+, SO_4^{2-}, Cl^- and NO_3^- observed from fine ash leaching and the addition of brine during hydraulic fine ash disposal. The initial analysed NaSO$_4$/Cl water type may have either originated from the local geology of alternating shale, sandstone and mudrock or from the addition of brine over many years of ash slurry deposition in the vicinity prior to the monitoring program or a combination of the two.

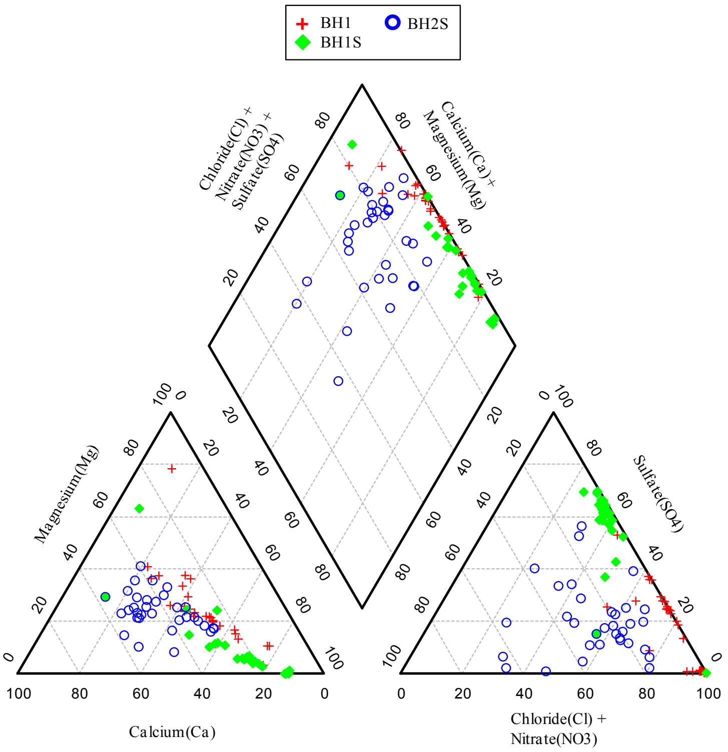

Figure 3*Piper diagram indicating the groundwater chemistry of boreholes downstream of a tailings dam.*

In addition to monitoring boreholes BH1 and BH1S, the adjacent shallow borehole BH2S was also affected by the downward migration of the fine ash leachate plume. Its water type altered from a CaMg-bicarbonate to a Ca/Mg/SO$_4$/Cl/NO$_3$ water type. Over time, the Ca and Mg concentrations decreased in the groundwater, while the concentrations of K, Cl and NO$_3$ increased due to leaching from dissolved salts in the fine ash tailings dam and possibly ion exchange in the host rock. The CaMg-bicarbonate water type could either be the natural water type derived from carbonaceous shales or more likely formed by percolating mine water from the ash disposal site. Similar results were also found in a study conducted by Spadoni *et al.* (2014) on the impact coal ash disposal has on the water quality. The groundwater was often found to be high in bicarbonate as a result of the addition of treated industrial water on the disposal site. Calcium and Mg decreased slowly in the groundwater because of processes involving cation-exchange, redox reactions and sorption/precipitation.

Borehole BH2S was monitored prior to most other boreholes and contained higher concentrations of Si and heavy metals (B, Fe, Mn, Cu, Cr, V and Zn) between 1990 and 2000, compared to that of other boreholes monitored from 2000 to 2014. This indicates a fast release of readily soluble elements from the surface of the fine ash particles during the early stage of fine ash leaching. Over time, the leached concentrations declined in the groundwater due to a slow release from less reactive primary and secondary minerals.

Aluminium, Mn, Si and Fe concentrations were very high in the shallow aquifer compared to the deeper aquifer during earlier years of monitoring. These initial high concentrations however declined rapidly to low and stable concentrations in the groundwater due to sorption onto particles of the host rock matrix as well as precipitation as (oxy)hydroxides. These processes most likely attenuated the metal transport in the leachate plume. A rapid decline in Al and Mn concentration and a lower but constant Fe concentration were also observed in the deeper aquifer because of further sorption and hydrolysis processes. The concentration of Mn and Fe remained relatively constant but high in solution when compared to the other detected metals in the groundwater. These elevated Mn and Fe concentrations were caused by their high solubility during fine ash leaching and possible further dissolution of Fe (oxy)hydroxides in the presence of a low groundwater pH. The B concentration increased during a period of 14 years in the groundwater of both shallow and deeper aquifers due to continuous leaching of B from the tailings dam. Boron occurs as an oxyanion which is not very likely to be adsorbed by clay and fine ash particles at a high pH as result of their high negative charge. Electrostatic repulsion between BO_3^{3-} ions and fine ash particles as well as minerals in the host rock enhances the leaching of B and increases its concentration in the groundwater over the years.

In general, most trace element concentrations in the shallow and deeper aquifers were high during the early onset of monitoring and then declined drastically to concentrations below the detection limit. This shows that most of the heavy metals detected were controlled by sorption and co-precipitation with oxides and hydroxides. Trace elements Li and Cr were found to rapidly leach from fresh and weathered fine ash at relatively high concentrations, but had too low concentrations to be detected in the groundwater. This suggests that these elements were mostly absorbed in the tailings dam. Barium, B, Cu, V and Zn were found in the groundwater indicating that fine ash was not able to store these trace elements under alkaline conditions, partly due to their oxyanionic properties.

Conclusions

Kinetic leaching indicated that the major and minor fine ash components, SiO_2, Al_2O_3, CaO, MgO, Na_2O and K_2O were leached at the highest rate from fresh and weathered fine ash and hence dominated the leachate chemistry. Overall, the highest release rates of most fine ash components were observed in fresh fine ash and in the saturated zone of the tailings dam. Three different trends of fine ash leaching were identified in the unsaturated zone of a tailings dam profile:

- Elements which had a decreasing release rate with depth (Ca, B, Al and Ba);
- Elements which had an increasing release rate with depth (V, Mo, Cu, Mn, Si, Li, Cr and SO_4); and
- Elements which had a constant release rate throughout the tailings dam profile (Se, Fe, MAlk, Na, Mg, K, Cl, NO_3 and Zn).

Elements which were released at high rates were found to dominate the groundwater type in the shallow and deeper lying aquifers in the vicinity of the tailings dam. As a result, the chemical composition of the groundwater surrounding the tailings dam was dominated by a $Ca/Mg/SO_4/Cl/NO_3$ water type. Major and minor elements and trace elements Ca, Mg, SO_4, K, Cl, Al, Si, Fe, Ba, B, Mn, Cu, V and Zn were found to leach into the groundwater and could pose a potential threat of groundwater pollution.

However, weathering processes such as secondary mineral precipitation, sorption of elements to negatively charged fine ash particle surfaces under alkaline pH as well as ion exchange were able to attenuate the leaching process of readily soluble elements. The formation of less soluble secondary mineral phases including amorphous clay, carbonates and Fe and Mn oxides co-precipitated a substantial amount of heavy metals. Furthermore, a low hydraulic conductivity of fine ash, the compacted and hardened surface of the tailings dam as well as the alkaline system lead to the storage of most heavy metals and toxic trace elements associated with fine ash leaching.

Each fine ash disposal site should be closely monitored as the leachate chemistry and leaching behavior is site specific. Leaching should be prevented and minimised by lining tailings dams with an impermeable layer prior to construction. A vegetation or clay cover after closure could also reduce the infiltration of precipitation and hence the leaching of fine ash.

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Surface Paste Disposal of High-Sulfide Tailings at Neves-Corvo – Evaluation of Environmental Stability and Operational Experience

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Abstract

The Neves-Corvo mine is a world-class underground copper-zinc mine located in the semi-arid south of Portugal. The mine has been operated since 1988 by Somincor (Sociedade Mineira de Neves-Corvo, SA), a subsidiary of Lundin Mining.

Pyritic tailings produced in the copper and zinc plants have a high acid generation potential and have historically been placed subaqueously since the startup of the mine. This disposal system at Somincor has provided safe and reliable storage of tailings. However, the tailings facility was predicted to reach full capacity in 2011 and alternatives for provision of sufficient tailings storage capacity were studied by Somincor. Surface disposal of paste was selected as the preferred alternative.

The feasibility of changing the tailings deposition method to sub-aerial placement of paste has been investigated since 2001. Work completed includes a laboratory screening program, a field cell monitoring program, a large-scale field trial, a feasibility study, basic engineering, detailed engineering, and commissioning of the paste plant, culminating in operational placement of paste commencing in late 2010. Co-placement of acid-generating waste rock occurs in the form of berms and dikes that contain the paste.

This paper summarizes the geochemical work conducted to evaluate the environmental stability of the paste. In addition, operational learnings and observations are presented.

Operational experience to date indicates that the environmental behavior of the paste is consistent with the predictions resulting from the field and laboratory geochemical testing programs, demonstrating the value of these extensive efforts. Despite the high acid generation potential of the paste, its surficial placement under controlled conditions results in responsible and reliable management of both tailings and waste rock.

Key words: Paste, tailings, surface, acid generation, operational, co-disposal, waste rock

Introduction

Environmental impacts resulting from surface disposal of acid generating waste are a common problem for base metal mines around the world. Sociedade Mineira de Neves-Corvo, S.A (Somincor), who own the Neves-Corvo underground copper-zinc mine and associated tailings facility in southern Portugal, have been investigating the possible application of paste technology since 2001 when a feasibility study indicated the potential for major long-term advantages. Given the long remaining mine life (current estimates indicate possible operations through 2034), the sub-aqueous disposal method would require substantial dam raises. In addition, the presence of a water cover in perpetuity as a closure option was considered a considerable challenge in the semi-arid and net evaporative climate of southern Portugal.

The Neves-Corvo deposit is a so-called volcanogenic massive sulfide (VMS) and, as such, the tailings contain significant quantities of pyrite (up to approximately 50 wt.%). Understanding the geochemical behavior of these sulfide-rich tailings was paramount as conventional sub-aerial disposal methods may facilitate and promote significant generation of acid rock drainage (ARD).

Evaluation of Environmental Stability

The geochemical investigation of the paste has had three principal objectives:

- Evaluation of the long-term environmental stability of the paste;
- Identification of operational constraints during operational placement of paste; and
- Assessment of closure options.

The program has included multiple phases, as follows:

- Laboratory bench-scale testing (2000);
- Field cell testing (2002 - 2005);
- Paste pilot program (2005 - 2010); and
- Operational monitoring (2011 - current).

The laboratory program was conducted in the Somincor laboratory (Figure 1) and involved a one-year screening-level assessment of different sub-aerial placement options, including wet paste (250-mm slump), stiff paste (150-mm slump) and filter cake, both with and without amendments (cement, lime, and bactericide). The results were consistent with expected relationships between moisture content, amendments, and sulfide oxidation. In summary, the best performance (i.e. the least oxidation) was observed for the samples with the highest moisture content (250-mm slump paste). Lime and cement amendments provided early buffering capacity, but not in the long term. Sulfide oxidation rates were not affected by the presence of lime or cement, while use of bactericide showed a short-term benefit only. More detail about this program can be found in Verburg et al. (2003).

Figure 1 *Laboratory Bench-Scale Testing of Paste.*

The geochemical study expanded to the field in 2002 with the construction of six field cells, each containing approximately 12 tons of tailings, to monitor the performance of the sub-aerial placement option. Based on the results of the laboratory testing, wet paste was selected for the field cell trials. The cells were monitored for three years, with routine collection and comprehensive chemical analysis of seepage and runoff (Figure 2).

***Figure 2** Field Cell Program.*

The field cell testing program provided data supporting the use of tailings paste as a viable disposal alternative. The results from this program demonstrated that, although sulfide oxidation occurred in the paste, due to the high degree of saturation of the paste, oxidation rates were reduced relative to those in dry tailings. In addition, due to its low permeability, contaminant transport was very slow, and the impact of sulfide oxidation on seepage quality was reduced through the presence of mineralogical controls that buffered pH. The results from the field cells further identified that, during active paste disposal, it would be the control of runoff, not seepage, which would govern the placement protocol. In particular, a lag time to acid generation was established that represented the operational window within which a previously-placed layer of paste needed to be covered by either a fresh paste layer, an interim cover, or a final cover to prevent an unacceptable degree of sulfide oxidation. More detail is provided in Verburg et al. (2006).

In 2005, a paste plant was commissioned in support of construction of a 50,000 cubic meter (m^3) pilot paste trial. This trial was initiated to investigate paste deposition techniques, co-disposal with acid-generating waste rock, and long-term performance of covers. Three cover scenarios were tested: 1) a low-flux cover without capillary break, 2) a low-flux cover with capillary break, and 3) a barrier cover (Figure 3). All three covers contained a component of acid generating waste rock. An exposed quadrant was present as a control cell. Monitoring continued for a duration of approximately five years and included collection of runoff and infiltration for chemical analysis. Data interpretation involved extensive geochemical modelling, unsaturated numerical flow modelling, and an impact assessment to evaluate seepage quality and quantity and potential associated effects on the receiving groundwater aquifer.

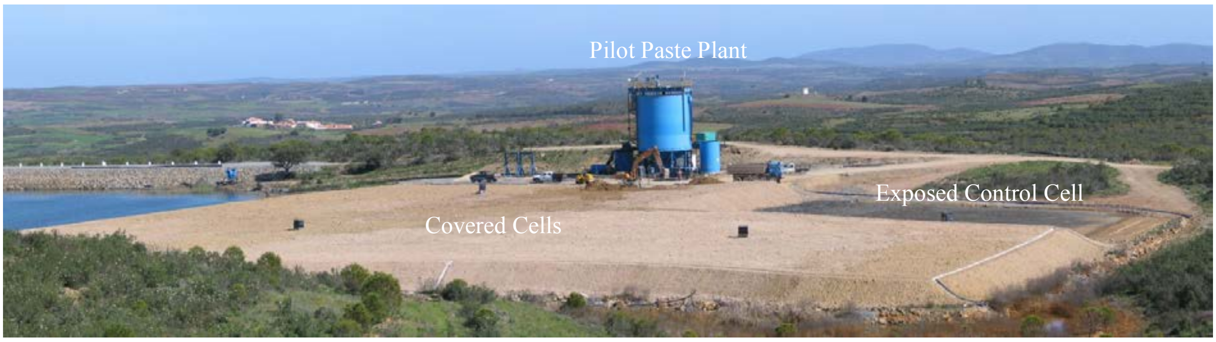

***Figure 3** Paste Trial after Construction.*

Monitoring results indicated significant reductions in sulfide oxidation in the covered cells relative to the control cell. Evaluation of draindown characteristics through unsaturated flow modeling identified that the highest degree of long-term saturation was achieved for the low-flux covers. This led to the conclusion that a cover system which strongly limits water infiltration, such as a barrier cover, is not always the best option for closure of acid generating tailings facilities located in arid and semi-arid climates. Instead, a cover that allows some infiltration was considered more reliable in terms of controlling ARD by maintaining a higher degree of saturation within the tailings. More detail on the geochemical findings of the program and draindown evaluation can be found in Verburg and Oliveira (2011) and Junqueira et al. (2009), respectively.

In late 2015, excavation of the covers in the paste trial provided an opportunity to conduct an informal assessment of cover performance. Based on visual observation, the extent of oxidation was limited to a few centimeters in all three cover designs, despite the presence of acid generating waste rock in the covers. It was further observed that the underlying paste had retained its moisture content.

Operational Monitoring and Experience

Operational paste placement commenced in late 2010. Paste is placed in cells separated by rock dikes constructed of acid generating waste rock (Figure 4). Alternating paste deposition between cells and limiting lift thicknesses promotes drying and densification of the deposited tailings. The sequential cell filling also provides for progressive closure and site restoration, as well as better control of acid generation and runoff during the operating years. An aerial overview of the paste placement scheme is presented in Figure 5. More detail on operational practices can be found in Oliveira et al. (2011) and Lopes et al. (2015).

Figure 4 *Operational Paste Placement.*

Figure 5 *Aerial View of Paste Placement Scheme.*

Operational monitoring includes visual observation, routine determination of paste pH in paste core samples, and collection and analysis of pond water. The paste pH measurements indicate that the depth of oxidation is limited to a few centimeters, even after extended exposure. Pond water quality is affected by this shallow oxidation, as evidenced by trends for pH and sulfate over time. The observed water quality is consistent with the predictions from the geochemical investigation program (Figure 6). Through 2014, pond water quality was amended by direct lime addition. This practice was discontinued in early 2015, and pond water is now routed to a collection pond prior to lime treatment in a water treatment facility.

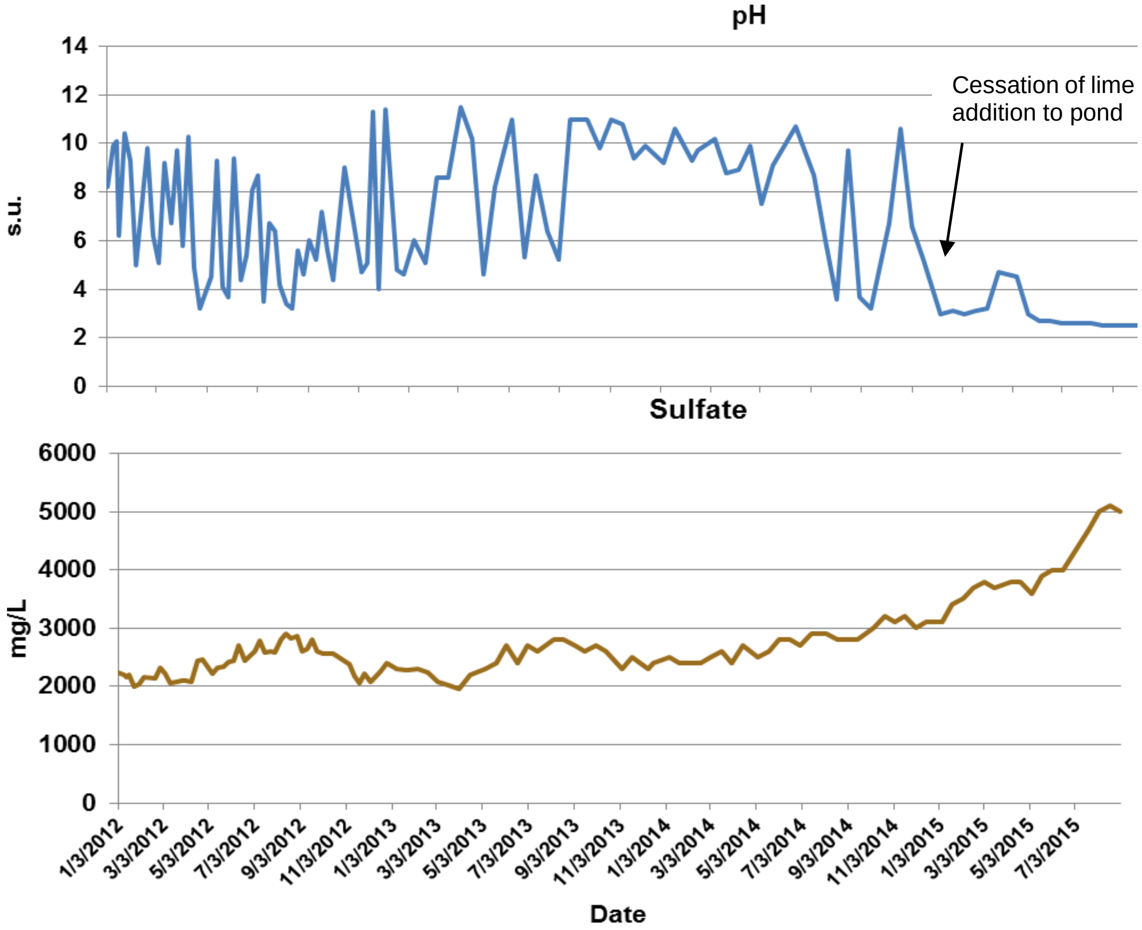

Figure 6 *Trends of pH and Sulfate Concentrations over Time in Pond Water.*

Placement of interim covers for operational purposes has provided an opportunity for qualitative evaluation of cover performance. Minor oxidation is observed at the base of the covers themselves, which consist of waste rock, but the underlying paste shows no visual signs of oxidation and has retained its moisture content. Future long-term cover testing, on a quasi-operational scale, is planned for quantitative demonstration of cover performance, while also presenting opportunity for gaining experience with cover construction. Additional ongoing operational learnings relate to berm construction, sequencing of paste placement, and water management.

Future Considerations

Somincor's 2014 life-of-mine (LOM) studies have established additional reserves and related demand for additional storage of tailings and waste rock beyond the current design. This LOM plan envisions two future scenarios:

- Base Case: operation until 2024; and
- Expansion Scenario: operation until 2034.

Both scenarios require evaluation of paste disposal options. A trade-off study is presently being conducted that evaluates the relative merits of higher stacking of paste tailings versus raising the perimeter dam.

Conclusions

Operational experience to date at Somincor's Neves-Corvo facility indicates that the environmental behavior of the paste is consistent with the predictions resulting from the laboratory and field geochemical testing programs, demonstrating the value of this decade-long, rigorous proof-of-concept effort. Despite the high acid generation potential of the paste, its surficial placement under controlled conditions results in predictable, responsible and reliable management of paste tailings. Co-placement of acid generating waste rock has proven feasible as well.

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Control of acid mine drainage by managing oxygen ingress into waste rock dumps at bituminous coal mines in New Zealand

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Abstract

In New Zealand, bituminous coal is mined in mountainous areas with temperate climate and with high rainfall (~6 m/y). Mine drainages from the Brunner Coal Measures (BCM) in New Zealand have low pH, high Lewis acidity and elevated concentrations of trace elements such as Zn, Ni, and Mn. At historic sites and upstream of mine drainage treatment, acid flux from waste rock dumps is dependent on rainfall with minimal dilution even through two orders of magnitude change in mine drainage flow volume. Current research focuses on improved long term management of acid load from New Zealand's bituminous coal mine. We present results that examine the impact of waste rock dump construction on oxygen ingress.

Sealed probes have been installed in three waste rock dumps where short lifts have been used during construction. The results indicate the oxygen concentration in waste rock pore spaces can decrease sharply with little distance into the dump. At 2-4m into the dump, the oxygen content is often around 10% and between 4-25 m into the dump the oxygen content is often less than 1%. In contrast, probes installed a dump constructed by side cast methods (pushing out a high tip head with a dozer) have oxygen concentrations between 11 and 21%

The findings of oxygen probe studies include.

- Oxygen ingress into waste rock dumps for mines in the Brunner Coal Measures can be limited by changing dump construction processes.
- The reduction in oxygen content in waste rock dumps that have short lifts is attributed to minimising grainsize segregation.
- For waste rock dumps constructed in short lifts and prior to capping and rehabilitation, acid loads could be calculated by assessing the surface area of the dump and the top ~2m using column leach studies. This differs from previous approaches where the total tonnage of waste is used for acid load calculations.
- Information from this study will be combined with autopsy studies, rehabilitation studies, revegetation studies to identify best practise for waste rock dump construction.

Keywords: coal mine drainage, oxygen ingress, waste rock dump, acid mine drainage, acid flux.

1. Introduction

Bituminous coal is mined on the West Coast of the South Island of New Zealand from Cretaceous Paparoa Coal Measures and Eocene Brunner Coal Measures. This mining district is mountainous, has high rainfall (~6m/y) and often mine operations are constrained by lack of space for waste rock dumps (WRDs). Generally disturbance of Paparoa Coal Measures during mining activities releases near neutral mine drainage, whereas mining of Brunner Coal Measures releases acid mine drainage (AMD) (Pope et al., 2010a,b). Typically this acid mine drainage has high Lewis acidity, and elevated concentrations of Zn, Ni & Mn. Acid can be released from either the coal measures or from the overlying marine rocks of the Kiata Formation which are also net acid forming at the base (Hughes et al., 2004.). Acid mine drainage flux from poorly managed (WRDs) at mines hosted in Bruner Coal

Measures increases linearly with flow at some sites indicating little or no dilution (Mackenzie, 2010; Davies et al., 2011) by the high rainfall.

Studies on oxygen ingress into WRD's at mines hosted in Brunner Coal Measures are limited. If WRDs are built well to minimize oxygen ingress then the ingress of oxygen is diffusion controlled (Weber et al., 2013; Olds et al., in press a & b). Where WRDs are built with no thought to controlling oxygen ingress then oxygen content of air within the dump can be ambient controlled by advection processes. Controlling the ingress of oxygen is mechanism for controlling long term acidity loads from WRDs where the dominant source of acidity is sulfide minerals.

We measure oxygen ingress at WRD's constructed with low lifts ~2-6m in height to minimise grainsize segregation. Grainsize segregation and increases as the tip-head height increases and is characterized by development of coarse rubble zones at the base of or within (chimneys) dumps. Grainsize segregation permits water ingress by permeability contrast and oxygen ingress by advection (Fala et al., 2003; Wilson, 2008). In a poorly constructed WRD, advection accounts for ~90% of oxygen ingress and that diffusion accounts for 10% (Brown et al., 2014). Therefore construction of WRDs to minimise grainsize segregation is likely to reduce oxygen ingress rates by approximately one order of magnitude.

We present results of oxygen ingress studies into Brunner Coal Measures WRDs where short lifts have been utilized to control advective ingress of oxygen.

2. Materials and Methods

Three WRDs at active mines operating within the Brunner Coal Measures where management techniques are being applied to minimize oxygen ingress have been selected. Arrays of probes to measure the oxygen content of air within the dumps have been constructed and repeat measurements have been taken over several months.

The dump air measurement probes consist of several (5-7) 15mm hose pipes installed in a trench ~ 1m deep in the active surface of the WRD. The trench is aligned perpendicular to the face of the dump and the end of each hose sits in a 0.3 m^3 gravel packed reservoir excavated an additional 0.5 m into the surface of the dump. The sample sites are spaced every 2 m for the first 8-10 m into the dump then 5-10 m to a maximum of 25 m. Bentonite seals are placed around the hose pipes to prevent pathways for air connection between the gravel packed reservoirs. Each hose has a standard compressed air line fitting at the face of the dump where sampling equipment can be attached. During sampling a low volume air pump draws an air sample from the gravel reservoir and the air sample is passed through an electrochemical gas analyser which reports oxygen content between 0.1 and 21% (ambient atmospheric oxygen content). The analyses are made on site and recorded, the electrochemical gas analysers are temperature compensated and regularly calibrated.

In addition, we present data from Stockton Mine that was collected from bentonite sealed piesometers into a dump to a maximum depth of 6m. This dump was constructed by dozing material from a tip-head down a steep face by side cast methods off Mt Frederick. These piesometers were also fitted with airline fittings and measurements were made with a similar electrochemical gas analyser.

3. Results

The three sites where oxygen probes were installed include:

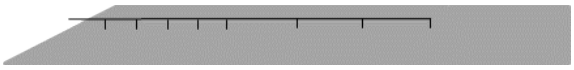
1. Cypress Northern Engineered Landform (ELF) at the Cypress Mine on Stockton Plateau
2. McCabes WRD at Stockton Mine on the Stockton Plateau
3. The Barren Valley ELF at Escarpment mine on the Denniston Plateau

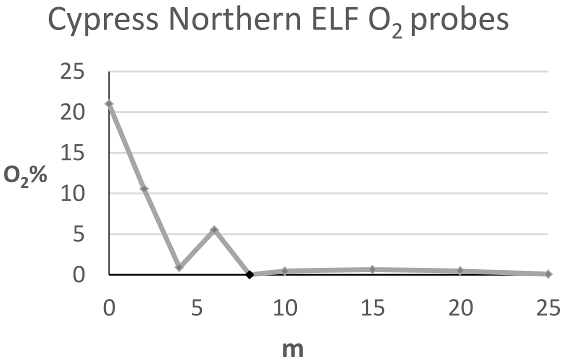
The site where the piesometers were installed is also at Stockton mine in the Mt Frederick WRD.

Cypress Northern ELF Oxygen probes.

Oxygen probes at the Cypress Northern ELFwere installed in July 2015 and the oxygen content measured in September 2015, January, February and March 2016. This dump is composed of mostly acid forming Kiata mudstone and the height of each lift is about 5m. For the first four months after installation no further dumping activity occurred over the oxygen probes. In December 2015 an additional 4m of overburden was placed over the buried probes (Figure 1).

Results indicate rapid decrease in oxygen content at many of the measurement sites from the time the trench was covered to the time of the first reading. In addition there is a sharp decrease in the oxygen content from the surface of the WRD batter slope so that 2 m into the dump, the oxygen content is between 8 and 14 % in the measurements made to date. The oxygen content 4 m into the dump is below 1% in all measurements to date. The oxygen content 6 m into the dump decreases from 5.5 to 2.3% during the between September 2015 to January 2016 and is below 1% in subsequent measurements. Beyond 6 m into the dump, all measured oxygen contents are below 1%.





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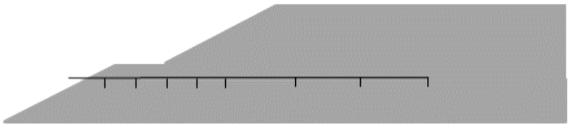

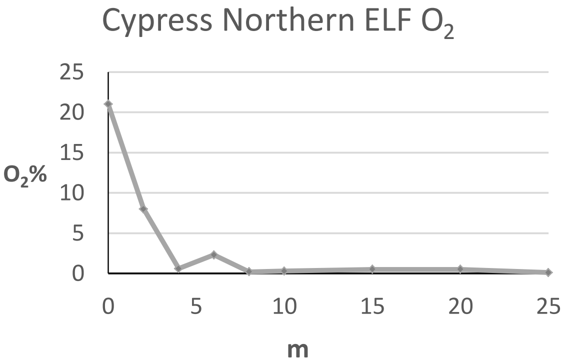

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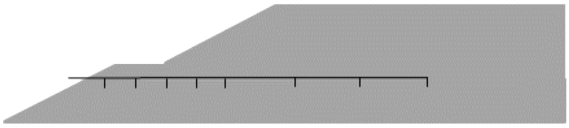

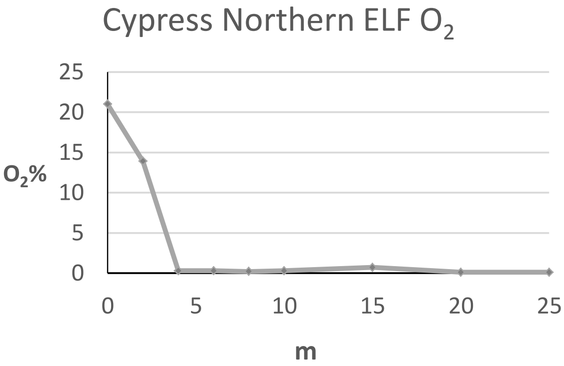

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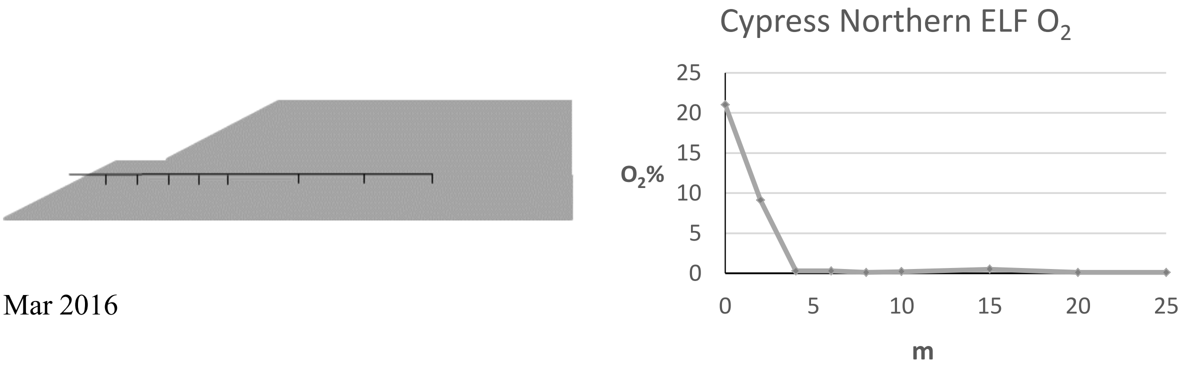
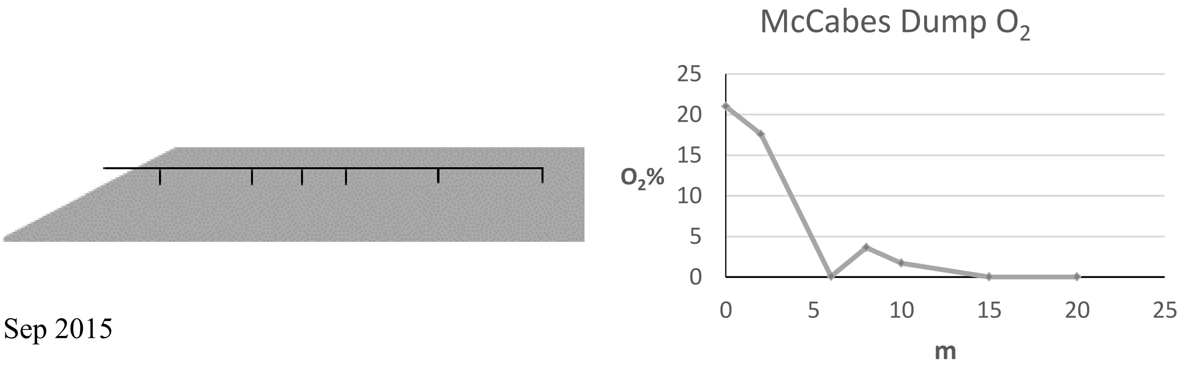


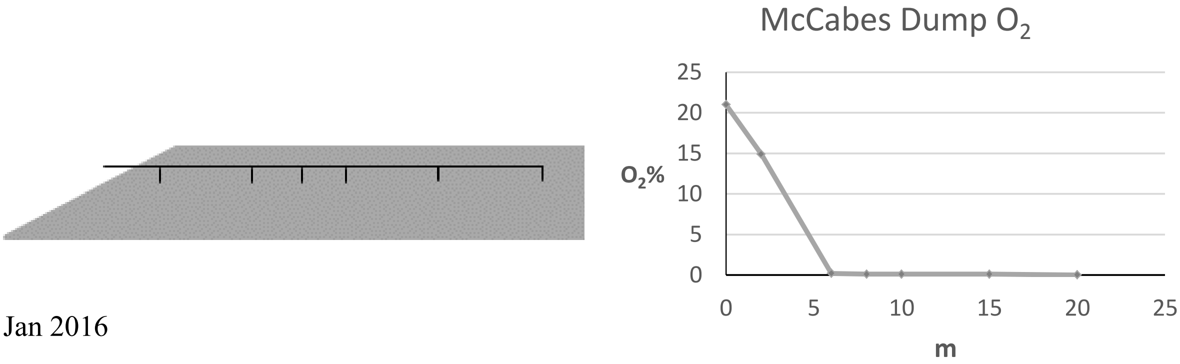
***Figure 1.** Oxygen content data and Cypress Northern ELF development. Rarely the oxygen probes were flooded and an air sample could not be obtained (recorded at 0% - black symbols on graphs).*

McCabes WRD oxygen probes

The McCabes WRD oxygen probes were installed in July 2015 and this dump is a mix of Brunner Coal Measures and Kiata Formation. The dump is constructed in lifts about 6m high. The oxygen content of air within the WRD was measured in September 2015, January and February 2016. No further dumping of waste rock has occurred at McCabes WRD so the oxygen probes are only covered by 1-2 m of waste rock.

Similarly to the Cypress Northern ELF, the oxygen content of the McCabes WRD (Figure 2) decreases quickly from ambient conditions at most of the sampling locations. In addition there is a sharp decrease in oxygen content with distance into the WRD horizontally from the batter slope. In September 2015 the oxygen content 2 m into the WRD was 17%, at 8 m into the WRD the oxygen content was 3.6%, at 10 m into the WRD 1.7% and other analyses were less than 1%. Subsequent measurements of oxygen content in air in the WRD are all less than 1% except at 2 m into the dump where the oxygen content decreases to 14.9% in January 2016 and 2.8% in February 2016.





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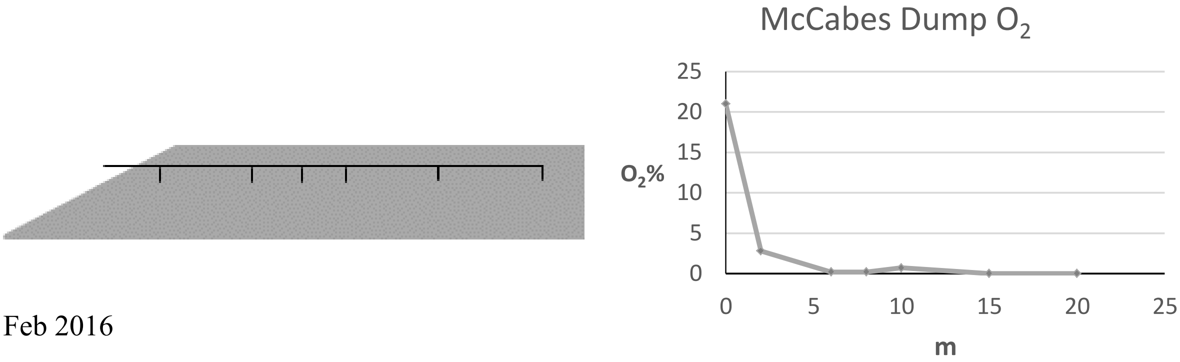

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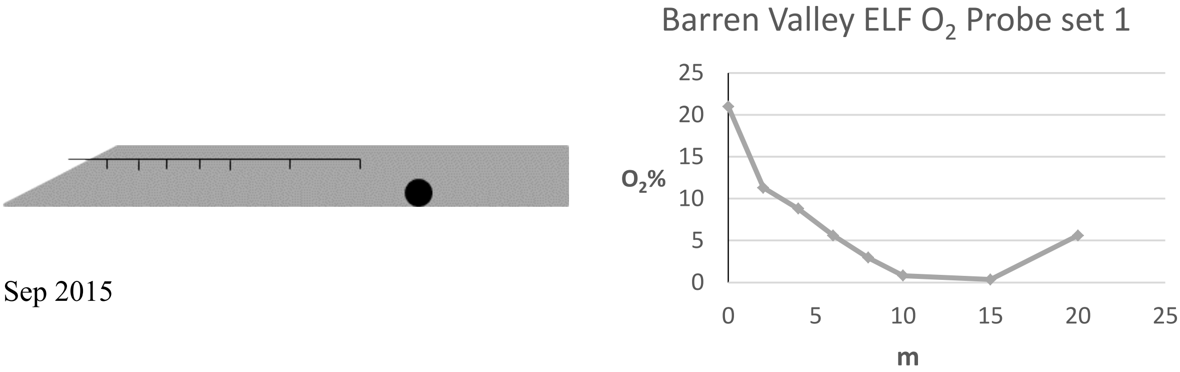
Figure 2. *Oxygen content data and ELF development McCabes Dump, Stockton mine.*

<u>Barren Valley ELF oxygen probes</u>

At the Barren Valley ELF oxygen probes were installed in July 2015. The dump consists of Brunner Coal Measures and this dump uses either paddock dumping of short lifts of about 2m. The WRD was re-contoured in January 2015 one week prior to measurement of oxygen contents and additional material was dumped over probes more than 10 m into the WRD. A second set of oxygen probes were installed in this WRD in January and oxygen readings commenced 2 days after the installation. The Barren Valley ELF contains an underdrain that is about 25 m into the WRD.

The oxygen content measured during September 2015 in the first probe set installed in the Barren Valley ELF (Figure 3) decreased gradually to <1% 10 m – 15 m into the dump and then increased to about 5% at 20 m into the WRD. The oxygen content measured in January 2016 showed a similar trend but with slightly higher oxygen contents. Oxygen contents measured in February and March 2016 showed a rapid decrease to about 1% at 2 m into the WRD, and then an increase to between 3 & 8% at 20 m into the WRD.



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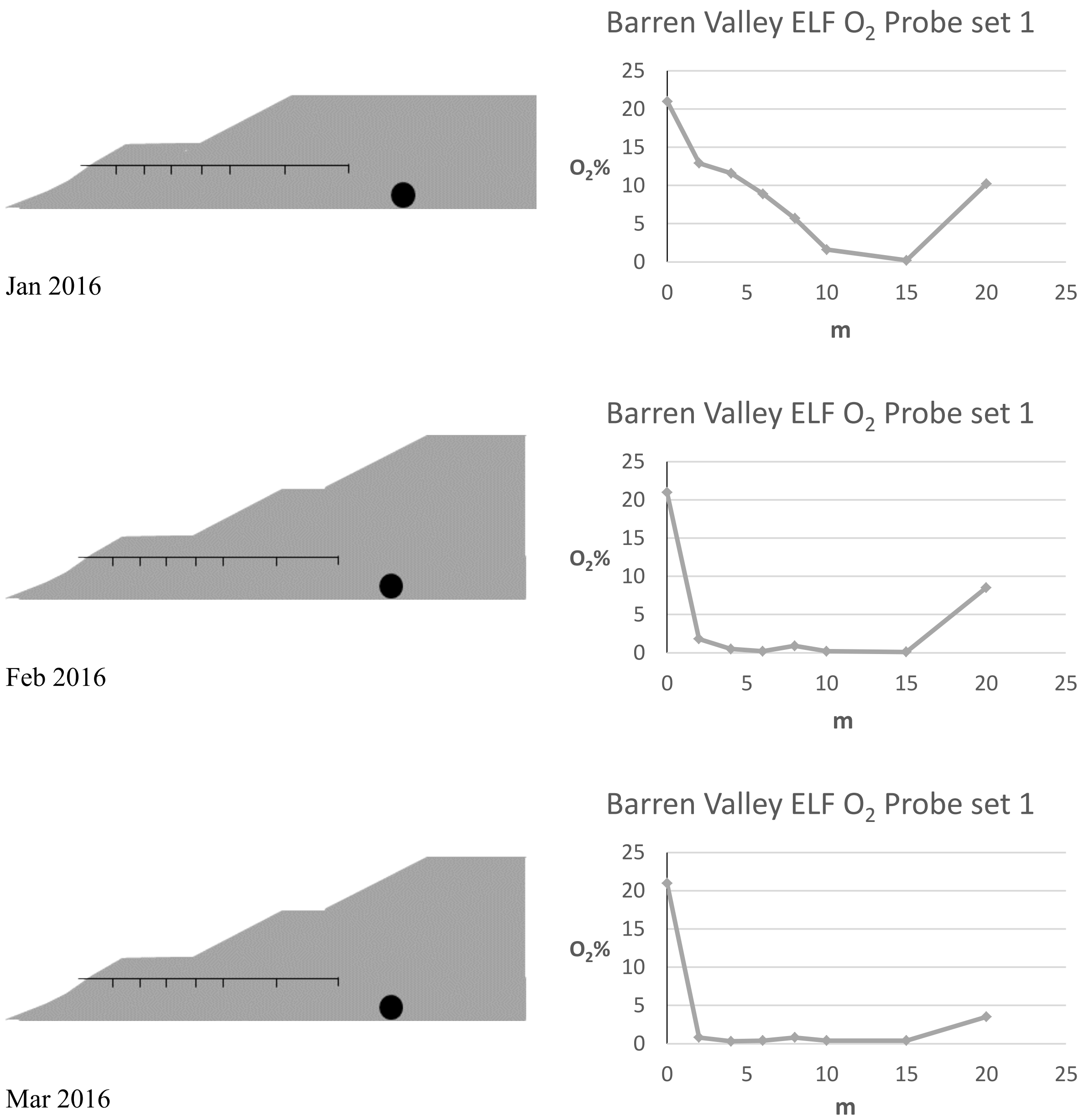

Figure 3. *Oxygen content data and dump development at the Barren Valley ELF, Escarpment Mine for probe set 1. Rarely the oxygen probes were flooded and an air sample could not be obtained (recorded at 0% - black symbols on graphs). Large black circle represents the location of the underdrain.*

The oxygen content measured during January 2016 in the second probe set in the Barren Valley ELF is relatively high >12% at all sites except 15 m into the WRD which is water saturated (Figure 4). Oxygen content measurements made during February 2016 show a rapid decrease in from the batter slope of the WRD so that probes at 2 m and 4 m have values of 2 & 7% respectively and all other oxygen contents are <1% except the probe at 20 m where the oxygen content is 7%. The oxygen content measured in March 2016 is <1% at all probes except the probe at 20 m where the oxygen content is just over 1%.

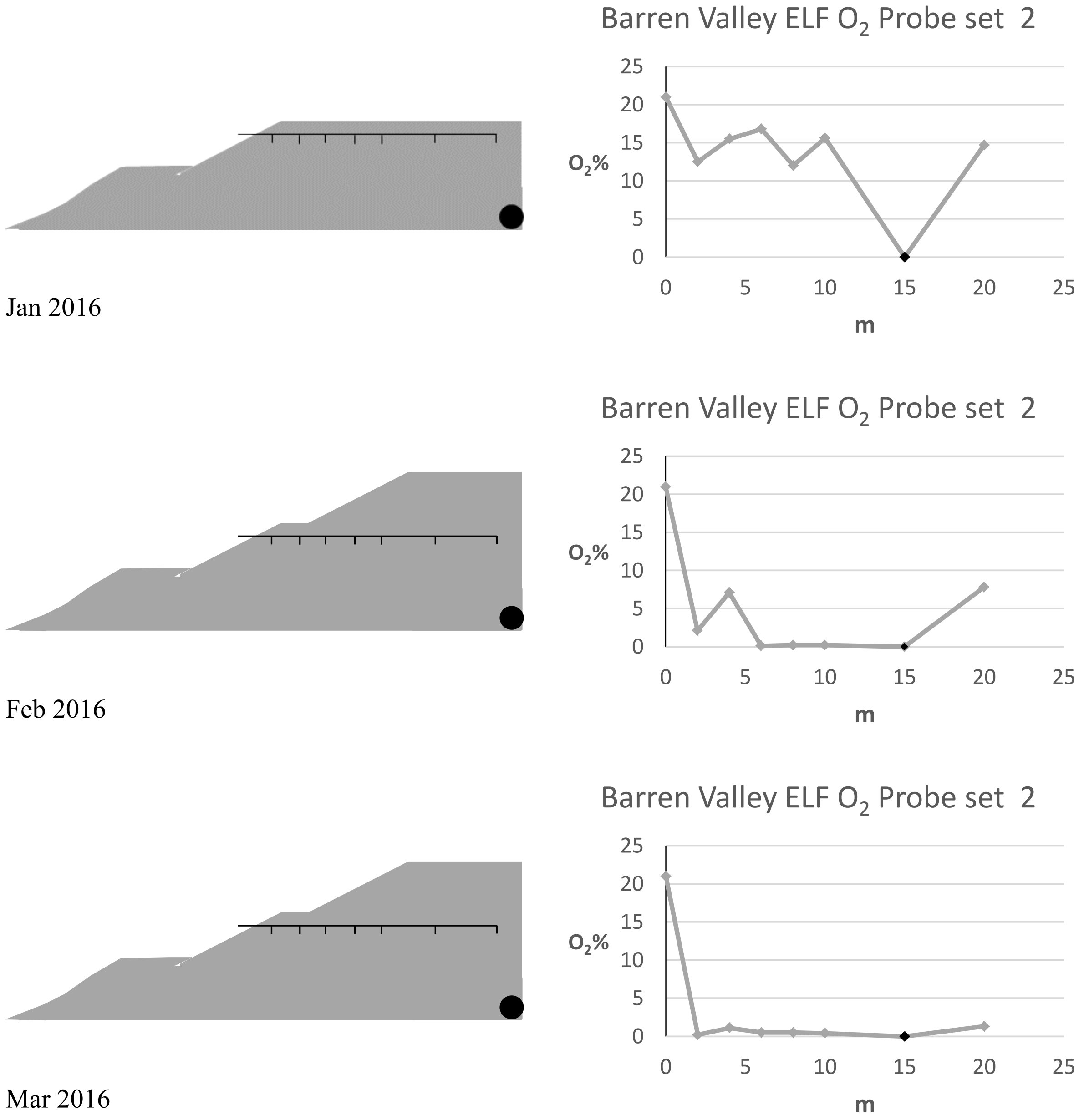

Figure 4. *Oxygen content data and dump development at the Barren Valley ELF, Escarpment Mine for probe set 2. Rarely the oxygen probes were flooded and an air sample could not be obtained (recorded at 0% - black symbols on graphs). Large black circle represents the location of the underdrain.*

Mt Frederick WRD piesometers

Data from two sets of piesometers in the Mt Frederick WRD indicate relatively high oxygen content for several years throughout the upper 6 m of the dump (Table 1 & 2).

Table 1. *Oxygen content (%) in piesometers in the Mt Frederick WRD (west). n = number of analyses*

depth (m)	2005	2006	2007	2009	2010
2	13	13	12	12	11
4	16	17	18	17	16
6	15	15	15	18	20
n	6	9	2	4	11

Table 2. *Oxygen content (%) in piesometers in the Mt Frederick WRD (east). n = number of samples*

depth (m)	2005	2006	2007	2009	2010
2	21	20	20	20	20
4	20	21	21	21	21
6	21	20	21	20	20
n	5	9	2	2	1

4. Discussion

Oxygen content data collected at Cypress and McCabes dumps indicate that there is a rapid depletion of oxygen away from the WRD batter slope and low or decreasing oxygen content at all sampling probes over the measurement period to date similarly to previous studies (Weber et al., 2013; Olds et al., in press a & b).

Oxygen content data from the Barren Valley ELF indicate slower initial oxygen depletion over the outer 10 m. In addition the data collected indicate that re-contouring of the WRD causes an increase in oxygen content, probably caused by disturbance to the WRD surface. However, once recontouring disturbance is complete and compaction had occurred, the oxygen content of the WRD rapidly decreased to less than 1%. The only exception to this is the oxygen probes located about 20 m into the WRD. At these sites it is interpreted that the underdrain provides a conduit for air this causes the elevated oxygen content. The underdrain is designed to have a swan neck with a water trap to prevent oxygen ingress however this has not been constructed yet.

These results confirm that construction of a WRD at mines in the Brunner Coal Measures using short lifts can reduce oxygen ingress compared to high tip heads or side casting. Dump construction using short tip heads to minimize grainsize segregation is therefore an important tool for management of AMD formation at mine sites where acid forming rocks are present.

5. Conclusion

Previous studies have shown the poorly managed or constructed WRDs at mines in Brunner Coal Measures release acid mine drainage in a manner that increases in a linear manner with rainfall (Mackenzie, 2010, Davies et al 2011). Typically these WRDs have been made with high tip heads or by side casting, or by dozing material out over large batter slopes. In these circumstances grainsize segregation with coarse material at the toe of the dump or within chimney zones allows relatively free oxygen ingress into at least parts of the dump and acid forming reactions proceed rapidly.

Data collected in this study indicates that the construction of WRDs in short lifts (<4 - 6 m), prevents oxygen ingress and therefore limits oxidation reactions to the margin of the dump. These data also demonstrate that oxygen ingress could be increased if the dump is disturbed after it is established (re-contouring) and that features like underdrains can provide a conduit for oxygen ingress.

Acid load prediction for these Brunner Coal Measures dumps prior to rehabilitation and capping can be calculated from the dump surface area and a zone about 2m thick covering the dump. For this part of the dump tests such as free draining oxygenated column leach trials (Pope & Weber, 2013) or humidity cell testing can be used to approximate acid loads. For the remainder of the dump acid release will be minimized by the limited availability of oxygen.

The oxygen ingress studies presented in this paper are linked to several other studies including dump autopsies, capping trials, rehabilitation, revegetation, and addition of neutralizing agents to acidic dumps. As we increase our dataset it is anticipated a new model for acid mine drainage release will be developed for WRDs associated with mines in the Brunner Coal Measures and other acid mine drainage forming rocks. The objective is to minimize rapid release of acid mine drainage, enable accurate long term prediction of acid load from mines in Brunner Coal Measures, to enable passive treatment as a long term closure plan and to develop a best practice waste rock dump construction method.

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Identification of major point sources in the severely contaminated alum shale area in Kvarntorp, Sweden

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Abstract

Scarcity of imported fuel led to oil production from alum shale in the Kvarntorp area, 200 km west of Stockholm, during 1941-1966. Remains from this are a 100 meter high waste deposit, Kvarntorpshögen, consisting mostly of shale ash and water filled open pits. As this shale is rich in sulphur and trace metals such as U, Ni and Mo, leaching from the waste deposit is feared. To elucidate the important question whether Kvarntorpshögen is the most important concern, or to what extent other sources might contribute with contamination, water sampling was extended to contain more localities than the ordinary control program. A new approach was the sulphur isotope analysis. The results point towards an area too complex for using sulphur isotopes for mixing calculations. Isotope fractionation during oil production is shown by the δ^{34} difference between shale and shale ash. Current isotope fractionation indicates sulphate reduction. Some localities indicate pyrite weathering and others rather show buffer capacities due to the presence of lime. Sr concentrations also suggest weathering. It is indicated that Kvarntorpshögen has an impact on the surroundings, but also that the water filled open pits as well as an industrial area affect the water quality. It is concluded that Kvarntorpshögen is one of the most important contributors of metal dispersion, but other point sources cannot be discarded as environmental risks.

Key words: Alum shale, Kvarntorp, Shale oil, Sulphur isotopes

Introduction

Faulting has enabled sedimentary rocks from the Cambrian and Ordovician periods to be preserved in the Kvarntorp area, some 200 km west of Stockholm. The gneissose and granitic basement is superimposed by sandstone, which higher up in the strata is followed by alum shale and limestone covered by till.

During World War II, shortage of imported fuel led to the search for alternative resources. Alum shale exists in several places in Sweden, but in most cases the oil content is too low for extraction. Svenska Skifferolje AB was formed in 1941, and Kvarntorp, where the shale contains 4.8% oil, was chosen for production (Schwartz 1945). Several methods were tested, for example an in-situ method, called the Ljungström method, which consisted in heating of holes drilled into the alum shale. Nevertheless, most of the oil was obtained by pyrolysis. This production lasted until 1966 and severely affected the area. The alum shale is from late Cambrian and is rich in for example sulphur, uranium, vanadium, nickel and molybdenum (Dyni 2006). Sulphur dioxide rich flue gas emissions (550 000 m^3/hour) damaged the forest, some 13 metric tonnes of dust were spread on a daily basis and polluted water reached the water courses (Kumla municipality 1979). Remains today are water filled open pits and a 100 m high waste deposit, Kvarntorpshögen, mostly consisting of shale waste in the form of shale ash (crushed and totally combusted shale) and fines (crushed but not further processed shale). There is also lime waste. The deposit still has a hot interior and increased metal leaching has been feared when it cools and more precipitation penetrates. Elevated temperatures are believed to be generated by pyrite oxidation (<100°C) and kerogen oxidation (>100°C) (Bäckström 2010). An important question is whether Kvarntorpshögen is the most important concern, or to what extent other sources might contribute with contamination.

In this study water sampling was extended to contain more localities than the ordinary control program run by the municipality of Kumla. A new approach was the analysis of sulphur isotopes.

Methods

Surface and ground waters sampled in March 2015 were analyzed with ICP-OES for metal and sulphur concentrations at Stockholm University (analytical precision within ±5%) and for uranium with ICP-MS at Örebro University. Sulphur isotope ratios were determined with IRMS, also at Stockholm University, after a precipitation of $BaSO_4$ was mixed with V_2O_5. The sulphur isotopes are calibrated against CDT and the standard deviation is ±0.2‰. Surface waters were sampled again in November and December 2015 as well as in January and February 2016. These samples were analysed with ICP-MS at Örebro University. Solid samples consisting of alum shale, shale ash, fines and limestone were also analysed for sulphur isotopes. The map in figure 1 shows the location of the area.

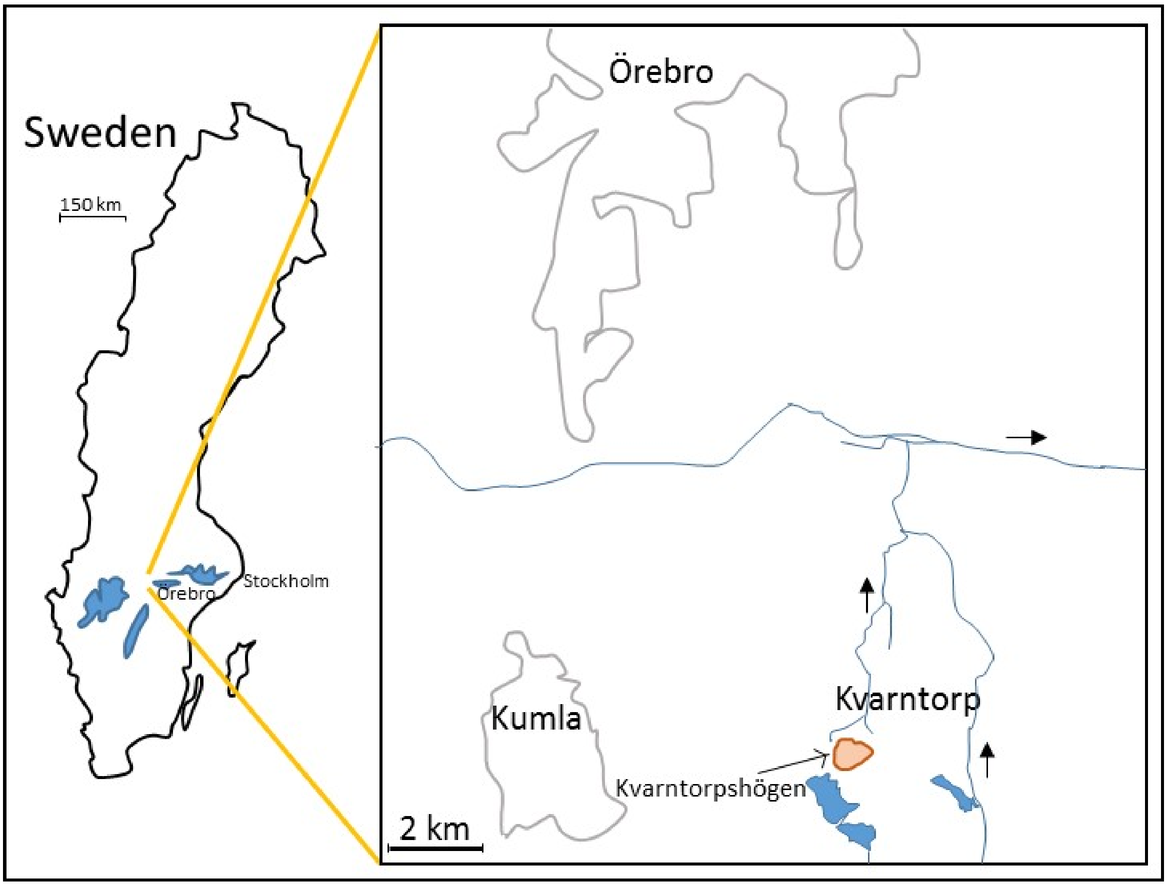

Figure 1 *Map showing the location of the Kvarntorp area and the waste deposit, Kvarntorpshögen.*

Results and discussion

Sulphur isotopes

A linear relationship between δ^{34}S values and 1/S would indicate mixing and enable sulphur isotopes to be used to calculate percentage of sulphur originating from a specific source, for example a mine or a waste deposit. No such linear relationship was found in this case.

During Cambrian the oceanic δ^{34}S was about +30‰ (Nielsen et al. 1991). Isotope analysis of solid samples from the area gave results as shown in table 1, with a range from +3.18‰ to +6.25‰. As the values are much lower for these samples than for the ocean at that time, this is an indication that the shale and the limestone do not show the isotopic composition of the ocean at their formation time, but an isotopic composition affected by biology and isotope fractionation. For surface water from the Kvarntorp area, the range in δ^{34}values is between -3.42‰ and +9.28 (see map in figure 2) and for groundwater the range is +2.83‰ to +15.77‰ (see table 2). The variety of δ-values in the different water samples is not explained by the sedimentary rocks examined in this study since they have a much narrower span. The $\delta^{34}S$ value for rainwater was +4.74, but as the sulphur concentration in this water was low compared to the surface waters, this is not an important contribution to the isotope signal in the area. All this suggests that there are several sources for sulphur. Furthermore, processes like pyrolysis and weathering might have had impact. The $\delta^{34}S$ difference between shale and shale ash indicates fractionation caused by pyrolysis. Negative values indicate oxidation of some kind.

The highest $\delta^{34}S$ values were found in some of the groundwater, indicating microbial activity where sulphate reduction has left the residual enriched in isotopic heavy ^{34}S. The result is that isotope values are too diverse in the Kvarntorp area to enable mixing calculations if solely sulphur concentrations and sulphur isotopes are used.

Table 1 $\delta^{34}S$ *values for solid samples.*

Solid sample	$\delta^{34}S$ vs CDT, ‰
Shale	+3.18
Shale	+4.47
Shale ash	+6.25
Fines	+4.39
Limestone	+4.08

Table 2 $\delta^{34}S$ *values for groundwater*

Groundwater	$\delta^{34}S$ vs CDT, ‰
G1	+2.83
G2	+3.42
G3	+5.52
G4	+15.77
G5	+6.12
G6	+3.68
G7	+9.00
G8	+10.47
G9	+9.75
G10 (deep)	+9.90
G11 (deep)	+10.63

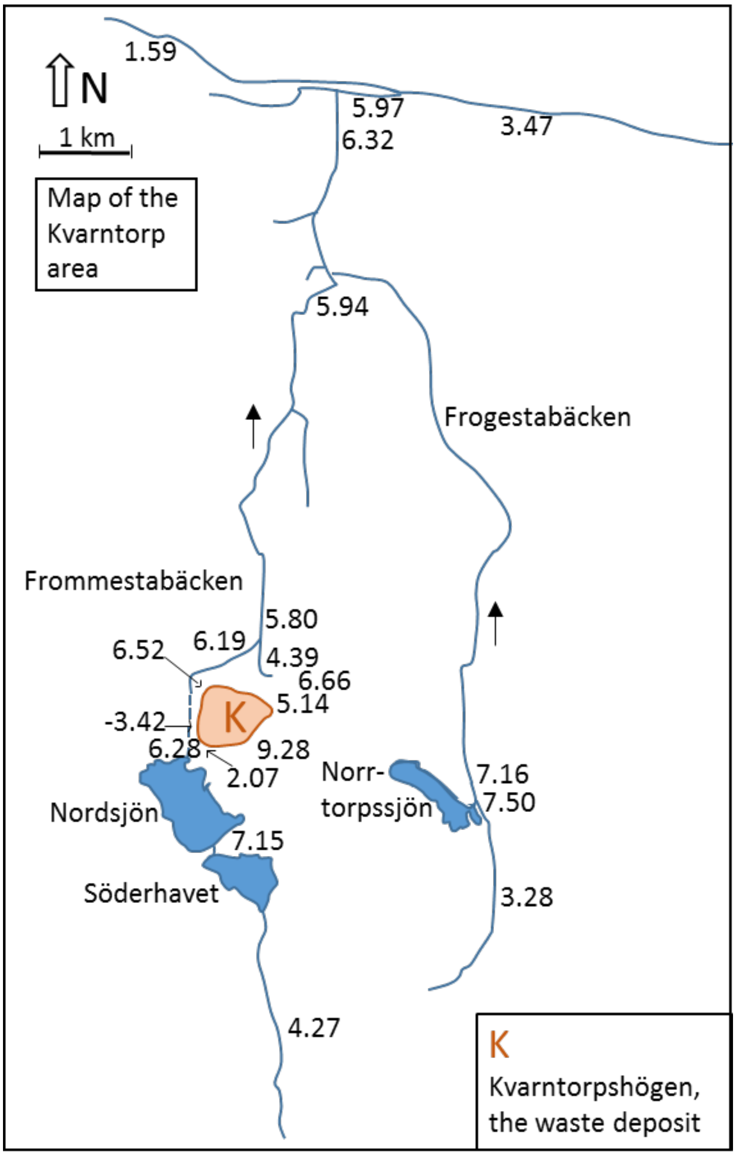

Figure 2 $\delta^{34}S$ *values for surface waters. The three lakes are water filled open pits.*

Metal analysis

Some of the localities for surface water sampling are shown in figure 3. A study of the western water course with a comparison between concentrations upstream (locality *a*) and downstream the waste deposit (locality *f*) shows an increase of metals and sulphur (see table 3) downstream the area, suggesting that the area affects the water.

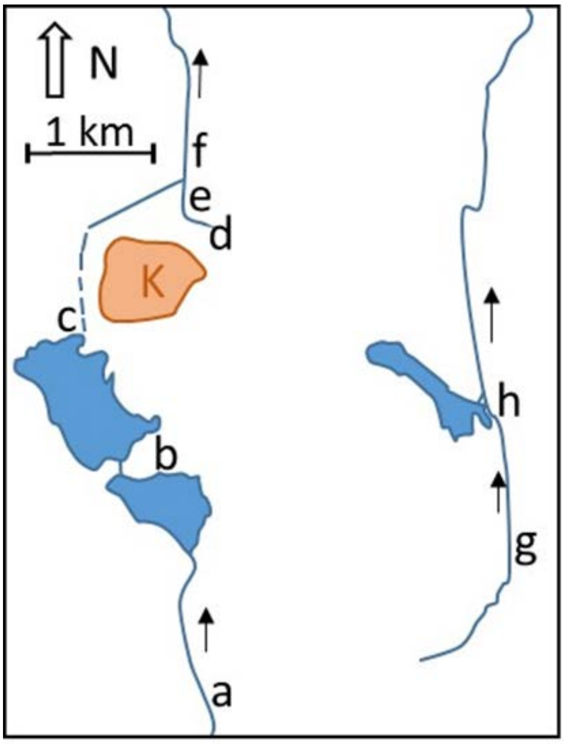

Table 3 *Concentrations for some of the surface water localities sampled in March 2015*

Locality	S, mg/L	Sr, µg/L	Ni, µg/L	Mo, µg/L	U, µg/L	pH
a	6.98	39.1	bdl	2.4	4.3	7.4
b	40	195	7.2	8.3	13.2	7.5
c	81	224	12.2	8.4	16.4	7.4
d	247	247	116	8.7	24.4	6.4
e	387	260	137	1.3	1.8	6.2
f	79.8	206	13.8	6.6	13.5	7.4
g	14	70.2	bdl	2.5	8.6	7.8
h	315	1280	5.4	4.9	24.0	7.1

Figure 3 *The Kvarntorp area with Kvarntorpshögen labelled K and six of the localities for surface water sampling* a-f*. The three lakes are water filled open pits.*

A plausible candidate for this influence is the waste deposit itself, but there might be other sources as well. The water passes two lakes which are now water filled former open pits. Water at locality *b*, the outlet of the southern lake, might contain weathering products from the exposed bedrock in the lake, but also water from a nearby waste treatment company, Ekokem.

Further downstream, the water enters a culvert at the outlet of the northern lake (locality *c*). Locality *d* consists of water from an industrial area whereas *e* is composed of surface water from the deposit after it has passed through a pond system, retaining some particles. In locality *f* water from *c*, *d* and *e* are already joined.

The diagrams in figure 4 show the concentrations of nickel, uranium, strontium and molybdenum in localities *a-h* for all four sampling occasions. For the western water course, nickel has its highest concentration in locality *e*, making the waste deposit the most important contributor of nickel. For uranium, on the contrary, locality *e* shows lower concentrations than the outlets of the lakes (*c*) and the water from the industrial area (*d*). For strontium locality *e* displays higher concentrations than the outlets of the lakes (*c*) and the industrial area. These concentrations, though, are much lower than for the highest concentration of strontium at the eastern water course (*h*).

Also the eastern water course passes through a water filled open pit, lake Norrtorpssjön, with locality *g* upstream and locality *h* at the outlet of the lake. There are higher concentrations of Ni, Sr, Mo and U at locality *h* compared to *g* for all sampling occasions. This is an indication of weathering of bedrock in the lake, but there might also be influence from the bedrock at the site where oil was obtained in situ. Water from this site is drained into the water filled pit and could affect its water. Also another open pit, now filled with industrial waste, is drained into Norrtorpssjön. The high Sr concentrations at the outlet of the eastern lake point towards weathering. A study by Lavergren et al. (2009) showed that neutral groundwater from both unprocessed shale and processed shale materials contained in excess uranium, molybdenum and some cadmium, nickel and zinc. Weathering of alum shale is a plausible source for the higher concentrations at the outlet of the lake, compared to upstream.

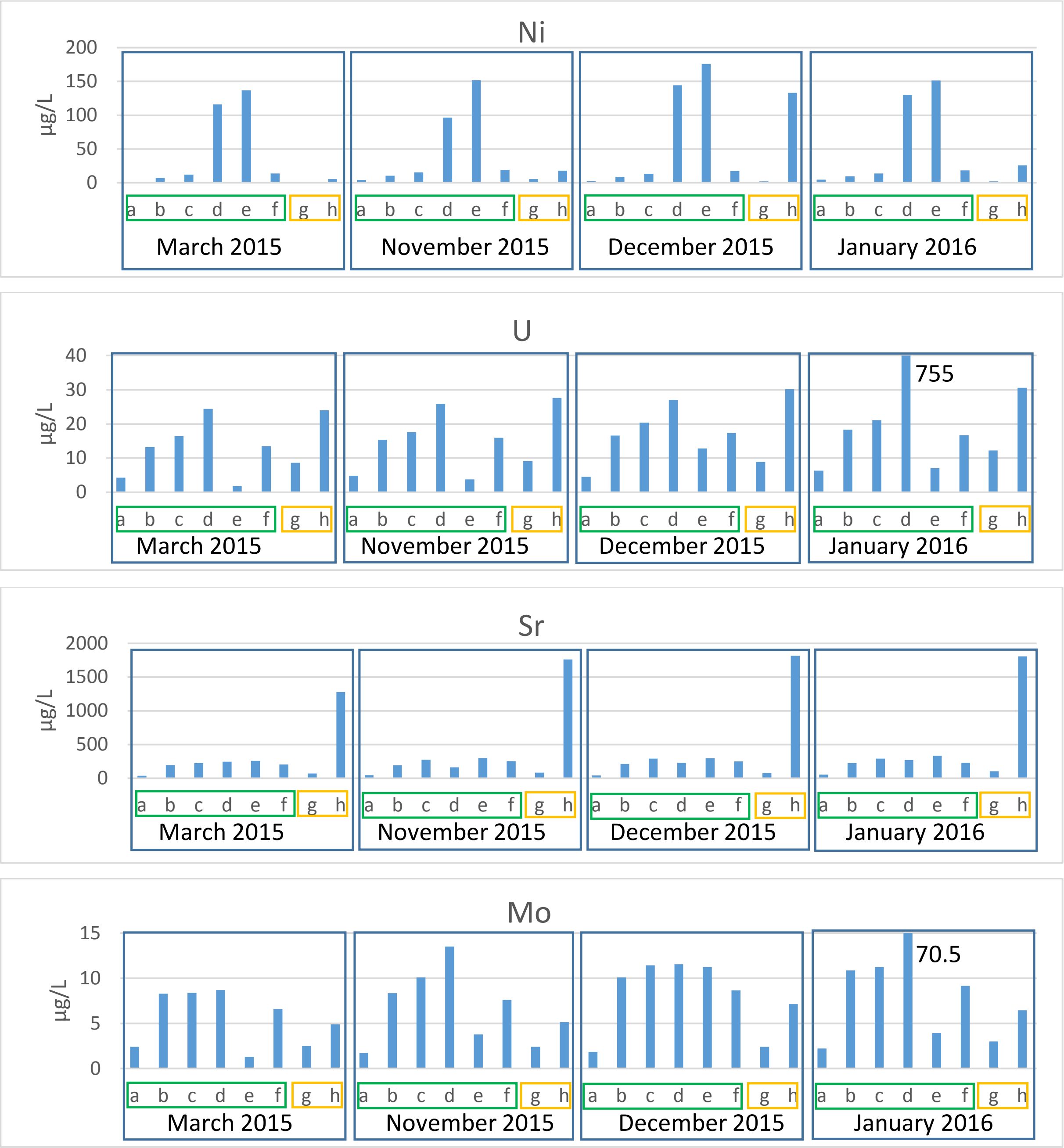

Figure 4 Diagrams illustrating the concentrations of nickel, uranium, strontium and molybdenum in localities a-h *for four sampling occasions. Localities* a-f *represent the western water course, and* g-h *the eastern.*

For some elements (e.g. uranium) the highest concentrations are not found in water originating from Kvarntorpshögen, while others (e.g. nickel) display their highest concentrations in water from the deposit. This implies that there are other several important point sources in the area, but also that Kvarntorpshögen is one of the most important contributors, even when water passes the pond system.

Analyses of groundwater and surface water around Kvarntorpshögen indicate that some localities are dominated by pyrite weathering, whereas at others, calcite is working as a buffer.

Conclusions

Sulphur isotopes have been subject to isotope fractionation in processes such as pyrolysis, making the isotope values too diverse to enable mixing calculations and estimations of percentage of sulphur originating from a specific source. Furthermore, current isotope fractionation processes are taking place in the area, indicating sulphate reduction.

Concentrations of elements such as nickel have shown that Kvarntorpshögen is one of the most important contributors of metal dispersion in the area. Elements such as uranium and molybdenum indicate that other point sources also affect the water quality. This statement is strengthened by the strontium concentrations in the eastern water course, indicating high weathering rates.

Figure 5 *Kvarntorpshögen seen from the south with the lake (open pit) Nordsjön in the foreground.*

Acknowledgements

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Aspects of the Environmental Monitoring on the Territory of Verhnekamskoye Potash Deposit (Russia)

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Abstract

For effective environmental management the system of complex environmental monitoring has developed in the southern part of Verhnekamskoye Potash Deposit − one of the biggest potash salt deposits in the world. Environmental monitoring includes hydrochemical, soil and biological monitoring in terrestrial and aquatic ecosystems. The main factor of potash mining effect on the environment is high solubility of wastes. High concentrations of Na^+, Cl^-, K^+, SO_4^{2-}, Mg^{2+} in waste and active water migration of these chemical elements caused salinization of the environment.

There are two types of technogenic bio- and geochemical salt anomalies. The first type of anomalies is localized near the salt tailings and plants as a result of air migration of pollutants. The second type of technogenic anomalies is more intensive and developed in river valleys. The main transport of salt components is surface and groundwater ones. Technogenic bio- and geochemical anomalies are characterized by high content of Na^+, Cl^-, K^+, SO_4^{2-}, Mg^{2+}, decrease of soil microbial biomass and invasion of salt-resistance species of terrestrial and aquatic ecosystems. Hydrogen sulfide settings and precipitation of iron-rich minerals in soils are developed in discharge areas of saline ground water.

Key words: potash deposit, environmental monitoring, anthropogenic salinization, surface and ground water, iron-rich precipitates

Introduction

Anthropogenic salinization of ecosystems was always serious problem for arid and semiarid environments and for cold and humid environments at last century. There are different sources of salt pollution, for example road salt (Kaushal *et al*. 2005), brines of old prospected oil wells (Svanidze *et al*. 2014) or salt production wells (Khayrulina & Maksimovich, 2015). Biggest salt source are associated with mining of evaporitic salt deposits, i.e. potash deposit (Rivers of Europe 2009, Beuer *et al*. 2005). Main factor of the environmental effect under mining of potash deposits is wastes of potash production that are accumulated in large amount in the field. For each tone of beneficiated ore 30 % becomes product, 70 % becomes waste (dry salt, slimes and brine). The wastes consist predominantly of high soluble potassium and sodium chlorides. These components are actively involved in the migration flows. Salinization of adjacent ecosystems has developed as a result of salt tailing piles deflation, plant emissions and drainage waters of salt tailing piles and slurry storage,

Intensive atmospheric precipitations percolate through the salt tailing piles and slurry storage and form saline drainage waters in great volume and may pollute the environment for long period after closing the mining (Beuer *et al.* 2005). Active migration of soluble components in water flows contributes salt pollution distribution trough ground- and surface water on considerable distance. Increase in salinity is a serious threat to the biodiversity of river ecosystems (Arle & Wagner 2013).

Effective environmental management must include a system of environmental monitoring. Monitoring has to consider special aspects of pollution distribution. Generally the environmental monitoring includes sampling of ground and surface water, biological monitoring of river ecosystems. The system of complex environmental monitoring is developing in the southern part of Verhnekamskoye Potash Deposit - one of the biggest potash deposits in the world.

Study area

The deposit is situated mostly on the left bank of the Kama river, tectonically belongs to the central part of Solikamsk depression of the Pre-Ural foredeep and is represented by the salt of Low- Permian halogeneous formation.

The area of deposit is about 6.5 thousand km ^{2}. The ore contains from 18 to 34% of KCl. Geological reserves of carnallite is up to 96,4 billion tons, sylvinite – 112,2 billion tons, halite – 4,65 trillion tons. Annual production of potassium-magnesium salts is about 40 million tons. Most of mines run flotation. Currently more than 270 million tons of halite wastes and 30 million m^3 of salt-clay slime have accumulated on the territory of the Verhnekamskoye Potash Deposit (Bachurin & Baboshko 2008).

Technological processes exclude brine release into the surface water. The main source of pollution on this deposit is uncontrolled discharge of drainage waters of salt tailing piles and slurry storage which were constructed 40-50 years ago without impermeable layer. Drainage water is a Cl – Na hydrochemical facies, has mineralization of about 300-400 g L^{-1} and pH 6.6. The concentration of water soluble components are: Cl − 20.7 g L^{-1}, SO_4 − 3.7 g L^{-1}, Na − 128.8 g L^{-1}, K − 20.6 g L^{-1}. Drainage waters are filtrated into groundwater and spread salt pollution on the environment.

Necessity of environmental research is caused by very intensive mining. New potash plants, salt tailing piles and slurry storage are under construction. Local streams, as a main pollutant transport, drain into the Kama River used for drinking-water supply.

Methods

Environmental monitoring includes hydrochemical, soil and biological monitoring in terrestrial and aquatic ecosystems. Samples of surface waters, springs were taken up 4 times in order to investigate fluctuations of salinity during the year. Sampling of soil, bottom sediments, plants and river biota was done once a year in July - August at different distance from plants and reservoir of wastes. Samples of snow were collected in the end of snow period (March) to analyze atmospheric pollution. Monitoring coveres ecosystems in natural and impacted state (fig. 1).

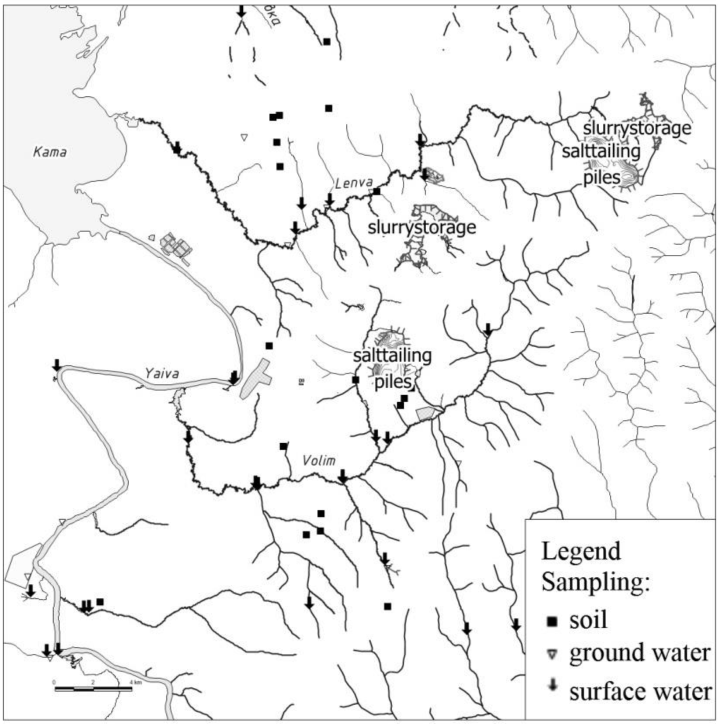

__Figure 1__ Schematic map of the southern part of Verhnekamskoye Potash Deposit with sampling sites of soil, surface and ground water.

Samples of surface and groundwater, soil- and bottom sediment were analyzed for NO_2^- , NO_3^-, NH_4^+, Cl^-, K^+, SO_4^{2-}, Ca^{2+}, Na^+, Mg^{2+} by using a capillary electrophoresis Capel-105, and pH of water extract , HCO_3^- and TDS – were investigating with traditional methods. Mineralogical analysis of soils and sediments was carried out by binocular microscope Nikon 104 with elutriation of soil and bottom sediment samples and removing of clay fractions less than 0.01 mm. Mineral components were analyzed by XRD using a D2 Phaser desktop diffractometer.

Results

Our research of anthropogenic salinization during 2009-2015 years revealed two types of bio- and geochemical anomalies. The first type is localized near the tailings and potash plants. This salt anomaly caused by air pollution. Soil salinization is not persistent and high (tab.1), because rainfall are actively leaching watersoluble minerals into groundwater or underlying landscapes.

Table 1 *Range in contents of chemical elements in soils (mg 100g^{-1}).*

Location	pH	Sum of toxic salts, %	Cl^-	SO_4^{2-}	Na^+	K^+
Near a salt piles (300 m)	5-6	0.090	1.4-7.5	0.6-4.8	0.8-1.8	1.4-5.6
Salt-affected valleys	4-8	1.582	22.6-1016.3	0.8-14.5	6.8-239.4	0.3-14.6
Background soils	4-6	0.011	1.1-2.3	0.8-1.9	0.6-1.0	0.3-1.7

Drainage waters entering into groundwater formed the second type of anthropogenic salt anomalies. Natural ground flows belong mostly to $Ca-HCO_3$ water type, in some cases – to $Ca-SO_4$ type. Drainage waters determine chemistry of groundwater: $Na-Cl$ water type, high concentrations of K^+ (5.85 g L^{-1}), SO_4^{2-} (2.19 g L^{-1}) and Mg^{2+} (5.18 g L^{-1}) (fig. 2). The ion exchange processes under the contact of saline water with carbonate and sulfate rocks set free Ca^{2+} into the ground water (Lucas *et al.* 2010, Beuer *et al.* 2005) and transform water type to $Ca, Na-Cl$ one.

Very large fluctuations in salinity were observed during monitoring. Some springs change the water type from $Ca-HCO_3$ to $Ca-Cl$ and $Na-Cl$ one for period of monitoring, salinity rose from background level of 256 mg L^{-1} –up to 27 g L^{-1}. These fluctuations may be determined by seasonal changes in the hydrodynamic regime.

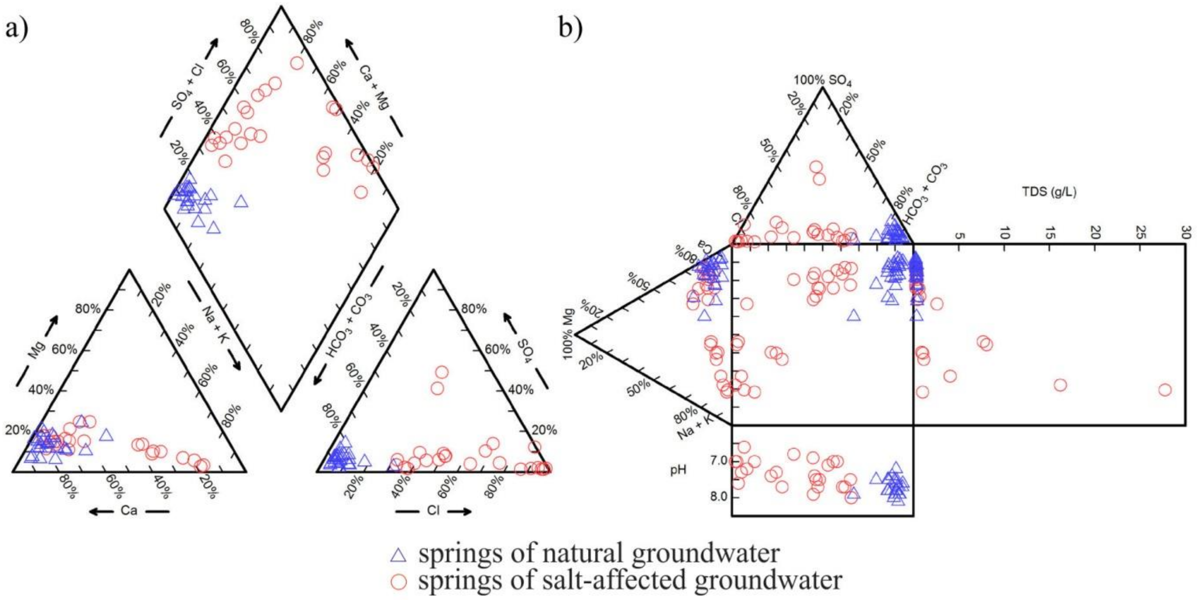

Figure 2 *Groundwater hydrochemical data on* ***a*** *Piper diagram and* ***b*** *Durov diagram.*

When saline groundwater meets confining beds it seeps to the surface in the river valleys and pollutes surface water. Chemistry of streams is derived from groundwater (fig. 3). Streams in natural state are $Ca - HCO_3$ water type; salt-affected streams are $Na - Cl$ and $Ca, Na - Cl$ water types. Chloride concentration in salt-affected streams now already exceed the maximum limit (300 mg L^{-1}) recommended for protection of freshwater life. The maximum Cl^- concentration in salt-affected streams is up to 34.63 g L^{-1}. High K^+ concentrations (up to 4.23 g L^{-1}) attribute the river salinization to the impact of potash mining.

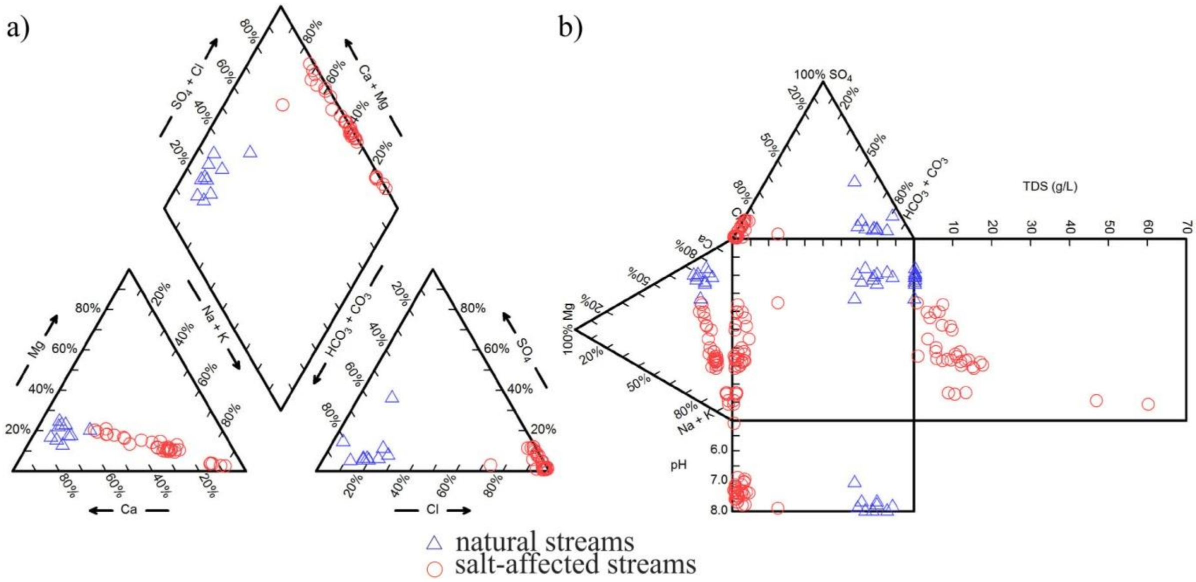

***Figure 3** Hydrochemical data of streams on **a** Piper diagram and **b** Durov diagram.*

Small rivers are experienced more intensive salt pressure, salinity some of them were up 100 times greater than salinity of natural flows. Concentration of water soluble salts of larger rivers gradually reduced by dilution of the non-affected streams. However increased chloride concentration can be propagated at substantial distance from salt sources, leading to negative effect on aquatic ecosystems.

Other aspect of groundwater salinization is sharp increase of Cl^-, K^+, SO_4^{2-}, Na^+ contents in valley soils (tab. 1). Water table in these landscapes is on 0-2 m depth. Saline ground water evaporates and causes minerals to precipitate. Increased concentrations of Cl^- and Na^+ in soils decrease soil microbial biomass and facilitate invasion of salt-resistance species of plants (Yan & Marschner 2012, Eremchenko & Lymar' 2007, Khayrulina 2015).

Some soil-change processes are associated with saline water-logging in seepage areas developed because of rising of water tables. In seepage areas bare soils acquired reddish-yellow iron-rich precipitates on their surface. This processes is described for arid ecosystems (Salama, Otto & Fitzpatrick 1999) High content of sulfates in the saline waters and microbiological activities lead to hydrogen sulfide settings in the soils. Mineralogical analysis of the upper soil horizons (0-3 cm depth) showed that the maximum total content of iron minerals was 84.9%, ferruginated plant - 20% (in the insoluble part of the samples). In the lower soil horizons (3-30 cm depth) hydrogoethite content reached up to 84% in the insoluble part of the sample. Other iron minerals (hematite and magnetite) were indentified. Source of iron in the soils is the iron-enriched rocks and saline ground water. The presence of dead trees in bare seepage areas was observed that this processes have been developing recently.

Conclusion

The system of complex environmental monitoring including hydrochemical, soil and biological monitoring in terrestrial and aquatic ecosystems revealed that the most damage of soil and water salinization were caused by drainage water filtration into groundwater. Saline groundwaters spread high concentrations in Na^+, Cl^-, K^+, SO_4^{2-}, Mg^{2+} and pollute streams and soils in river valleys. The salt pressure on terrestrial and aquatic ecosystems changed the species composition of vegetation for salt-resistant and decreased microbial communities.

Sulphurous settings in soils are formed with iron-rich precipitates on the surface of soils in areas of saline groundwater discharges. Appearance of reddish-yellow iron-rich precipitates may indicate increasing of polluted ground water zone.

Acknowledgements

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Geophysical Electromagnetic Measurements for Mine Site Groundwater Monitoring

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Extended Abstract

Water management at the mine sites is an important topic and developed as one theme in Finnish Green Mining programme during 2013 – 2016. Research programme is funded by the Finnish Funding Agency for Innovation, TEKES. Geosto Oy has been developing efficient geophysical methods for improved control of groundwater quality and waste area monitoring in its NOVEL-EM project. Needs arise from environmental safety, water resource protection and trend of increased mining areas. The presentation discusses the methodology, example surveys executed and new advances gained.

Direct current electrical methods have been used for a long time in groundwater investigations. New versatile electromagnetic induction (EMI) based instruments have also recently been made available. They particularly offer suitability to fast near-surface mapping of electrical resistivity and soundings in the depth range of 0 – 15 m. Instruments also suit to varying ground conditions. Integrated use with groundradar (GPR) offers improved discrimination of soil layers and their electrical properties. In addition, for greater depth penetration larger coil spacing (Slingram type), VLF-resistivity, audio- and radiomagnetotelluric and time-domain transient measurements can be selected depending on the surveying requirements of the mine site [1].

Development work has included methodological tests as well as stability and calibration studies have been important part of the EMI development. Example of a baseline measurement setting is described in Figure 1. During monitoring phase time-lapse measurements are compared and differences evaluated. Hydrological background variations are compensated and final data levelling applied.

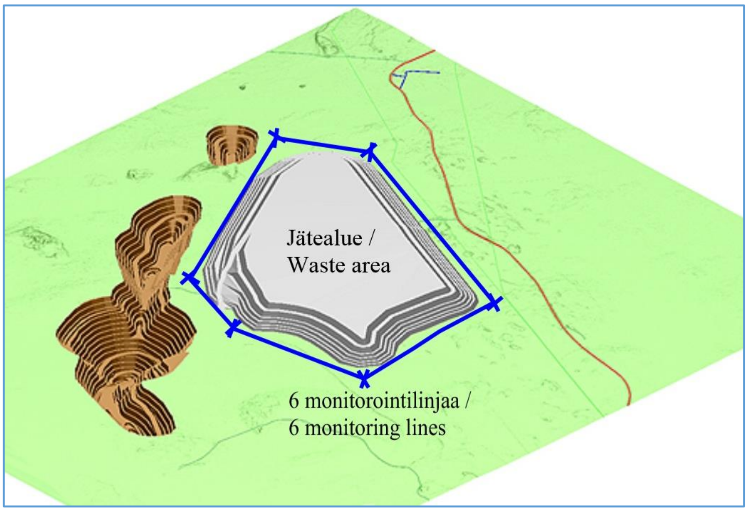


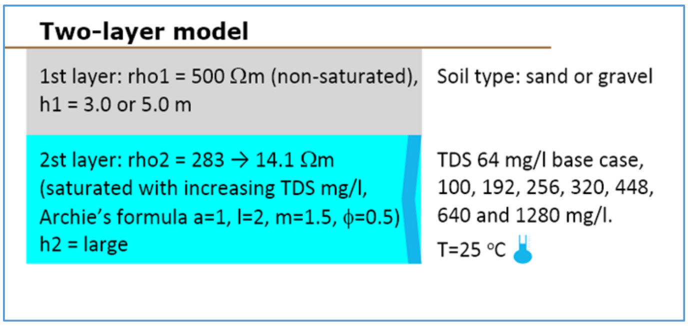
***Figure 1**: Basic example setting for electrical conductivity monitoring line network.*

If several surveying methods are used, the best interpretation result is achieved if data modelling scheme can do joint inversion and knowledge from soil-rock layers and structures, their proper-ties can constrain the calculation process. The use of multiple datasets in inversion and a priori soil structural model has been one key areas of development in NOVEL-EM project.

Baseline measurements have provided also useful supplementing data of hydrogeological site conditions. Accurate system calibrations and follow-up during the measurements have proved to be necessary [2]. These include static offsets, drift, user influence and documentation of site conditions and possible changes between measurement rounds. Compensation of hydrological and physical base parameters must be considered. Influential parameters include soil tempera-ture, saturation degree variations and groundwater level fluctuation (distance from ground surface).

Results show that change detection down to 50 – 100 ppm in total dissolved solids (TDS) content in groundwater is possible. This is exemplified with calculations made for hand-held EMI system (GSSI system EMP-400 Profiler) and for groundwater layer at depth of 3.0 m from the ground surface. The electromagnetic induction response imaginary (Im) component values were calculated over frequency range 400 – 40000 Hz. Groundwater base case has salinity 64 mg/l (electrical resistivity 100 Ωm). Then salinity is increased in steps to values shown in Figure 2, from 1.5x times to 20x the base case. Coloured curves depict the increase of Im-component response with water salinity increase. Detection limit is typically around 10 ppm, so 20 ppm was taken as detection threshold limit. Figure 2 shows that with higher >15 kHz frequencies even small 35 mg/l salinity increase is observable. Salinity increase of 130 mg/l from base level is clearly detectable over large (>4 kHz) frequency range as well as all higher than 130 mg/l salinity contents.

a)



b)

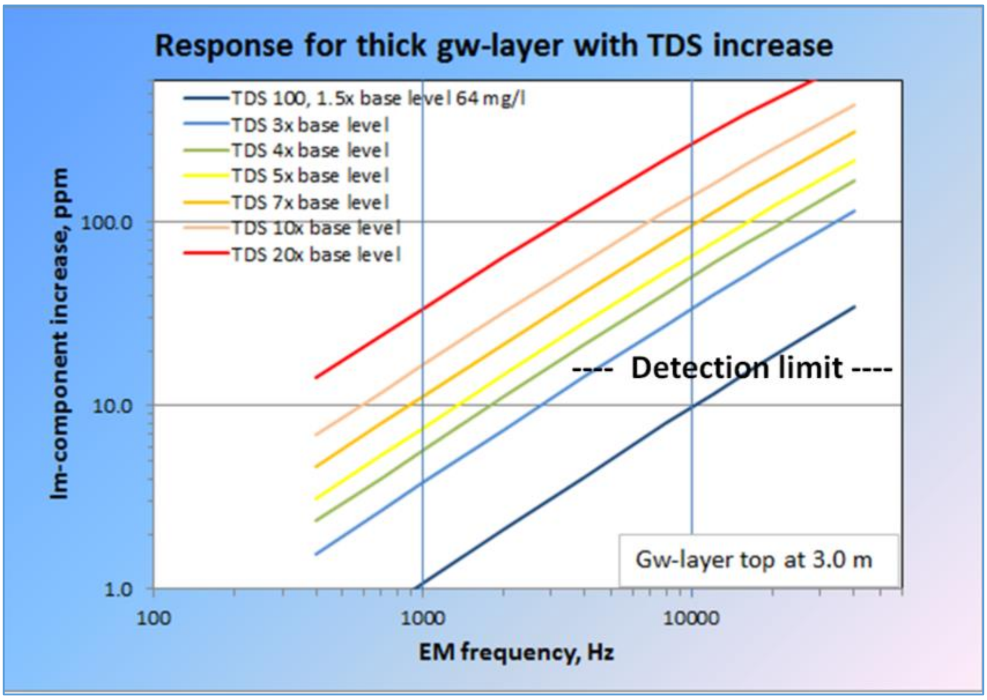


***Figure 2**: a) used model parameters, b) detectability of groundwater layer with increasing salinities over EMI frequencies.*

If the groundwater layer is deeper seated or as middle-layer has limited thickness (from sounding point of view), the measurable responses are weaker and so the detectability limit gets higher. Soil type can also have significant influence to responses: soils containing fine-grained component like clay, silt and moraines have higher electrical conductivities by nature and groundwater quality changes are less distinguishable. Similar situation applies if the baseline water salinity is very high – change detection limits arise.

If influence of distinct aqueous ions as electrolyte is of interest, an electrolyte was formulated in the NOVEL-EM project where solute ionic contents can be entered and resulting electrical conductivity of the solution is calculated. This is also useful if there are electrically conducting metals and minerals mixed with the solute that sums up in the total conductivity estimation.

Changes in surface water chemical variations can also take place and can be distinguished from subsurface variations. Locating of the change areas is vital for verification and other actions. For example, watercourse areas where sulphate layering has occurred and deposits settled to lake bottom, can be mapped for remediation actions.

In direct leakage detection variations in soil and bedrock geology are mixed with groundwater originating responses. Importance of background data and its interpretation plays a larger role. Particularly this can be challenging in mining areas if within the surveyed areas there are miner-alised bedrock volumes close to the ground. On the other hand, we have noted that sometimes the observed mineralisations can explain elevated metal and other substance levels and so prevent false environmental alarms.

Same methodology can be used also in earth dam structural investigations and monitoring although depth range can be larger depending on the dam measures. Example measurement tested against known leakage channel indicated positive and high-resolution localisation capability, Figure 3.

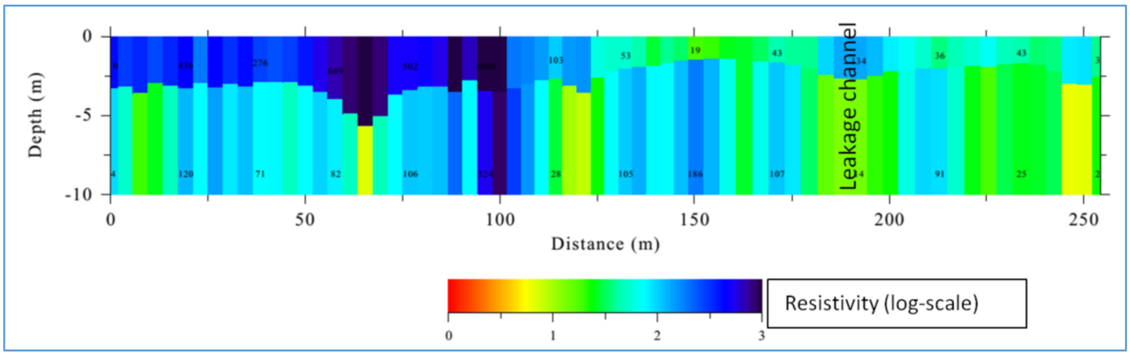


Figure 3*: Measured and modelled two layer resistivity profile over a leakage channel.*

Main uses for groundwater quality monitoring are to supplement the groundwater standpipe and well chemical data and provide comprehensive coverage around the waste disposal areas at the mine sites. This leads to improved environmental safety. In addition, several other uses can be found for water management like positioning of new monitoring wells, pumping wells for contamination remediation or dewatering purposes.

Key words: Mine wastewater, dam, monitoring, geophysical measurement, electrical conductivity

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AMD formation and dispersion of inorganic pollutants along the main stream in a mining area

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Abstract

The highveld coalfields area in Mpumalanga Province of South Africa is well known for the intensive mining activities focusing mostly on coal processing. The imminent impact of these activities on the water systems has been addressed by the mining companies over the years but the potential threat to the degradation of surface and ground waters quality has resurfaced (BFAP, 2012). This study aimed to quantitatively evaluate the level of mine pollution indicators in the surface water around the mining areas and particularly the implication efflorescent salt iron phase on the acidification of water. Water and efflorescent salts samples were collected along the stream from the mining areas in summer. These samples were analysed for their geochemical properties, anions and metal concentrations. High level of potentially toxic elements such as As, Cd, Co, Cu, Fe, Ni, Pb, U and Zn were detected in the main stream from mining areas that was very acidic (pH < 4) with high level of sulphate (2000 to 9000 mg/L). The efflorescent salts formed from acidic water were characterized using XRD and Mossbauer. Mikasaite, romerite, greigeite, cesanite, merwinite, maghemite, magnetite, nickelhexahydrite and thernardite were the dominant minerals in the salt samples. These results are indicative of acid mine drainage resulting from mining activities in the region. The formation of efflorescent salts near the stream with the potential to further acidify water and release metal pollutants was further indication of the presence of permanent threat to the degradation of water quality.

This study highlights the potential of formation and the characteristics of a typical acid mine drainage as well as the impact of mine wastes on the quality of environmental water in the neighborhood of mining activities.

Key words: Acid mine drainage, efflorescent salts, pollution, Mössbauer

Introduction

Coal is known to be the primary source of energy in South Africa; apart from contributing to 96% of the country's electricity generated in coal fired power plant, coal is also used as feedstock for the production of considerable fraction of the country's liquid fuels (Hancox and Gotz 2014). The country is among the largest producer of coal in the world and will certainly rely on coal for energy generation for several decades.

The highveld coalfields area in Mpumalanga Province of South Africa is well known for the intensive mining activities focusing mostly on coal processing. Coal mining and processing has significant environmental impact in the form of noxious gases generated during combustion and exposure of acid generating rocks which contribute to acidification of underground and surface waters. In the later case poor management of deposits accumulated over several years has resulted in the oxidation of pyrite and other sulphide minerals which further acidify rain water which percolates through the tailing dumps leading to the mobility of toxic metals and pollution of surrounding aquifer (Marsden 1986; Naicker et al. 2003). Iron sulphide minerals are reported to be the main source of sulphide oxidation products present in coal beds or strata overlying and undelying the coal exposed to oxygen and water (Qureshi et al. 2016; INAP 2009; Lottermoser 2007; Montero et al. 2005; Jennings et al. 2000). The formation of acid mine drainage (AMD) from mining areas expending to the farming and residential areas through rivers and streams has constituted a serious threat for the water reserve, farm development and conservation of touristic sites in the country during the past few decades.The imminent impact of these activities on the water systems has been addressed by the mining companies over the years but the potential threat to the degradation of surface and ground waters quality has resurfaced (BFAP 2012). Some of the methods implemented include: limiting oxygen ingress into closed mine workings, acid neutralization, water purification, controlled release and soil protection. However, most of these techniques have been abandoned because ineffective or too costly (McCarthy and Pretorius 2009). With such inconsistency in the management of coal wastes, monitoring of the environmental impact of AMD in the area becomes a necessity to evaluate the performance of remediation strategy. Understanding of the impact of effluents from mine requires geochemical studies that predict dispersion of key pollutants such as acidity and metals along the river basin; this also implies consideration of salt crusts which have a storage potential of pollutants and are susceptible to negatively impact the quality of receiving water depending on the solubility of the minerals in the crust. The Mossbauer technique is recognized to determine various phases of iron which impacts on the solubility of iron suphide minerals.

This study aims at determining the pollution potential of acid mine effluents around the mining areas in the highveld coalfield and predict the persistence of pollution impact downstream and overtime.

Methods

Water sampling and analysis

Sampling strategy consisted to follow the flow of the effluents from mining area to the different paths in the surrounding community, such as to establish the extent of pollutants dispersion in the surface water system.

The samples were collected close to the surface inside the pounds in the premises of the mine, in the dams at the vicinity of the mine and along the effluents network on a distance of approximately 5 Km, using previously rinsed 500 mL plastic bottles. The following physico-chemical parameters were measured in-situ using a pH combined electrode with integrated temperature probe (portable Lovibond SensoDirect 150 multi-parameter water quality meter): Temperature (°C), pH, Electrical conductivity EC (mS/cm), Dissolved oxygen DO (mg/L), and Redox potential Eh (mV). The pH-meter was calibrated before analysis in the field, using reference buffer solutions. (....). The samples were then stored in the cooler bag containing ice packs until taken to the laboratory for analysis. . The concentrations of sulphate (SO_4^{2-}), nitrate (NO_3^-) and cyanide ($CN^{-)}$ were measured using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA).

The metal ions in the samples were measured using the inductively coupled plasma optical emission spectrometer (ICP Expert II, Agilent Technologies 720 ICP-OES).

Efflorescent crust sampling

Efflorescent crust (salt) was carefully collected at the top 5 cm of the deposit along the stream bank in the vicinity of the mine. Samples were collected in the polypropylene clean plastic bag and transported to the laboratory. The samples were spread at the flat surface in the lamina flow hood and air dried for 72 hours. The dried samples were screened using a 150 µm mesh sieve size to remove large debris and stones. Screened samples were then analyzed using XRD and Mossbauer.

X-Ray Diffractometer (XRD) analysis

The efflorescent crust samples were dried at 50°C overnight in the oven and ground in a mortar; for the determination of the mineralogical phase, they were subjected to X-ray diffraction (XRD) analysis using the Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV; Programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2θ range: 4-79.98; step size: 0.017°. The proportion of elements in the suspended solids was determined by X-ray fluorescence (XRF) using the MagiX PRO & SuperQ Version 4 (Panalytical, Netherland); a rhodium(Rh) anode was used in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

Mössbauer analysis

The Mössbauer analyses were conducted on the powedered samples with the aid of a Halder Mossbauer Spectrometer as described by Waanders et al. (2014). The samples were placed between perplex plates and then irradiated with γ-rays from a 50 mCi57Co(Rh) radioactive source to obtain a room temperature Mossbauer spectrum. The Mossbauer spectrometer was calibrated using α-Fe as the reference and the product species were identified as the basis of their quadrupole and isomer shifts with reference to the values available in the literature.

Results and discussion

Spatial distribution of pollutants from mine effluent

Water samples collected along the drainage from the coal mine were analyzed to determine the nature and the spatial distribution of pollutants. The physicochemical qualities of the mine effluent from the upstream to the downstream points are recorded in Table 1. There was consistency in the level of pH at the proximity of the mine, in the dams and downstream in the residential area; it was characterized by acidic pH in the range of 2.24 – 3.35 which is typical of acid mine drainage (Gray 1998). The EC level was generally high (2.41 – 11.85 mS/cm) at all the sampling points; the EC being an estimate of the total dissolved solid (TDS), it could therefore signify that the water was highly polluted. This corroborated with very high concentrations of SO42-, CN-, Cl-, Al, Ca, Fe, Mg, Mn and Na which reached maximum concentrations of 18090 mg/L, 671 mg/L, 700 mg/L, 433 mg/L, 719 mg/L, 3145.8 mg/L, 1362 mg/L and 532.7 mg/L, respectively. Overall, the trend of pollution seems to be increasing from the mine till the mid points and then decrease downstream; the lowest concentration of pollutants were recorded at the farthest point from the mine in the residential area, indicating that the pollutants tend to precipitate along the stream. While the lowest pH and highest EC were recorded inside the dam (point ID) which also coincided with higher concentration of Fe and SO42-, implying that the acidification probably resulted from the oxidation of pyritic particles in the dam; similar results were reported in our previous work (Fosso-Kankeu et al. 2015). However, it was also observed that at the highest pH (3.35), a significant drop of the concentration of Fe which was due to precipitation; it is known that iron is less soluble at pH value close to 4.

***Table 1** Measured values of major pollutants in the water samples*

Samples ID	In-situ variables			Major anions				Major cations						
	pH	Ec	Eh	SO_4^{2-}	NO_3^-	CN^-	Cl^-	Al	Ca	Fe	K	Mg	Mn	Na
		mS/cm	mV	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
UDB	2.55	8.42	215	7550	0	286	466.7	257.0	584.4	2516.7	17.9	451.8	104.9	149.7
NDB	2.64	8.46	212	18090	0	264	333.3	252.5	583.3	2495.4	17.3	443.5	103.4	153.9
NDA	2.65	8.58	210	18090	0	363	466.7	253.7	581.1	2608.9	16.3	446.2	103.8	150.0
ID	2.24	11.85	230	17085	0	671	666.7	358.6	531.1	3145.8	5.7	662.0	160.6	174.9
IAD	3.35	9.59	175	15075	74.8	88	700.0	433.1	699.7	7.7	68.8	1362.8	532.7	457.3
IAD2	2.55	6.55	216	7035	123.2	242	400.0	212.7	691.5	1402.6	12.1	426.1	95.6	149.0
FD	2.5	6.71	219	14070	262.5	440	666.7	218.5	715.9	1450.6	12.3	444.9	95.6	155.9
DDU	2.46	6.65	221	5285	4.5	264	600.0	213.4	719.2	1415.8	142.1	438.4	94.2	239.4
DU	2.64	2.41	220	2265	23.1	11	366.7	35.2	175.6	45.3	12.8	88.6	13.0	104.5

The most problematic pollutants as far as water quality is concerned, mostly occurred in trace amount (Table 2). Metals such as U, As, Ni and Pb were the dominant trace elements which were randomly distributed along the drainage; noticeable high concentrations of uranium (4.57 mg/L) in the dam and arsenic (67.14 mg/L) at point NDB compared to other points were recorded. Although the overall concentrations of trace metals decreased at the farthest point downstream (sampling site DU); U, As, Ni and Pb were still present at non-permissible levels based on the drinking water recommendation by the South African Bureau of Standard (SABS 2005). The spatial distribution of pollutants along the drainage shows that the pattern varies depending of the pollutants; while some of the concentrations of some of the pollutants may decrease moving downstream from the mine, it is not the case with other pollutants for which the concentrations increase along the drainage. It is therefore likely that dissolution of minerals may take place simultaneously with precipitation. Efflorescent salts deposited on the bank of the river were therefore analyzed to better understand their contribution to the contamination of water.

***Table 2** Measured values of trace metals in water samples*

Sampling sites	Concentration of minor cations in water (mg/L)							
	Ag	U	As	Cd	Cu	Ni	Pb	Zn
UDB	0	2.4	0	0.45	0	13.06	43.57	8.82
NDB	0.42	1.89	67.14	1.66	0.77	5.61	8.34	12.44
NDA	0	1.69	14.57	0	0.5	24.57	60.04	5.51
ID	0.38	4.57	0	0.79	0.18	30.38	38.68	12.41
IAD	0.08	1.85	31.64	0	0.19	8.47	10.89	11.44
IAD2	0.41	1.82	8.39	0	0	37.36	53.92	4.36
FD	0.02	1.76	9.51	0.99	0	20.43	33.93	5.22
DDU	0	1.44	0	0.79	2.64	22.21	0	13.64
DU	0	1.59	6.42	0.18	0	33.8	29.7	1.53

Mineralogical composition of efflorescent salts

Specific sampling sites were selected before and after the dam to better understand the influence of efflorescent salts (shown in Figure 1) on the pollution upstream and downstream.

***Figure 1** Efflorescent crust at the bank of the acid mine drainage*

The mineralogical composition of efflorescent salts was determined using the XRD analysis. The results in Table 3 show that Goethite and hematite were found in salts at all the sampling points, while SO_4^{2-}, Fe, Mg and Mn were predominant in salts at all the sampling points; this confirms the results obtained from the analysis of water as these were among the major elements occurring in the drainage. It could be suggested that the salts are likely to contribute to the pollution of water; it was reported in previous study that electrical conductivity could increase while pH decreases following dissolution of effluorescent crust (Tutu et al. 2011).

***Table 3** XRD results of efflorescent salts at sampling sites*

Minerals	Formula	Samples			
		ND	NDBB	NDAB	IAD
Apjohnite	$Mn\,Al_2\,(SO_4)_4\,(H_2O)_{22}$	X	X		
Goethite; Goethite, syn	$FeO\,(OH)$	X	X	X	X
Mikasaite, syn	$Fe_2(SO_4)_3$	X			
Hematite, syn	Fe_2O_3	X	X	X	X
Kaolinite	$Al_4\,(OH)_8\,(Si_4O_{10})$		X	X	
Magnesium sulfate hexahydrate	$MgSO_4(H_2O)_6$		X		X
iron(III) sulfate	$Fe_2(SO_4)_3$			X	
Pickeringite	$(Mg_{0.93}\,Mn_{0.07})\,Al_2\,(SO_4)_4\,(H_2O)_{22}$				X

Fe-components in efflorescent salts

From the XRD analysis all the samples contain some hematite which was not detected in the Mössbauer experimental runs. According to the XRD results samples 3 and 4 should contain 10% and 16% hematite respectively and should have been seen in a Mössbauer spectrum run at 10 mm/s, which was however not detected. Both samples contain similar amounts of goethite, which was detected in the Mössbauer experiments (Table 4). Since the hematite has a hyperfine magnetic field in a Mössbauer spectrum the samples 3 and 4 were run at 10 mm/s but only the doublet was observed and to ensure a better resolution of the doublets all samples were run at 4 mm/s velocity to ensure a better resolution between the doublets and the parameters found for the goethite fall well in to known literature values (Stevens et al. 2005). In addition sample 3 had an iron sulphate species present as was also observed in the XRD spectrum

It should be noticed that the mineral Mikasaite is rare on earth and was detected on Mars (Nomura et al. 2005; Dyar et al. 2013) and thus doubtful that they are in the samples originating from a dam or stream. Mikasaite was found in sample 1in the XRD spectrum and not observed in the Mössbauer spectrum.

***Table 4** Hyperfine interaction Mössbauer parameters of Fe-components found in this investigation*

Sample	Component	IS	QS	H	Relative intensity
		mms^{-1}	mms^{-1}	Tesla	(%)
		(±0.02)	(±0.02)	(±0.3)	
Sample 1 ND	Doublet goethite	0.337	0.771		100
Sample 2 NDBB	Doublet goethite	0.36	0.726		100
Sample 3 NDAB	Doublet goethite	0.34	0.74		40
	Doublet iron sulphate	1.58	2.85		60
Sample 4 IAD	Doublet goethite	0.371	0.858		100

Note: IS = Isomer shift relative to α-Fe, QS = Quadrupole splitting
H = Hyperfine magnetic field strength

Conclusions

The physicochemical analysis of mine effluent considered in this study showed that it was typical of acid mine drainage containing very high load of pollutants which were distributed all along the stream moving down to the residential area. There is concern with the very acidic pH and the high concentrations of heavy metals in leached from the mining sites and sustain by the progressive dissolution of salts at the bank of the stream. The Mössbauer and XRD results have confirmed the occurrence of goethite in all the salts which is much likely to be involved in the oxidation or dissolution process and contribution of high level of Fe in water. The impact of the AMD formation on the stream downstream in the residential area was quite pronounced as the levels of pollutants especially heavy metals were above the permissible values recommended by the national guideline for drinking water. There is therefore an obvious risk of destabilization of the aquatic ecosystem, intoxication of farm animals and human relying on that stream.

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Persistent Secondary Contaminant Sources at a Former Uranium Mill Site, Riverton, Wyoming, USA

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Abstract

Milling activities at a former uranium mill site near Riverton, Wyoming, USA, contaminated the shallow groundwater beneath and downgradient of the site. Uranium mill tailings have been removed, and groundwater modeling predicted that natural flushing of the groundwater aquifer to a nearby river would achieve compliance with applicable groundwater protection standards by the year 2097. From 1989 to 2009, contaminant concentrations below the former mill site and downgradient of it were declining steadily; however, local flooding in 2010 mobilized stored contaminants in the downgradient floodplain and resulted in an increase in groundwater contaminant concentrations. These stored contaminants or persistent secondary contaminant sources were not considered in the original conceptual site model and groundwater modeling predictions with natural flushing.

Additional data collection was performed on the floodplain in 2014 and 2015 to assess the possibility that secondary contaminant sources (specifically uranium) have been retained at the surface and in the subsurface through various processes. Data collection activities included surficial sediment sampling, trenching for direct subsurface observations, sonic drilling for core collection and multilevel well installations, and hand augering for shallow core collection and the installation of pore-water samplers.

Results indicate that uranium is being concentrated and stored in surface and subsurface evaporites and naturally reduced zones (NRZs) with high organic carbon and sulfide content. The evaporites and NRZs contain up to 66 and 140 mg/kg uranium, respectively, with resulting pore-water concentrations up to 2.68 mg/L uranium in the NRZs. These values compare to <1.3 mg/kg uranium in the typical underlying sand and gravel aquifer solids and up to 1.7 mg/L uranium in the current groundwater. It appears likely that the NRZs provide a mechanism to concentrate uranium under reducing conditions. Subsequent oxidation of the NRZs provides a release mechanism for uranium to the overlying unsaturated zone pore waters and the underlying groundwater. Due to a shallow water table and arid conditions that produce high evapotranspiration rates, the uranium-rich pore waters provide a mechanism to form overlying uranium-rich evaporites. The presence and understanding of these persistent secondary contaminant sources can be used for more informed management of the Riverton site.

Key words: uranium, persistent contaminants, evaporites, naturally reduced zones

Introduction

Milling activities at a former uranium mill site near Riverton, Wyoming, USA, took place from 1958 to 1963. Uranium mill tailings were removed, and surface reclamation was completed by the U.S. Department of Energy (DOE) in 1989. However, shallow groundwater beneath and downgradient of the site is still contaminated (fig. 1) with up to 2.1 mg/L uranium in 2012 and up to 1.7 mg/L uranium currently. Groundwater modeling predicted that natural flushing of the groundwater aquifer to a nearby river would achieve compliance with applicable groundwater protection standards by the year 2097 (DOE 1998). Initial data from 1989 to 2009 indicated that overall, contaminant concentrations below the former mill site and downgradient of it were declining steadily. However, local flooding in

2010 mobilized stored contaminants in the downgradient floodplain and resulted in an increase in groundwater contaminant concentrations, including uranium (fig. 2), which lead to additional site characterization (DOE 2013). These stored contaminants or persistent secondary contaminant sources were not considered in the original conceptual site model and groundwater modeling predictions with natural flushing (Dam et al. 2015).

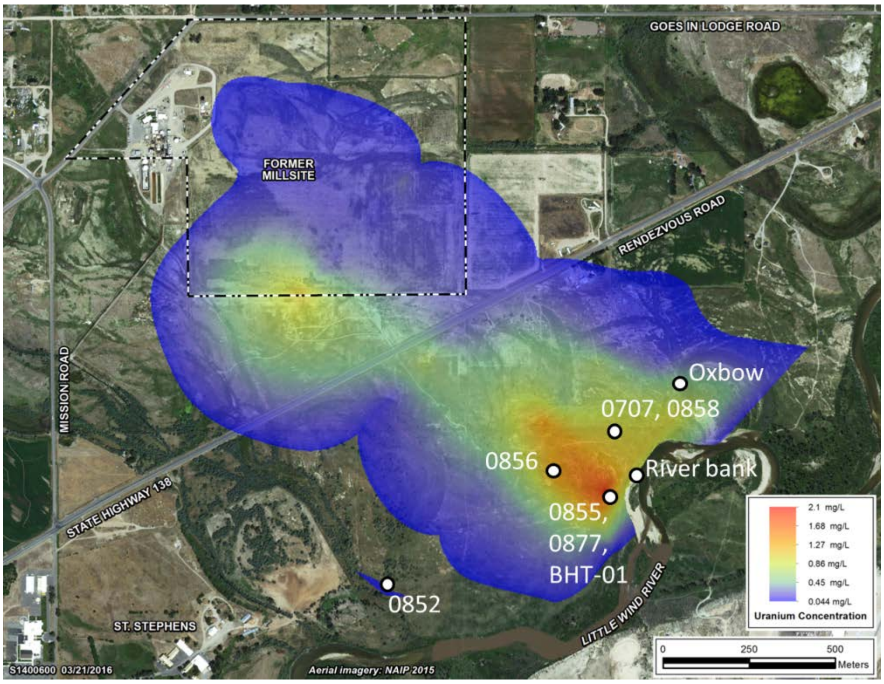

Figure 1 *Uranium plume at the Riverton site in 2012 with key sample locations.*

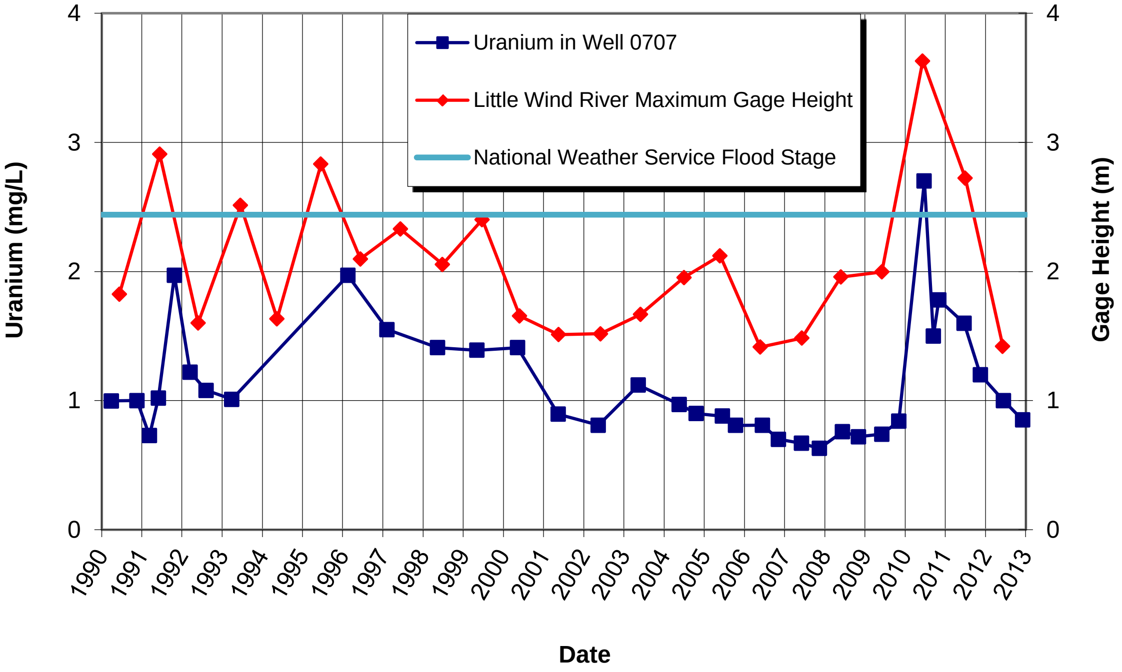

Figure 2 *Hydrograph for the Little Wind River compared with uranium concentrations at well 0707 (see location in fig. 1).*

This paper focuses on additional data collection performed on the floodplain in 2014 and 2015 to assess the possibility that secondary contaminant sources (specifically uranium) have been retained at the surface and in the subsurface through various processes. Data collection activities included: surficial sediment sampling, trenching for direct subsurface observations, sonic drilling for core collection and multilevel well installations, and hand augering for shallow core collection and the installation of pore-water samplers.

Methods

Solid-phase samples were analyzed for trace metals and cations using a total acid digestion with subsequent inductively coupled plasma mass spectrometry (ICP-MS). Some solid-phase samples were analyzed using x-ray fluorescence (XRF). Solid-phase anions were analyzed using a water leach and subsequent ion chromatography (IC) analyses.

Multilevel well installations were completed using continuous multichannel tubing (CMT) that was cut in the field based on the geology to provide three sampling ports with depth. The CMT was attached to a traditional plastic well riser pipe with a bottom screen to provide a fourth groundwater sampling interval. Water sampling was done using a peristaltic pump, and water analyses were completed using IC and ICP-MS techniques. Pore water was sampled using hand pumping suction devices with an end filter (suction lysimeter) installed directly into the ground, either in the side of trench walls or subsurface in hand-augered holes.

Evaporites

Surficial evaporite deposits or efflorescent salt crusts (fig. 3) can be found along the river banks. Background concentrations of uranium in these deposits are approximately 1.4 mg/kg uranium, but the uranium concentrations in surficial evaporites over the plume are as high as 66 mg/kg uranium (DOE 2014).

Figure 3 *Evaporite deposits found along the Little Wind River.*

The general stratigraphy at the Riverton site is a 0.76 to 1.37 m silt layer (fig. 4b) underlain by 1.92 to 4.63 m of sand and gravel (fig. 4c), which is then underlain by lower-hydraulic-conductivity bedrock (Wind River Formation). The silt layer is generally above the water table but can be within the capillary fringe depending on the time of year and the water-table stage. This silt layer appears to be concentrating a variety of constituents (not shown) in subsurface evaporites. The presence of subsurface evaporites was visually confirmed in the sides of trench walls, hand-augered material, and in sonic drilling cores (fig. 4b). The concentrations of elements that occur naturally, such as chloride, appear to be independent of mill-related plume concentrations (fig. 4). However, the anthropogenic source of uranium does appear to concentrate in the subsurface evaporites in areas over the uranium plume (fig. 5), with up to 8 mg/kg uranium in the silt over the plume compared to approximately 1.5 mg/kg uranium from the silt in borehole 0852 outside of the plume.

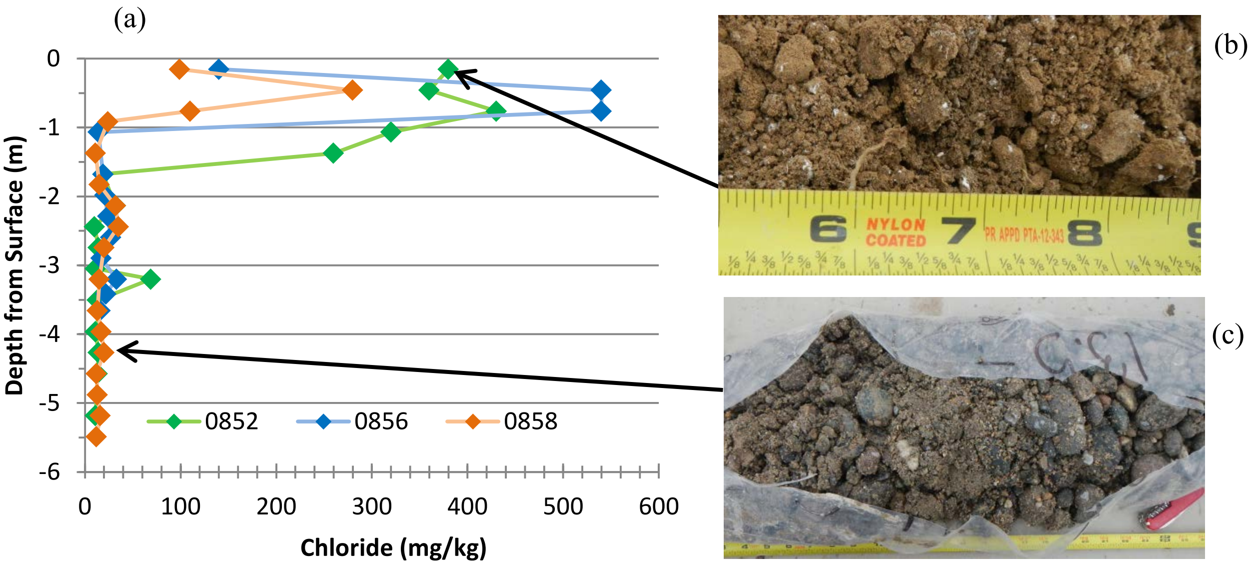

Figure 4 *Solid-phase chloride concentrations with depth (a) with photographs of silt with white evaporites flecks (b) and underlying sand and gravel (c). Borehole 0852 is outside of the uranium plume, and boreholes 0856 and 0858 are within the uranium plume (see locations in fig. 1).*

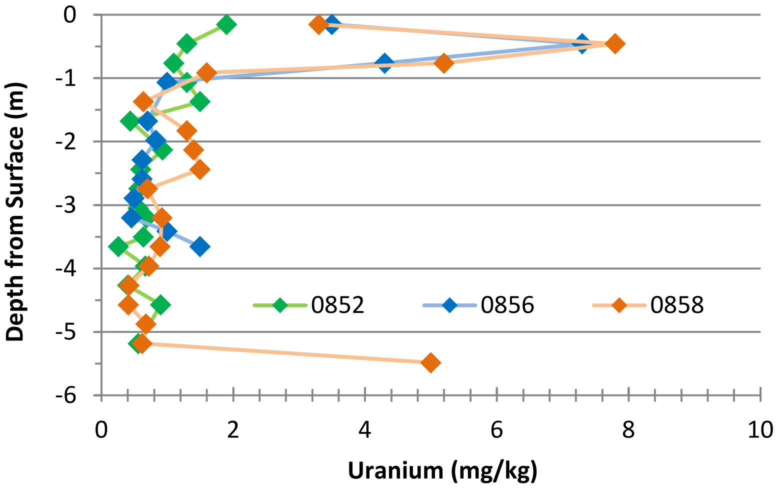

Figure 5 *Solid-phase uranium concentrations with depth. Borehole 0852 is outside of the uranium plume and boreholes 0856 and 0858 are within the uranium plume (see locations in fig. 1).*

Naturally Reduced Zones (NRZs)

NRZs at the Riverton site occur in sediments within the area of a river cutoff meander that has formed an oxbow lake (fig. 6a), in sediment near the riverbank (fig. 6b), and in subsurface sediments away from the river (figs. 7a and c). The defining characteristics of these NRZs are fine-grained sediments with enough organic carbon to produce sufficient reducing capacity to maintain anoxic conditions when saturated. Under these conditions, uranium is less soluble in water and tends to sorb and/or precipitate on the solid phase. As a result, XRF data for the oxbow and riverbank NRZs range from 22 to 140 mg/kg uranium. Subsurface NRZs have concentrations up to 22 mg/kg (fig. 7a) compared to generally less than 2 mg/kg uranium in the underlying sand and gravel. Uranium concentrations in the subsurface evaporites that occur above the NRZs (fig. 7b) range from about 4 to 10 mg/kg uranium (fig. 7a), which is similar to those of evaporites that do not occur over an NRZ, which range from 3 to 8 mg/kg uranium (fig. 5).

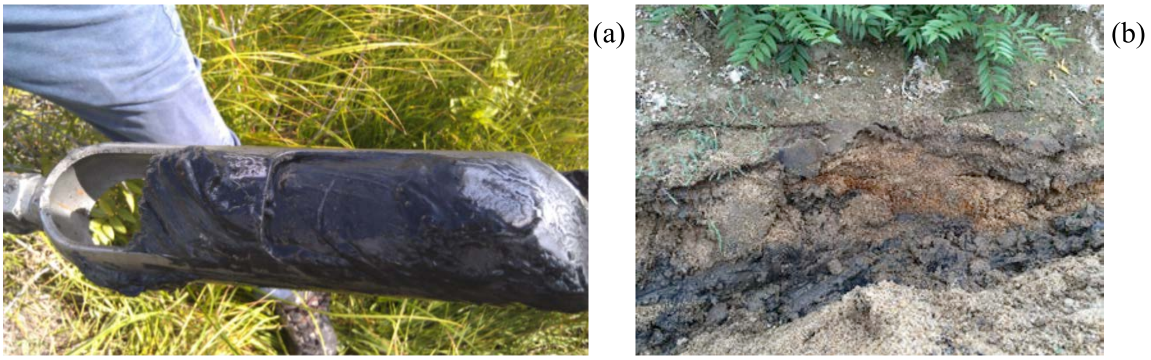

Figure 6 *Hand-auger sample of oxbow sediments (a) and a cross-sectional view of an NRZ at the riverbank (b). For sample locations see fig. 1. Note the oxidized top portion in (a) with iron hydroxide staining.*

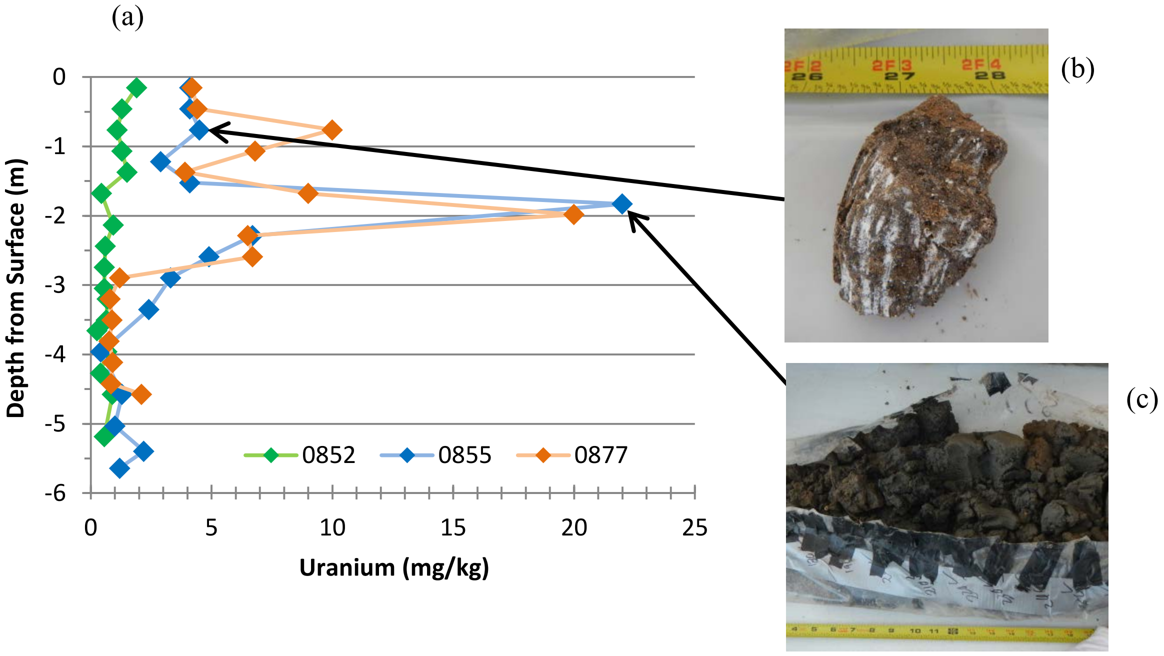

Figure 7 *Solid-phase uranium concentrations with depth (a) from borehole 0852 outside of the uranium plume and boreholes 0855 and 0877 within the uranium plume (see locations in fig. 1) along with photographs of evaporites (b) and an NRZ zone (c).*

Groundwater

Uranium in pore water within and above an NRZ zone was sampled from a trench in May 2015 (fig. 8a) and then again in August 2015 using pore-water samples installed in a hand-augered hole (fig. 8b). Uranium concentrations in groundwater from the multilevel well installations (three points at greater than 2 m depth) were sampled in September 2015 and are plotted along with the August 2015 pore-water data and compared to uranium concentrations in the solid phase (fig. 8b). In August/September 2015 the uranium concentrations in water are highest in the bottom half of the NRZ and in the underlying groundwater compared to the above pore water and the groundwater below 5 meters (fig. 8b). The water table in this area likely reaches the top of the NRZ in the spring at approximately 1.3 m in depth but was close to 1.6 m in depth in August/September 2015. With a lower water table in May 2015 at above 1.7 m, before the spring snowmelt and high river stage, the upper part of the NRZ is unsaturated and has likely been oxidizing though the fall and winter months. This results in higher uranium concentration in pore water (fig. 8a) in the upper part of the NRZ, up to 2.68 mg/L. By August/September 2015 the pore water in the upper part of the NRZ was likely flushed to the underlying groundwater, thereby decreasing the uranium in the upper zone to less than 0.7 mg/L and increasing the uranium in the bottom part of the NRZ from 1.17 mg/L to 1.4 mg/L (fig. 8).

Overall, it appears likely that the NRZ zone can maintain a groundwater uranium concentration of 1.4 mg/L compared to the underlying uranium concentration of 0.86 mg/L in the sand and gravel just above the bedrock interface, which may represent upgradient plume water. Seasonal measurements of uranium in the pore water and groundwater in and above this NRZ zone are ongoing. These seasonal measurements should assist in better understanding the contributing amount of uranium to the groundwater from overlying evaporites compared to the underlying NRZs. Release of uranium from the evaporites does require a higher water table and/or flood conditions such that these evaporites become saturated, with a resulting release of uranium to the groundwater. As such, uranium release from the evaporites may not occur every year, while uranium release from the NRZs may occur on a more seasonal basis.

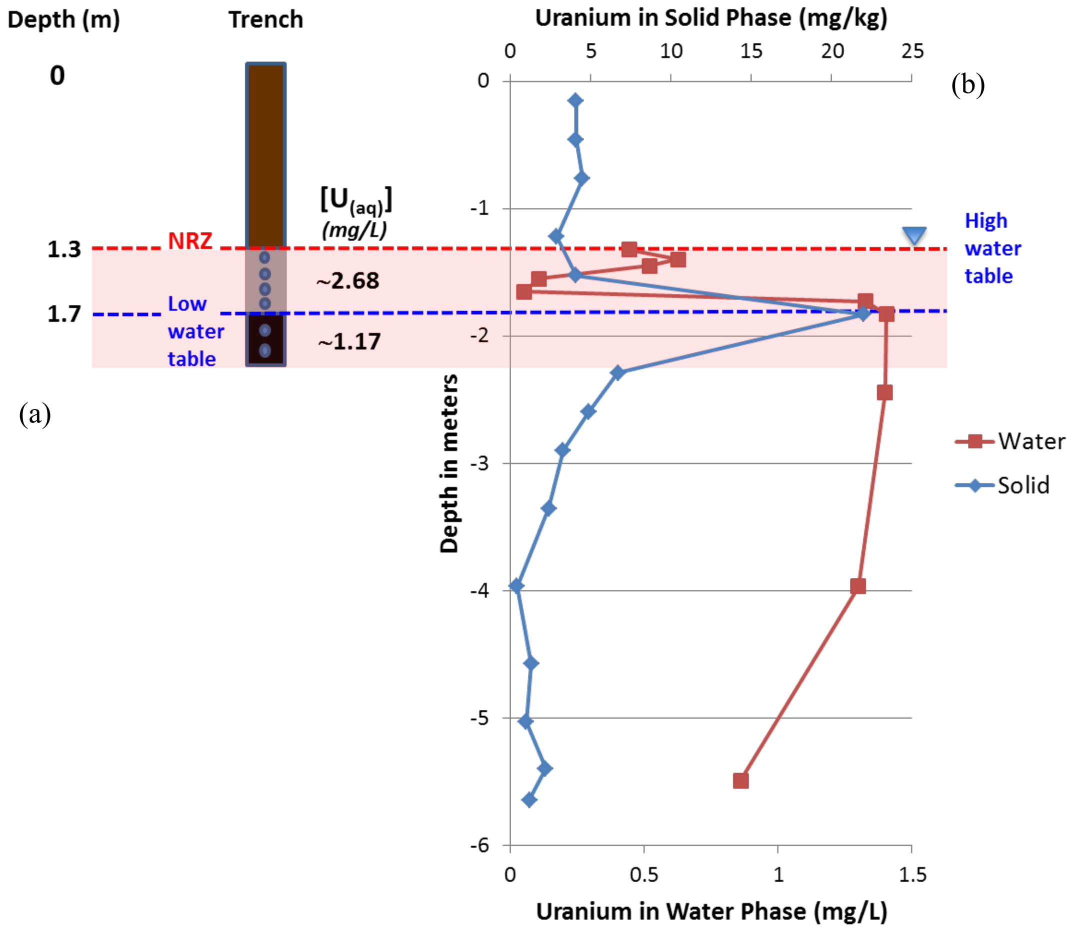

Figure 8 *Pore-water uranium concentrations in May 2015 from trench BHT-01 (see location in fig. 1) with an NRZ (a) and pore water and groundwater uranium concentrations in August/September 2015 compared to solid-phase uranium concentrations (b) from the same general location.*

Conclusions

Measured solid-phase uranium concentrations in evaporites and NRZs indicate higher concentrations of uranium and provide potential secondary contaminant sources that can delay natural flushing at the Riverton site. Due to a shallow water table and arid conditions that produce high evapotranspiration rates, the underlying uranium-rich plume waters provide a mechanism to form overlying uranium-rich evaporites (with or without NRZs). The reducing conditions produced by NRZs provide a mechanism to concentrate uranium; however, subsequent oxidation of the NRZs provides a release mechanism for uranium to the overlying unsaturated zone pore waters and the underlying groundwater. Seasonal measurements of pore water and groundwater at the site near the evaporites and NRZs are ongoing in order to better understand the amount and rates of uranium release. Overall, the presence and understanding of these persistent secondary contaminant sources and how they relate to plume persistence can be used for more informed management of the Riverton site.

Acknowledgements

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Waste Rock Characterisation versus the Actual Seepage Water Quality

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Abstract

Proper characterisation is needed to predict the long term behaviour of mine waste material and to successfully close a waste facility. The objective of this study was to compare the performance of commonly used prediction methods with the actual seepage water quality from closed or active mine sites. This was carried out by characterising waste rock material and seepage waters from seven mine sites. The prediction methods included static tests, NAG leachate, shake flask test and hot *Aqua Regia*.

Differences were observed between the methods predicting acid production potential (APP) and the actual acidity of the seepage waters. The study indicated that the laboratory tests were often too pessimistic in comparison with the pH values measured from the seepages. Therefore, the use of several different methods, as well as mineralogical data, is recommended for the APP prediction.

According to the results of the different examined leachability tests, the hot *Aqua Regia* extraction had the best correspondence with the actual seepage water quality in predicting which elements will be present in the effluents. In general, performance of the NAG test leachate was reasonable, but it underestimated the metal concentrations when NAG leachate pH was higher than around 4. The shake flask test was observed to be the most unsuitable for the effluent quality prediction.

The results obtained from the *Aqua Regia* extraction and NAG leachate can be used to predict the elements that will appear as elevated concentrations in the effluents, considering that the concentrations are only approximate, not exact. Elevated concentrations in any of the evaluated leaching tests indicate a possibility of increased element loads in the seepages.

Key words: Mine waste characterisation, mine water, drainage quality, prediction

Introduction

Mining wastes and waste facilities are usually the most fore standing sources of harmful drainage at a mine site. Proper characterisation is needed already before actual mining operations, to predict the long term behaviour of disposed waste material, for example, for the environmental impact assessment, and for the planning of waste and seepage water management methods and their closure. Therefore, selection of suitable characterisation methods is crucial. Seepage water quality can be predicted, for example, by using geochemical characterisation, geochemical modelling, or analogies between similar deposit types (REFs?).

To determine acid production potential (APP), the acid base accounting (ABA) tests are the most commonly used static test methods. These tests characterise if sample material is either non-acid producing, i.e. neutralisation potential (NP) exceeds acid production potential (AP), or potentially acid generating, i.e. AP exceeds NP (Sobek et al. 1978, White et al. 1999). Also the net acid generation (NAG) test can be used to assess the risk for acid generation, either as a standalone tool (Miller et al. 1997), or as a supplement to other static tests, e.g. the ABA test (Jambor 2003).

Leachability of potentially harmful elements can be evaluated with several methods. According to the European legislation concerning mine waste characterisation, the leachability of metals, oxyanions and salts over time should be evaluated by pH dependence leaching test, and/or percolation test and/or time-dependent release and/or other suitable testing, and for sulphide-containing waste, static or kinetic tests should be carried out in order to determine acid rock drainage and metal leaching over time (European Commission 2009). In Finland, to fulfil the requirements of the European Commission and to predict metal leaching, one of the most common selective extractions used for mine waste characterisation is the hot *Aqua Regia* leach (Doležal et al. 1968, Niskavaara 1995). Also the NAG test leachate can be analysed to assess the harmful element mobility during long-term acid generation reactions (Räisänen et al. 2010). Furthermore, the leachability of elements can be assessed using the two-stage batch leaching test/shake-flask test SFS-EN 12457-3, which complies with the waste disposal related Decrees 202/2006 and 403/2009 of the Finnish Government.

The objective of this study was to compare performance of various prediction methods with the actual seepage water quality from closed and active mine sites. This was carried out by characterising waste rock material and seepage waters from seven mine sites. For the prediction of APP, suitability of modified ABA and NAG test was evaluated. Dissolution of metals and metalloids during hot *Aqua Regia* extraction, NAG test and two-stage shake-flask test was investigated and performance of these methods to assess the mobility of contaminants during the long term waste rock storage was evaluated.

Methods

Seepage water and waste rock samples were collected from seven operating or closed mine sites, in total from nine waste rock areas originating from varying commodities and with different disposal periods (Table 1). From the mine sites 3 and 6 samples were collected from waste rocks piles of different disposal periods, i.e. from a waste rock pile, in which waste rock disposal had ceased already some 15-20 years ago, and from a waste rock pile, in which disposal was still active.

Table 1 *Commodities of the studied mine sites and disposal periods of the waste rock piles*

Target Site	Commodity	Time of waste rock disposal
Mine 1	Au	2011 -
Mine 2	Cu, Co, Zn, Ni	1972 - 1985
Mine 3 (old)	Talc, Ni	1982 - 2000?
Mine 3 (fresh)	Talc, Ni	2004 -
Mine 4	Cu, Co, Zn, Ni, Au	2011 -
Mine 5	Ni, Co	1970 - 1993
Mine 6 (old)	Apatite	1975 - 2000?
Mine 6 (fresh)	Apatite	2000? -
Mine 7	Cu, Zn	1973 - 1986

Seepage waters were collected from the edges of the waste rock piles from points where the water surfaces from the pile. The pH was measured in the field using a portable multi-parameter YSI meter. Filtered (0.45 µm), HNO_3-acidified samples were collected for dissolved cations and trace element analyses, and measurements were made by ICP-OES/MS.

Waste rock samples were collected as 10-15 kg composite samples of fist sized subsamples taken from the waste rock pile surface above the seepage points. The amounts of carbonate carbon and total sulphur were measured using pyrolytic methods. The APP of the waste rock material was studied with ABA (CEN-EN 15875) and NAG (AMIRA 2002) tests. *Aqua Regia* was used to dissolve the samples according to the modified ISO-11466 standard. Leachability of elements was further studied by analyzing trace metal concentrations from the leachates of the NAG test, and using the shake-flask test/batch leaching test (SFS-EN 12457-3). The trace element were measured from the leachates with ICP-OES/MS.

Results and discussion

Table 2 shows the results of the acid production potential of the rock samples measured with the modified ABA and NAG test, the contents of carbonate carbon and total sulphur, and the *in-situ* measured pH values of the seepage waters. Based on the results, the ABA and NAG tests revealed differences in assessing the acid production potential of the rock samples. According to the ABA test, six samples were likely to produce acid rock drainage (NP/AP < 1) and three samples were non-acid generating, whereas based on the NAG test, only four samples were potentially acid forming (PAF) and five non-acid forming (NAF) (tab 2).

The samples that showed differences in assessing the APP were sample Mine 3 (old) and Mine 4. The NAG test assessed both samples as non-acid forming, while the ABA tests indicated both samples to be likely acid generating. For the classification of acid generation, the AMIRA guidebook (2002) further recommends the use of the net acid production potential (NAPP) together with the NAG results. When applying the NAPP to the NAG results, the APP of sample Mine 4 classified as uncertain, and the sample 3 (old) as NAF but close to the uncertain field. Based on the results, the contradictory results between the two tests can be expected with samples falling under the uncertain category of APP.

Table 2 *Carbonate carbon and total sulphur concentrations, APP test results and the actual seepage water pH at the mine sites. NAF = non-acid forming, PAF = potentially acid forming.*

Sample	C carb (%)	S (tot) %	NAG	ABA	Seepage pH
Mine 1	0.8	0.1	NAF	None	6.7
Mine 2	0.2	1.7	PAF	Likely	6.3
Mine 3 (old)	1.3	1.4	NAF	Likely	7.3
Mine 3 (fresh)	1.4	2.3	PAF	Likely	7.7
Mine 4	0.7	4.3	NAF	Likely	7.1
Mine 5	0.1	3.4	PAF	Likely	6.7
Mine 6 (old)	2.8	0.1	NAF	None	6.5
Mine 6 (fresh)	0.8	0.2	NAF	None	7.0
Mine 7	< 0.1	1.6	PAF	Likely	3.9

Furthermore, clear differences between the test results and the actual measured seepage water pH values were observed. The laboratory tests, especially the modified ABA test, gave principally too pessimistic estimates on the APP compared with the realized seepage water pH at the mine sites.

The sums of dissolved heavy metals in the extracts produced in the NAG test and the *Aqua Regia* leach, and in the waste rock seepage waters are presented in Figure 1. The batch leaching / shake-flask test results are not shown in the Figure, because element concentrations were mainly low or below the detection limit of the analytical method. The concentrations presented in Figure 1 should not be considered as exact estimations of seepage water quality, but merely as approximates of potentially elevated metal concentrations.

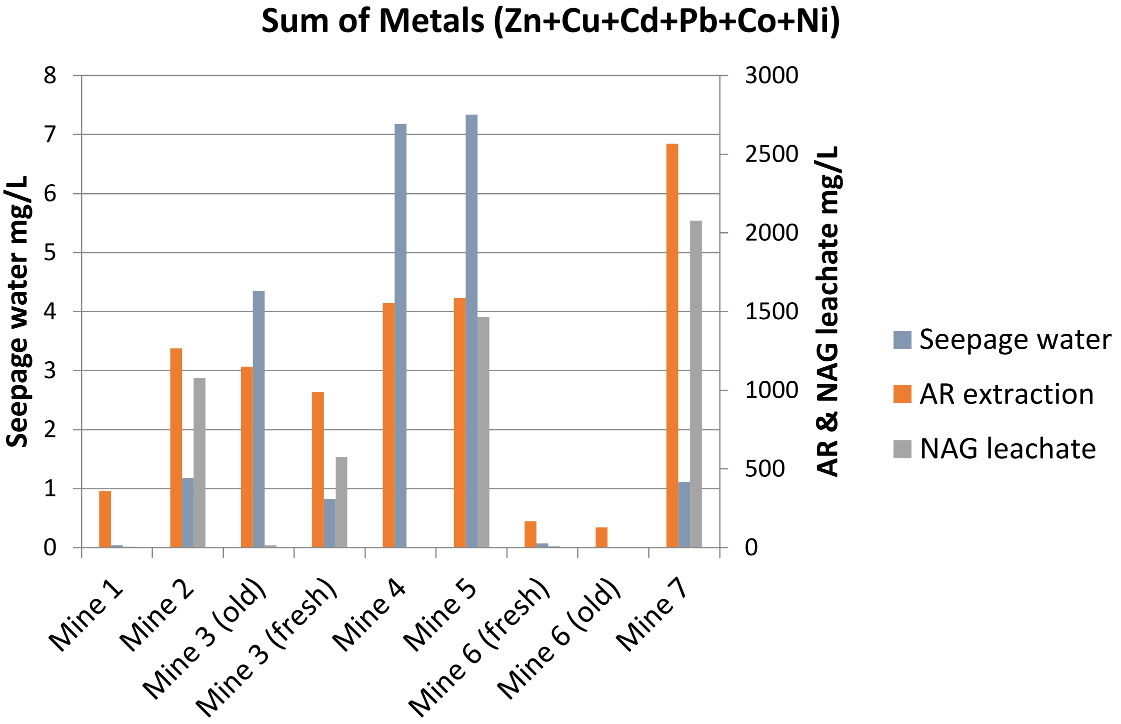

Figure 1 *The sums of dissolved heavy metals in the extracts from the NAG test and the Aqua Regia leach, and in the waste rock seepage waters.*

The *Aqua Regia* extraction seems to have the best correspondence with the elevated metal concentrations in the actual seepage waters. The NAG test leachate underestimated the metal load in the cases of sample Mine 3 (old) and Mine 4. In general, performance of the NAG leachate test was reasonable, but it underestimated the metal concentrations when the NAG leachate pH was higher than around 4, which is due to the precipitation processes (Räisänen et al. 2010, Charles et al. 2015).

The batch leaching test seems to be the most unsuitable for the seepage water quality prediction, as the results were mainly under the detection limit of the analytical method even though seepage waters showed elevated concentrations of trace metals. The solvent used in the batch leaching test (distilled water) is probably too weak and the reaction time too short for crystalline waste rock materials. Based on the results, elevated concentrations in any of the tests used in this study indicate a possibility for dissolution of trace metals from the rocks.

Interpretation of the results is complicated by the representativeness and weathering grade of the samples. Seepage water qualities should be monitored for a longer time period to detect the seasonal and annual variation in the quality.

Conclusions

Based on the results, the performance of the studied characterisation methods to predict acid rock drainage and metal leaching over time could be compared and evaluated. Differences were observed between the modified ABA and NAG tests predicting APP and the actual acidity of the seepage waters. The results indicated that the laboratory tests, especially the ABA test, were often too pessimistic in comparison with the real measured pH values at the mine sites. Therefore, the use of several different methods, together with mineralogical data, is recommended for comprehensive APP prediction.

According to the results of the different evaluated leachability tests, the hot *Aqua Regia* extraction had the best correspondence with the actual seepage water quality in predicting which elements will be present in the effluent waters. In general, performance of the NAG test leachate based test was reasonable, but it underestimated the metal concentrations when the NAG leachate pH was higher than around 4. The shake flask test was observed to be the most unsuitable for the effluent quality prediction, probably due to a weak solvent used in the test (water) and the too short reaction time for the crystalline waste rock material.

According to this study, the results obtained from the *Aqua Regia* extraction and NAG leachate based test can be used to predict the elements that will appear as elevated concentrations in the effluents, considering that the concentrations are only approximate, not exact, and that the pH of the NAG test leachate is sufficiently low. Elevated concentrations in any of the evaluated leaching tests indicate a possibility of increased element concentrations in the seepage waters.

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Mine Water approach using Tracers in South African abandoned Coal Mines

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Abstract

Surface water and groundwater quality in areas of South Africa continues to be degraded by acid mine drainage (AMD), a legacy of coal mining. The majority of abandoned coal mines consist of complex multiple level workings connected to a drainage tunnel discharging AMD, in lower lying regions. This decanting mine water poses severe problems to the receiving environment. Thus, there is a need, to define hydrologic connectivity between surface water, groundwater and mine workings to understand the source of both water and contaminants at the decanting points. South Africa has limited studies into the feasibility of using tracer techniques, especially in mine water studies to understand underground water dynamics. Locally, there are no regulations and/or standard procedures for such activities. Wolkersdorfer (2008), states that in some countries such as Germany, there are regulations that govern the use of tracers.

In a case study that is currently in progress as part of the use of tracers in mine water, water samples were collected from different discharge points in and around a flooded and abandoned coal mine, within the Witbank coal fields of the Permian Karoo Supergroup. This was done to classify the different water types as a pre-assessment for using tracer techniques. Our preliminary results demonstrated that the water samples collected have high concentrations of major elements such as SO_4, Cl, Na, Mg, Al, K, and Ca.

Key words: Mine water, tracer, discharge, South Africa

Introduction

A major environmental problem relating to mining in many parts of the world is the uncontrolled discharge of contaminated water from abandoned mines. The general consensus is that this phenomenon is responsible for costly environmental and socio-economic impacts. While South Africa has made the paradigm shift in addressing mine closures and mine water management through rigorous legislation and regulatory changes, vulnerabilities in the current system still remain. Commercial coal mining in South Africa started in about 1864 when the first colliery opened near the town of Molteno in the Eastern Cape Province (De Korte 2010). Since then, many mines were discovered and mined in different localities around the country. Subsequent to their closure, some of these were left abandoned. After the closure of the mines, many parts of the mines collapsed and subsided, resulting in a combination of problems including acid mine drainage and spontaneous combustion, eventually causing further subsidence and air pollution due to spontaneous combustion. Following mine abandonment, pumping from the active mine is terminated and mine voids are allowed to flood (Donovan *et al*. 2000).The flooding of abandoned mines will mostly continue until the groundwater achieves a new equilibrium, either by the surface discharge of mine water or by controlled pumping and treatment. The hydrodynamics controlling the flow and transport of the mine water in flooded underground mines is generally not well understood in South Africa. Much of the research carried out over the past decade in South Africa has focused on the treatment of polluted water and the prevention of water ingress, making it possible to implement certain ingress control measures immediately while other measures require minimal preparatory work. The prevention of pollution will always be more sustainable than pumping and will obviate or reduce the need for perpetual treatment of AMD.

Tracer tests are well established in groundwater studies where they are commonly used to investigate the hydraulic parameters or interconnections of groundwater (Käß 1998). Most of the techniques used are well described and, depending on the aims of the tracer test and the hydrological situation, a range of tracers or methods may be chosen. Published results of tracer tests in abandoned underground mines are not common. This is mainly as a result of the complex infrastructure of underground mine workings and poor conceptualisation of the hydrological system. However, over the past decade, a number of tracer tests in underground flooded mine workings were conducted with the aim of understanding the hydrodynamics of the subsurface and support remediation procedures (e.g. Younger *et al* 2002, Wolkersdorfer 2002,Aldous and Smart 1988, etc). A tracer is any substance (compound, trace metal, heat, micro-organism, etc.) that can be carried by water in order to provide information about the direction and velocity of the water as well as the transport of potential contaminants (Davis *et al.* 1980). Tracer tests techniques may be used to generate new knowledge, research and advancement in the field of mine water in South Africa

Methodology

The overall program that this work fits into is generally based on bringing solutions into mine water problems in South Africa. As a part of that, this task is aimed at scientifically quantifying and apportioning pollution sources from mining activities. Several methods have been proposed over the past decade, such as principal component analysis/multiple linear regression, tracer and isotopic techniques and numerical modelling (Cowie *et al* 2014). Owing to the complexity of mining water environments, regulators and decision makers are often confronted with significant challenges in their efforts to manage the full scope of water resources. Characterisation of the spatial variations and source apportionment/determination of water quality variables (analysis using piper, stiff, SAR and duvor diagrams) offers an improved understanding of the environmental conditions and can help researches to establish priorities for sustainable water management.

Tracer techniques

Tracer tests are used to investigate the hydrodynamic parameters or interconnections of groundwater flow, however, the use of tracers in flooded mines to monitor the hydrodynamics of groundwater is a field that still requires exploration. Tracers are classified into environmental/natural and artificial. Environmental tracers are ambient, natural or artificial compounds widely distributed in the earth's near-surface. They may be injected naturally into the hydrological system from the atmosphere at recharge and/or are added/lost/exchanged inherently as waters flow over and through materials (Elliot 2004). In flooded underground mines, both types of tracer tests can be used to evaluate flow paths and seepage of water, connections from the surface to the mine (Wolkersdorfer 2002).

Wolkersdorfer (2008) reported that in some countries, such as Germany, there are regulations that govern the use of tracers because water has to be managed for the security of the general public and in accordance with the welfare of individuals. Although tracer tests may have been conducted locally by academic institutions, mining houses, etc. the information is not freely available for review or is rarely published. Internationally, more and more publications on tracer tests are developing. In a tracer test review by Davis *et al*. (1994) it was noted that although there are two types of tracers, natural and artificial, it is importance to collect sufficient data in order to assess the compatibility of a tracer with the environment and tracers needs verification.

Fluorescent dyes are often used as an applied tracer, with the use of fluorescent dye to trace groundwater dating back to at least 1877 when sodium fluorescein (uranine) was used to evaluate the connection between the Danube River and the Aach spring (Käß, 1998). Fluorescent dyes are commonly chosen applied tracers for groundwater studies in areas with low clay content. Recent studies have found dye tracers to work well both in karst and fractured crystalline rock settings (Himmelsbach, *et al*, 1995). However, the use of such dyes is problematic in AMD, because below a pH of 6, the sorptivity of uranine increases and its fluorescence intensity diminishes. Smart and Laidlaw, 1977 demonstrated that the fluorescence of uranine may be reduced by as much as 50% below a pH of 5. An additional difficulty in dye tracer application in groundwater and mine systems is accurately quantifying the mixing reservoir. The reservoir represents all waters (mine pools and inflows of surface and groundwater) with which the tracer could mix between the injection point and the sampling point and which will influence the mass of tracer applied in order to produce appropriate dye concentrations in collected samples. If the mixing reservoir is overestimated, the resulting dye concentrations may become toxic or exceed the dynamic range of the instruments, whereas an underestimated reservoir will result in low dye concentrations, possibly below analytical detection. Therefore, a multiple tracer approach is often recommended for complex hydrologic settings with a limited access point and unknown flow-through times, especially when fieldwork time and logistical support are limited (Wolkersdorfer, 2008).

Isotope techniques

The variability of isotope ratios has proved valuable when studying a wide variety of geological and environmental problems. The study of Pb isotopes, in particular, has been applied to problems such as determining the source and extent of anthropogenic Pb contamination in a variety of environments (Chow and Johnstone 1965, Patterson *et al*. 1976, Monna *et al.* 2006, Coetzee and Rademeyer 2006). Stable isotope ratios in water ($\delta^{18}O$ and $\delta^{2}H$) are used to understand the origins of water in various environments (Clark and Fritz 1997). Isotopes of water are generally non-reactive in aquifers over relatively short time scales. At the surface, isotopic signatures of water can be altered by evaporation and, in the subsurface, isotopic signatures of water may be altered over long time scales by geothermal exchange and water-rock interactions (Clark and Fritz 1997). Studies have demonstrated the use of isotopes in order to understand water sources in mining environments (Cowie *et al* 2014) and in fractured-rock aquifers.

Multivariate statistical analysis

The effectiveness of the application of multivariate statistics to any problem in the geosciences field is a function of data availability. Many areas in South Africa suffer problems in respect of data scarcity, and a lack of effective monitoring of water resources remains a problem. However, the coal fields have received considerable attention over the past years and substantial amounts of data have been generated in the process of mine operations and closures. Multivariate analysis techniques are very useful in the analysis of data corresponding to a large number of variables. Analysis using these techniques produces easily interpretable results. Multivariate data consist of observations on several variables for a number of samples (sample vectors or individuals). Data of this type arise in all branches of science, ranging from physiology to biology, and methods of analysing multivariate data constitute an increasingly important area of statistics.

Various multivariate analysis techniques are available. The choice of the most appropriate technique depends on the nature of the data, the problem and objectives. The underlying theme of many multivariate analysis techniques is simplification. One fundamental distinction between the techniques is that some analyses are primarily concerned with relationships between variables, while others are primarily concerned with relationships between samples. Techniques of the former type are called variable directed, while the latter are called individual directed (sample directed) multivariate analyses. In the analysis of dependence between variables, if the variables do not arise on an equal footing, multivariate regression analysis is recommended. The multivariate statistical techniques such as cluster analysis (CA), factor analysis (FA), principal component analysis (PCA) and discriminant analysis (DA) have widely been used as unbiased methods in the analysis of water quality data for extracting meaningful information (Helena *et al* 2000). The multivariate treatment of data is widely used to characterizse and evaluates surface and freshwater quality and it is useful for evidencing temporal and spatial variations caused by natural and anthropogenic factors linked to seasonality (Helena *et al* 2000). Cluster analysis is useful in grouping objects (cases) into classes (clusters) on the basis of similarities within a class and dissimilarities between different classes. The class characteristics are not known in advance but may be determined from the analysis. The results of CA may be used to interpret the data and indicate patterns (Vega *et al* 1998). FA, which includes PCA is a very powerful technique applied to reduce the dimensionality of a data set consisting of a large number of interrelated variables, while retaining as far as possible the variability present in data set. This reduction is achieved by transforming the data set into a new set of variables, the principal components (PCs), which are orthogonal (non-correlated) and arranged in decreasing order of importance. Mathematically, the PCs are computed from covariance or other cross-product matrices, describing the dispersion of the multiple measured parameters to obtain eigenvalues and eigenvectors. Principal components are the linear combinations of the original variables and the eigenvectors (Wunderlin *et al*., 2001). In contrast to the exploratory features of CA, DA provides the statistical classification of samples and is performed with prior knowledge of membership of objects to particular group or cluster (such as the temporal or spatial grouping of a sample which is known from its sampling time or site). In addition, DA is useful in grouping the samples sharing common properties. Although not as common as CA and FA/PCA, DA has recently been applied successfully to water quality sets (Wunderlin *et al*., 2001) and other data sets.Hierarchical cluster analysis (HCA) is commonly applied to classify observations so members of the resulting groups are similar to one another but distinct from other groups (Lambrakis *et al*., 2004 and Thyne *et al*., 2004). This method possesses a small space distorting effect, uses more information on cluster contents than other methods, and has been proven to be an extremely powerful grouping mechanism (Lambrakis *et al*., 2004).

Case study

A study area has been identified in eMalahleni, about 100 km east of Pretoria in the Mpumalanga Province. The site comprises a number of coal mines that were abandoned in the early–late 1950s, including the Transvaal and Delagoa Bay Colliery, the Middleburg Steam Coal and Coke Colliery and the Douglas No. 1 and 2 Collieries. The site is found in the Upper Olifants subarea of the Olifants Water Management Area (B11 catchment) in Quaternary catchment B11K. Two major streams flow through the catchment, the Brugspruit (from south to north of the catchment passing through the Transvaal and Delagoa Bay Colliery) and the Klipspruit (which drains into the Brugspruit towards the north of the catchment. Towards the east of the catchment, the Blesbokspruit stream drains into the Klipspruit. The land has not been utilised for some time, owing to ground instability, although recently opencast coal mines have been developed on some of the previously mined sites, to extract coal left behind in the earlier mining phase. The area is covered with a grassland type biome (and alien species such as *Acacia mearnsi* and *Eucalyptus globulus*) and covered with sandy-clayey and clay soils.

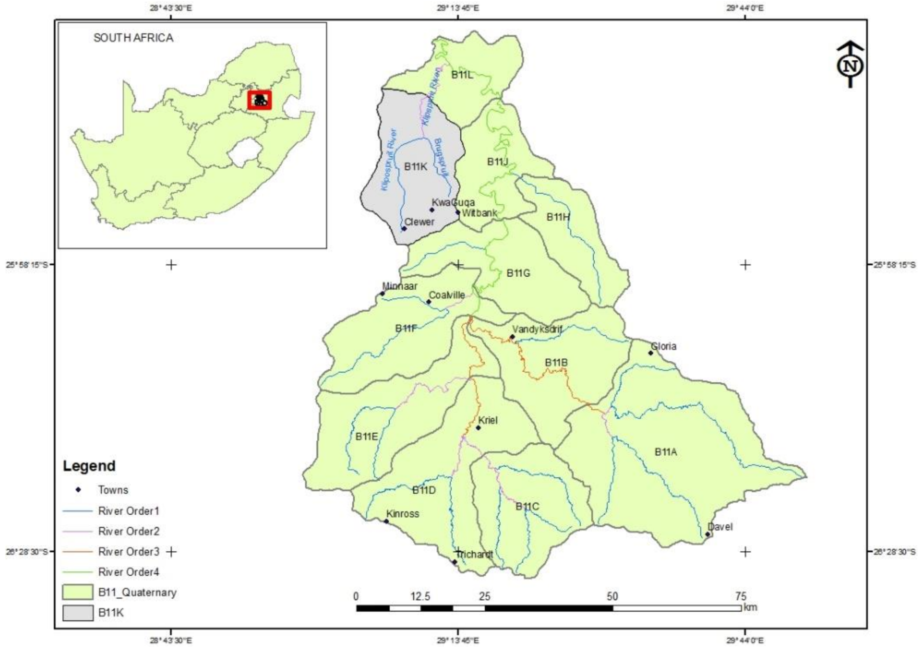

Figure 1: *Location map for B11K quarternary catchment*

The overall aims of this study are to:

- Develop an effective methodology/technique for conducting tracer tests in South African coal mine waters.
- Identify a tracer (environmental/artificial) that will be ideal to be used in mine waters characterised by high metal content and high acidity without local environmental interference.

- Determine the velocity of groundwater flow to determine possible contaminant transport and flow characteristics of the study area
- Investigate if there is any connectivity between the underground workings of site identified using tracers

Surface and groundwater sampling points were selected for the purpose of understanding the background of the study area of which preliminary water assessment and study area delineation was conducted. Physico-chemical data and water sampling is conducted quarterly and samples are analysed by ICP-MS and IC. Table 1 provides averages of physico-chemical and some major chemical data collected from different sampling points in and around a flooded and abandoned coal mine. This was done to classify the different water type as a pre-assessment for using tracer techniques. Our preliminary results demonstrated that the water samples collected have high concentrations of minerals such SO_4, Cl, Na, Mg, Al, K, and Ca.

Table 1 *Analytical results for the samples used in this study*

Sample ID	pH	EC	TDS	HCO_3	Ca	K	Mg	Na	Cl	SO_4
		uS/cm	mg/L							
SINKHOLE	7.0	3490.0	2243.5	67.7	182.8	72.9	110.4	10243.7	58.3	14494.8
BOREHOLE	5.0	4330.0	2783.5	0.000	161.3	118.4	66.2	8039.7	115.5	8637.3
7 SEEPAGE	7.5	659.0	423.6	106.2	39.9	5.9	26.7	27.5	12.0	110.6
T-DB	5.0	12423.0	7985.9	0.0	390.1	38.5	179.6	2248.5	60.1	4646.5
9 SEEPAGE	4.5	9969.0	6408.4	0.0	345.4	34.4	183.7	2881.2	146.3	-
DAM	4.0	1852.0	1190.5	0.0	106.4	3.6	70.1	9.6	1.80	247.7
14 WEIR	3.5	2404.0	1545.4	0.0	144.1	7.1	96.7	78.4	29.3	970.8
13 WEIR	3.5	2404.0	1545.3	0.00	116.4	6.	74.6	55.4	19.7	904.2

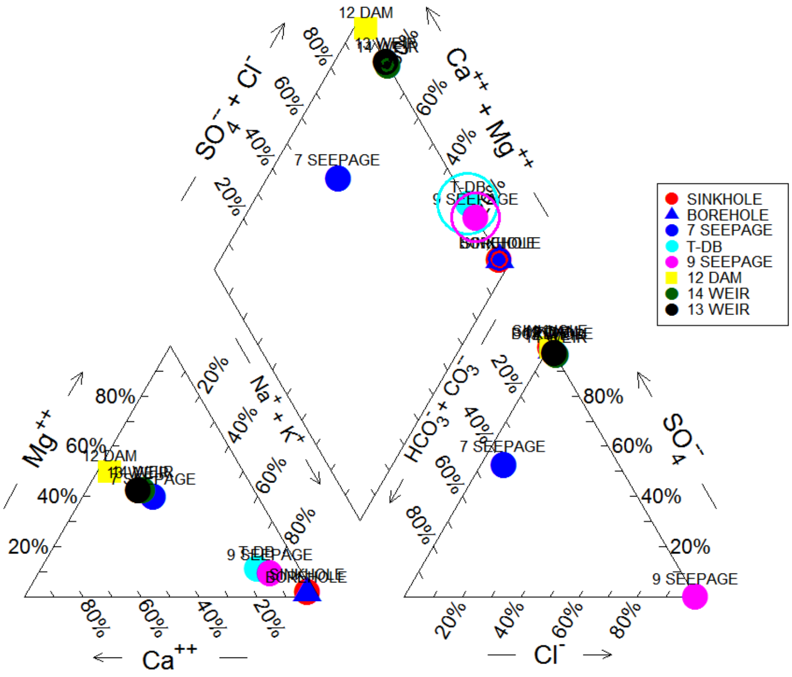

Figure 2: *Piper diagram for samples collected in the T&DB Area.*

Preliminary water assessment and classification have demonstrated that the samples collected towards the south (13 Weir, 14 Weir and 12 Dam) of the study area, have a dominant Mg-Ca-SO_4 water type, while those collected towards the north (Sinkhole, 2Borehole and T-DB) having a Na-SO_4 water type and samples collected towards the centre displaying mixing (*fig 2*).The distribution of the water chemistry on the stiffs (*fig 3*) for the Mg-Ca-SO_4 shows a similar trend but with an introduction of magnesium and calcium at the T&DB shaft.. The water collected from the dam and weirs have a similar distribution of water chemistry with elevated magnesium and calcium concentrations.

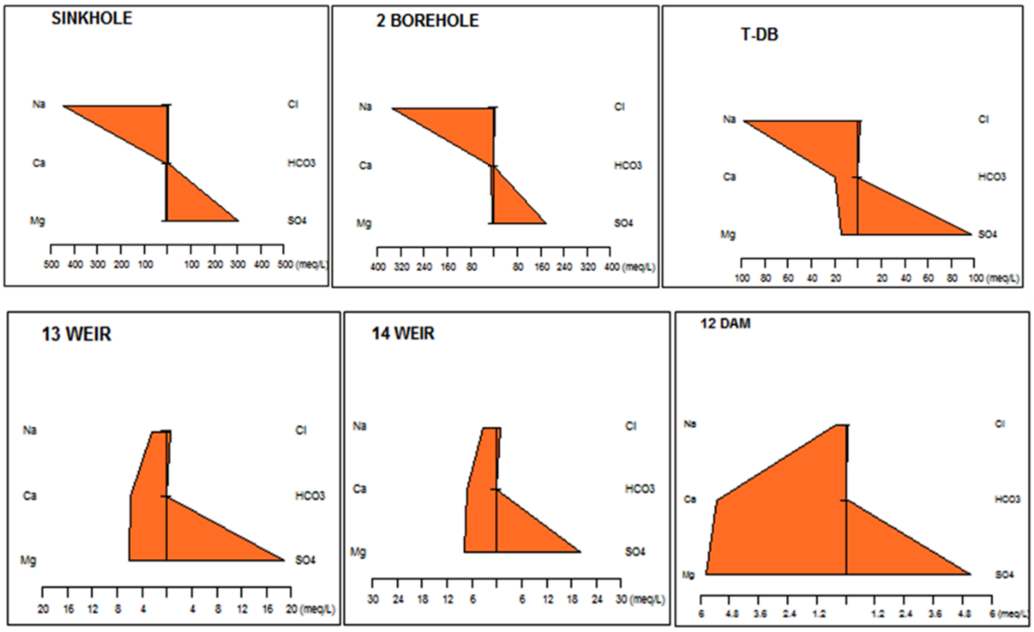

Figure 3: *Stiff diagram for samples collected from the sinkhole, borehole and T&DB which are classified as having Na-SO_4 type of water.*

The second phase will seek to scientifically quantify the environmental risks associated with existing and historical mining activities and therefore look at applying the following elements and techniques:

- Source identification using geochemical and solute mass transport modeling,
- Stable isotope analysis of $\delta^{18}O$ and $\delta^{2}H$ and multivariate statistical analysis
- The use of natural and applied tracers to guide targeted remediation efforts in acid mine drainage systems.

Conclusion

The case study is a baseline for understanding the different types of waters discharging at an abandoned coal site. Using tracer techniques we can characterize the sub-surface and surface water in terms of geochemistry, estimate its flow and storage properties, which are vital aspects in mine water management, treatment and remediation. Using tracers in a complex mining environment requires an integrated approach. This can have the added benefit of identifying targeted remediation strategies that address the feasibility of actually reducing or eliminating the generation of AMD at its source. It is critical for a mine water tracer study that the conceptual models and the associated water balance calculations are correct. These factors will be verified during phase 2 of the present project, which will deal with more data collection. The ultimate goal will be to develop a tool that can be used for mine water management at a local scale.

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Modeling Cyanide Degradation in Heap Leach Systems: From Laboratory to Reality

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Abstract

Heap leaching is a common technique used to extract gold and other metals from generally low grade ore. Gold is typically mobilized by leaching with cyanide; the success of this technique is driven by its reasonable cost. However cyanide toxicity requires that management strategies be put in place during operation and after closure to prevent any impact to the environment and potential receptors.

This case study presents a gold cyanide leach operation where the aim was to quantify and predict the life expectancy of cyanide species after closure in order to assess closure options and design appropriate mitigation strategies. This duration was predicted by modeling the flux of cyanide through the heap leach, determining the speciation of cyanide between the different reservoirs of the system and assessing the effects of natural degradation mechanisms.

The predictions were run for 20 years and the results indicate that the majority of the cyanide mass at any given time is within the core mass of the heap, while the lowest concentration occurs on the upper heap leach pad. From an initial Total cyanide concentration in excess of 900 mg CN/L at closure, the simulations predict cyanide concentration to remain above local comparable regulatory values for up to 10 years.

Based on the approach here, closure of this heap will require significant inventory reduction through evaporation or water usage or active treatment prior to environmental release.

Key words: case study, cyanide degradation, heap leach, modeling

Introduction

Heap leach mining is a technique used to extract gold and other metals from generally low grade ore where the target material is placed on an impermeable liner and sprinkled with a leaching solution. Gold is generally mobilized using cyanide; the success of this technique is driven by its reasonable cost. However cyanide toxicity requires that management strategies be put in place during operation and after closure of the mining operation (Botz and Mudder 2000) to prevent any impact to the environment and potential receptors.

The ore, deposited on the heap leach pad ore is leached using cyanide solution. Where leachable copper is present in the ore then the rate of cyanide usage is comparatively high, and the resultant cyanide concentrations in the barren and pregnant leach solutions are high; typically in excess of 300 mg/L cyanide.

At closure the active irrigation of the heap leach pad will cease, however, draindown of cyanide bearing fluids will continue for an extended period. Completion of the closure phase of the mine may be dependent upon the cyanide concentrations decreasing to within acceptable limits. Cyanide removal from the system occurs through three main processes, the volatilization of the cyanide into the atmosphere, degradation into breakdown products through biodegradation and cyanide photodissociation by ultraviolet light (Mudder et al., 2000; Parshley et al 2012).

This case study aims to quantify and predict the life expectancy of cyanide species after closure in order to assess closure options and design appropriate mitigation strategies. This duration was predicted by modeling the flux of cyanide through the heap leach pad, determining the speciation of cyanide between the different reservoirs of the system and assessing the effects of natural degradation mechanisms.

Method

Case study

This paper considers a heap leach gold mine using cyanide to mobilize gold. In order to anticipate closure and the different closure strategies SRK modeled the heap leach system once operations have stopped. After mine closure the solution circuit will be shut down and the solution will no longer be processed. Due to a large copper load in the system the cyanide concentrations are anticipated to be high (in excess of 900 mg/L) and the seepage volume from the heap will exceed the volume of the Storage Pond. The solutions will therefore be managed by continuing to irrigate the heap with solution from the Storage Pond.

Conceptual model

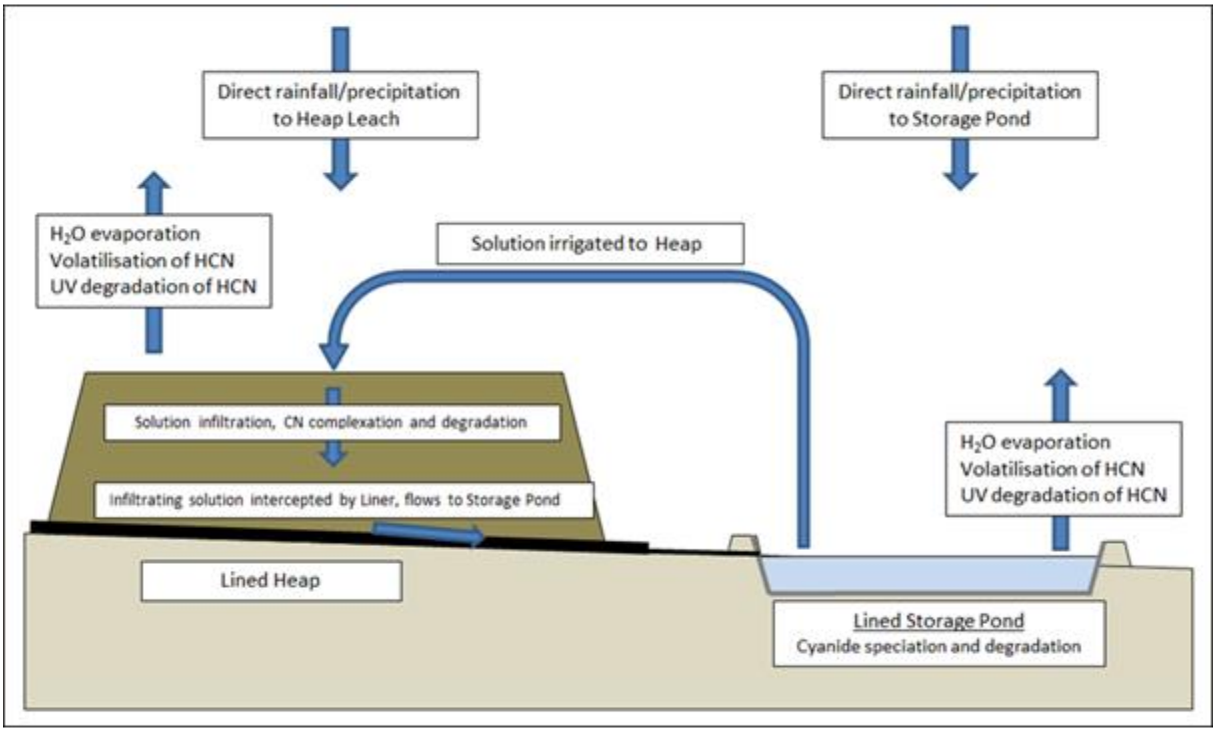

Figure 1 *: Conceptual model of the system*

The conceptualization of the post-closure fluid handling is shown schematically in Figure 1. Solution draining from the heap will flow to the Storage Pond, which will be spray-irrigated back to the Heap Leach. The only additional water inflows to the system are from direct rainfall/snow, it will percolate through the heap to the liner, where it will drain to the Storage Pond. Whilst the cyanide concentrations are elevated there will be no discharge of the waters. Therefore, the only solution losses from the circuit will be evaporation from the Storage Pond and from the heap. Evaporation is determined to significantly exceed rainfall/snow, such that the circuit will lose water over time. As the solution inventory decreases the rate of drainage will decrease, as will the degree of saturation of the Heap Leach.

Cyanide bearing solution will drain from the heap to the Storage Pond. Cyanide concentrations in the Storage Pond will decrease primarily as a result of the breakdown of cyanide by ultraviolet light and the volatilization of HCN gas into the atmosphere. The rates of cyanide degradation will be dependent upon cyanide speciation e.g. iron cyanide and copper cyanide complexes must first degrade to free cyanide species (CN^-) before the cyanide can be lost by breakdown or volatilization. Spray irrigation of the Storage Pond solution to the surface of the heap will permit further losses of cyanide by volatilization to the atmosphere and degradation by UV breakdown. Solution at the near surface of the heap will be subject to further volatilization, but not to UV breakdown.

As solution migrates through the heap mass there will be further attenuation/breakdown of cyanide by bacteria and/or oxidation processes, however, these processes are much slower than losses to the atmosphere and via UV breakdown and were therefore neglected in this study.

Numerical model

The numerical model for the draindown/water balance calculations of solution from the heap leach pad is based upon the HLDE model Version 1.2 (JBR Environmental Inc. and Newmont Mining Corporation 2011). However, a bespoke model was developed in order to incorporate the calculation of cyanide degradation/losses at different stages in the model.

As illustrated in Figure 1 the model has two main reservoirs – the heap leach pad and the storage ponds, from which water is transferred by pumping and irrigation, moved by seepage and lost by evaporation, each resulting in a change in storage for the different reservoirs on a daily timesteps. In order to allow for different cyanide attenuation mechanisms the water balance split the Heap Leach Pad into two 'reservoirs', an Upper Heap Leach Zone, and a Lower Heap Leach Zone, with the seepage from the Lower Heap Leach then draining to the Storage pond.

The Upper Heap Leach Zone is a thin zone (0.5 m) at the surface of the heap where evaporation and cyanide volatilization losses can occur. Solution in the Upper Heap layer is allowed to infiltrate through to the Lower Heap layer at a rate equal to the irrigation rate.

The Lower Heap comprises the bulk of the heap and contains the majority of solution and cyanide mass. Degradation of cyanide in the Lower Heap is limited to conversion/equilibration of cyanide species and a slower rate of degradation; there are no losses of HCN by volatilization, and no degradation of HCN by UV light.

Solution draining from the Heap Leach enters the Storage Pond. Within the Storage Pond the cyanide is subject to volatilization as HCN and degradation by UV light, including the photolysis of complexed metal-cyanide species to HCN and CN^-.

The HLDE model is based on the Corey and Brooks (1964) equation to represent how the hydraulic conductivity varies with saturation. Because water flows more easily through saturated media, as the degree of saturation decreases the hydraulic conductivity will decrease proportionally. This model also applies the Brooks and Corey (1964) equation to correct the drainage rate as the moisture content decreases.

$$K(\theta) = K_S \left(\frac{\theta - \theta_r}{\theta_{sat} - \theta_r} \right)^{\gamma}$$

Where: Θ is the volumetric moisture content

K_s is the saturated hydraulic conductivity

Θ_r is the residual moisture content

Θ_{sat} is the porosity or saturated moisture content

γ is an empirical parameter related to grain size distribution

Gamma is an empirical factor, and data are not available for it. The gamma value is dependent upon the pore size distribution, with crushed ore the value is typically less than10. Gamma values greater than one indicate that the K_{sat} decreases rapidly relative to moisture content, whilst gamma values less than one mean that K_{sat} decreases rapidly reducing moisture content. The hydraulic conductivity of the heap is assumed to remain moderately high with reducing moisture content, and as such a gamma value of 0.5 has been applied to the model.

Cyanide speciation and breakdown rates

Cyanide speciation in water is complex, with cyanide partitioning between various soluble and gaseous phases depending upon the solution pH, temperature and other solute chemistry. Each cyanide species behaves differently with respect to dissociation and breakdown. Cyanide interactions in natural systems are complex, and cyanide species can undergo volatilization, chemical oxidation, biological oxidation, hydrolysis, precipitation, complexation and sorption.

Studies report that the volatilization of hydrogen cyanide accounts for 90% of the cyanide removed from tailings impoundments (Botz and Mudder, 2000), with the other 10% losses occurring through other mechanisms. The main natural attenuation mechanisms of cyanide destruction occur through degradation under Ultraviolet (UV) light, and through biodegradation, with those processes occurring once the cyanide occurs as free cyanide (HCN and/or CN^-).

Therefore, the key mechanisms for cyanide loss and destruction, as depicted schematically in Figure 2, are dependent upon the conversion of complexed cyanide species to the free cyanide forms. This free cyanide will be subsequently volatilized and/or destroyed. It is understood that the loss of HCN by volatilization occurs according to a first-order rate equation which is directly proportional to the hydrogen cyanide concentration (Botz and Mudder 2000, Simonvic, 1984).

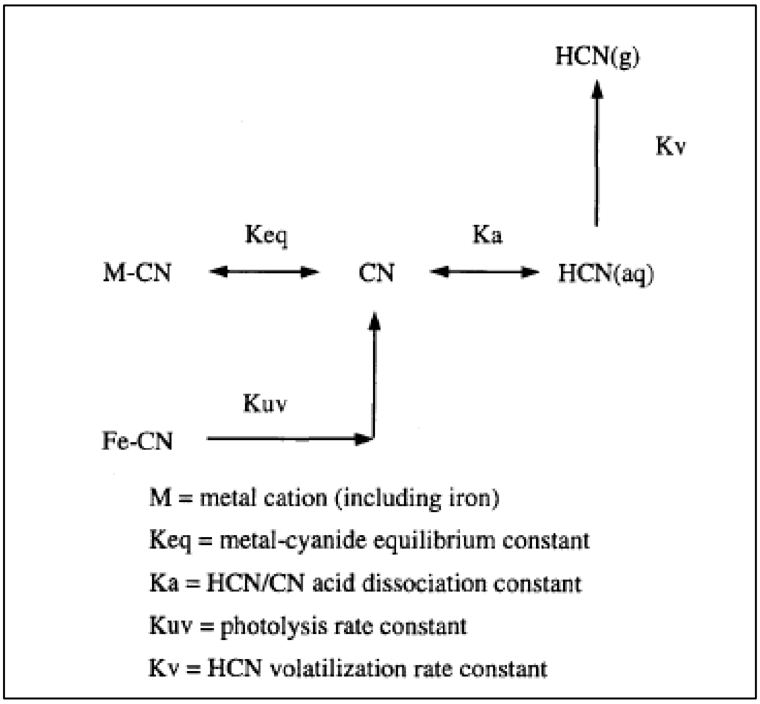

Figure 2: *Routes to Hydrogen Cyanide volatilization (from Botz and Mudder, 2000)*

The relationships shown in Figure 2 can be summarized as follows:

- HCN is lost by volatilization,
- CN^- is at equilibrium with HCN based on the equilibrium constant,
- Photolysis converts Fe-CN to Fe(dissolved) and CN^-,
- Me-CN complexes convert to metal ions (dissolved) and CN^- based on equilibrium constants.

The slowest steps in the process are the dissociation of Fe-CN and Me-CN to release cyanide. These processes are therefore the rate determining steps for the release and loss/destruction of cyanide.

Measurement of specific individual elemental-cyanide complexes is rarely undertaken. However, the cyanide speciation was calculated using the site aqueous metal concentration and the cyanide concentration. This speciation was used to define the initial cyanide distribution between the different cyanide species/complexes. The solute chemistry model includes speciation for different cyanide species, primarily to assess the partitioning of cyanide into HCN which can then be lost by volatilization. The majority of the cyanide in solution is retained as copper complexes, which then are assumed to rebalance the distribution as HCN is lost. This approach avoids the assumption that all cyanide can be lost as HCN.

It was assumed that the cyanide speciation can be calculated using the same proportional distribution of cyanide species as per the initial cyanide source term, with most of the cyanide occurring as copper complexes, with some partitioning into HCN which can then be lost to degradation/volatilization. These proportional distributions may not hold true at low cyanide concentrations where more exact speciation calculations may be warranted. However, given the elevated cyanide concentrations within the heap, this is considered an acceptable simplification for the initial models.

Cyanide speciation is also sensitive to pH, where a greater proportion of the cyanide exists as HCN at pH values below pH 9. This model does not couple the pH and cyanide complexation, instead relying on the assumption that the pH will remain around pH 9. This may be a fair assumption, as the seepage pH will be equilibrated with carbonate species, given the extensive liming of the leach pad that will have been conducted to maintain the operational process solutions around pH 11.

Results

Base Case Model results: Heap Leach draindown

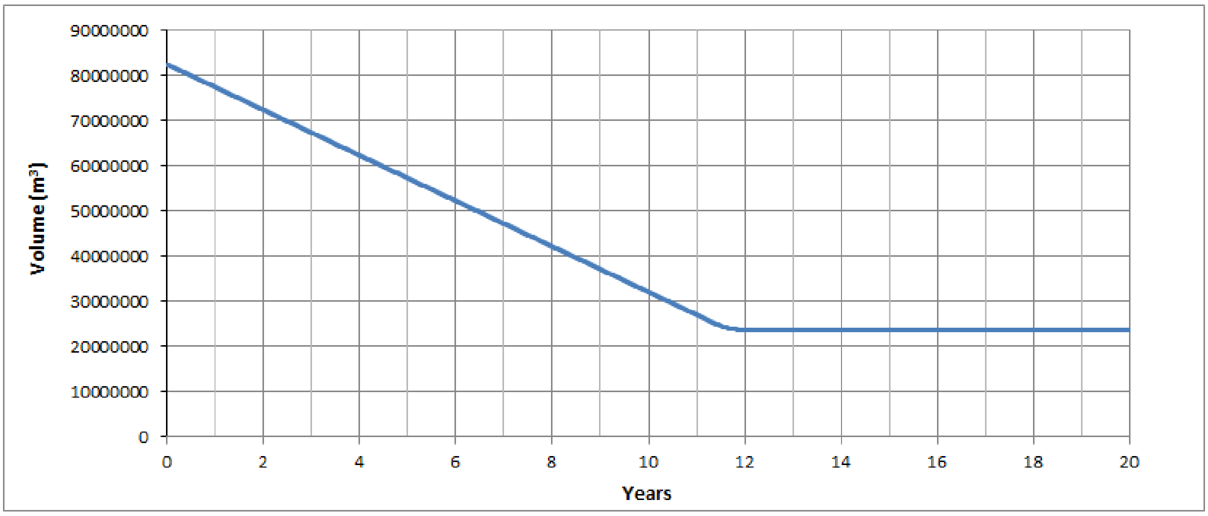

Figure **3** shows the modeled change in water volume within the heap as the draindown period progresses. The change in rate of the heap draindown and the moisture content are plotted in

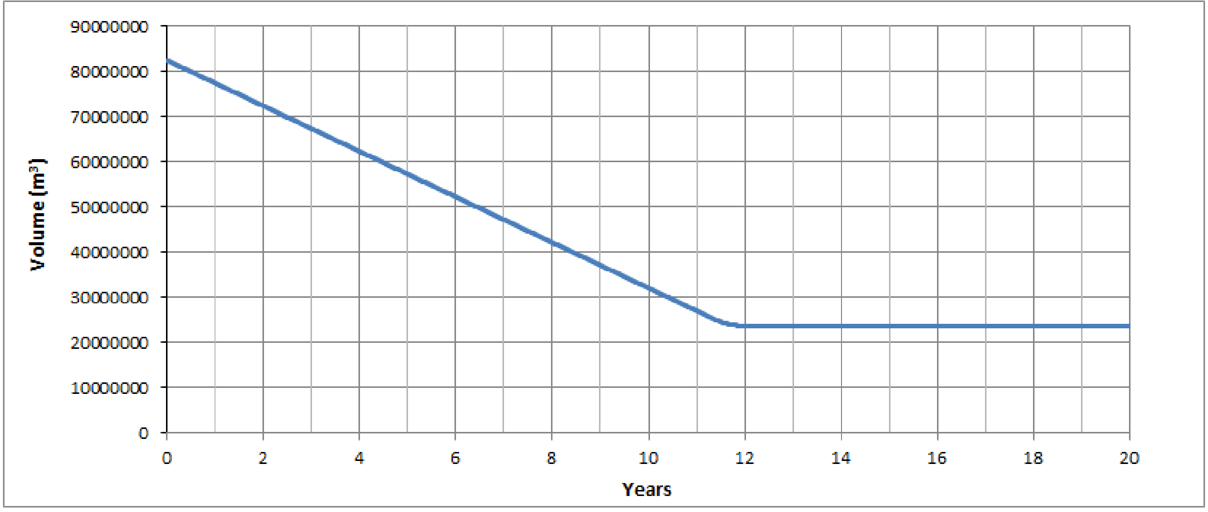

Figure **3**. As the degree of saturation the heap decreases, the rate of seepage also decreases, due to the reduction in the effective hydraulic conductivity. The moisture content within the heap steadily decreases to a point at which the moisture content reaches the specific retention value (assumed to be 10%) such that the net moisture entering the system as recharge is effectively equivalent to the rate of seepage discharging from the base of the heap.

Once the rate of pond evaporation exceeds the seepage rate it is assumed that pumping and irrigation of the water is stopped, and the pond then acts as a net sink of water: water enters from the heap and by rain/snow, and water is lost by evaporation. No pumping or discharge of water occurs. The model predicts that after around 11 years the seepage rate from the heap is less than the pond evaporation rate and that pumping ceases. At that stage the moisture content in the heap remains constant and there is a net loss of water from the storage ponds.

The decreasing volume/moisture content of the heap is linear through time as the simplified water balance assumes that the pumping rate from the heap decreases steadily through time, maximizing the volume stored in the pond and irrigated, thereby optimizing the rate of evaporation and cyanide destruction. Therefore, the average rate of water pumped from the pond and irrigated to the heap is equal to the rate of water draining from the heap to the pond, after accounting for direct rainfall and evaporation.

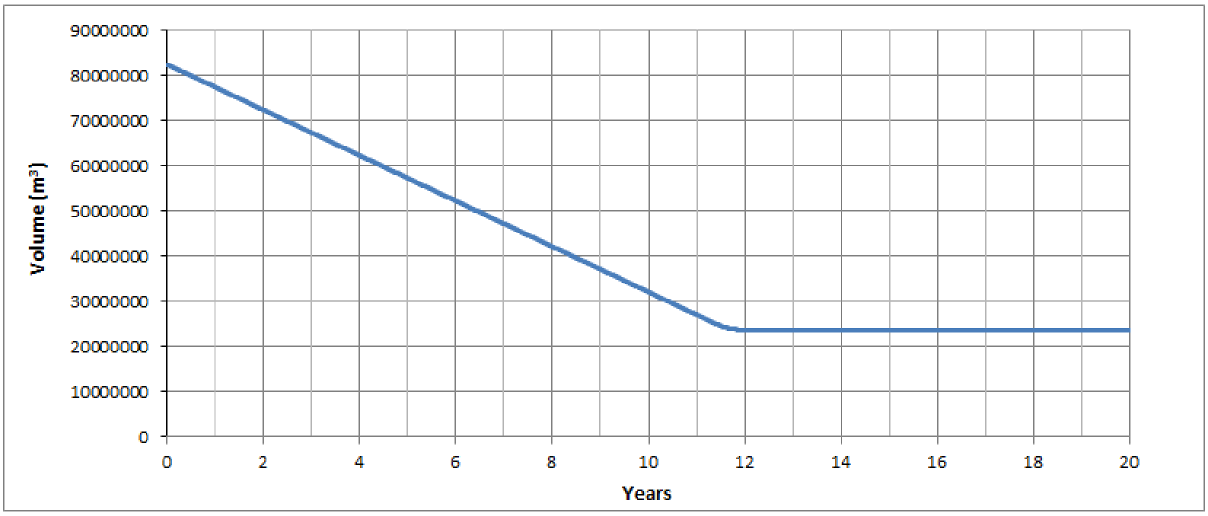

Figure 3: *Reduction in water stored within the Heap Leach Pad for Base Case model*

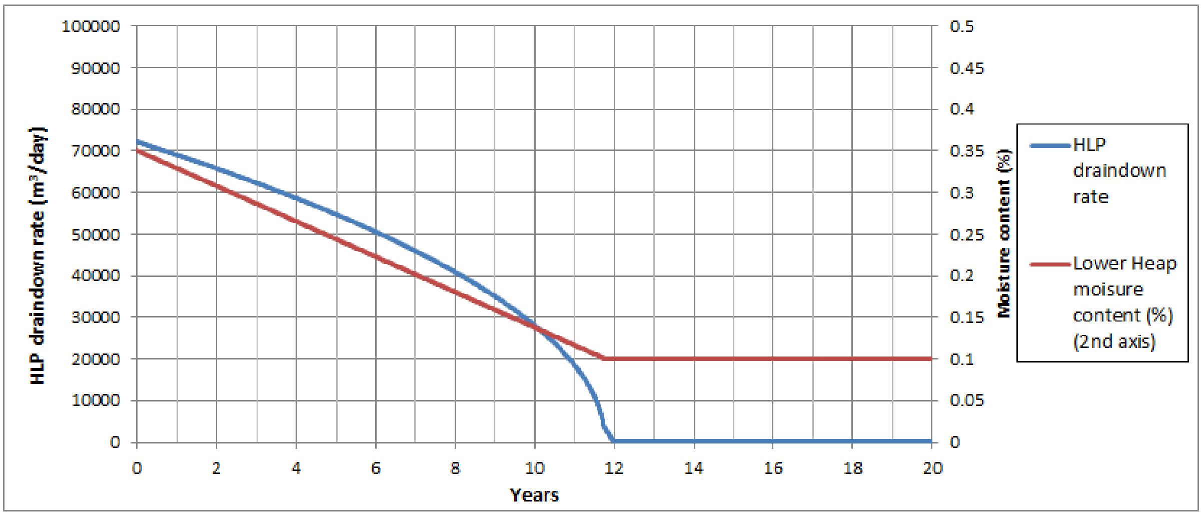

Figure 4 : *Draindown rate and change in heap moisture content*

Cyanide concentrations

The model results are presented as Total Cyanide concentrations to account for all cyanide species present. The modeled cyanide concentrations are presented in

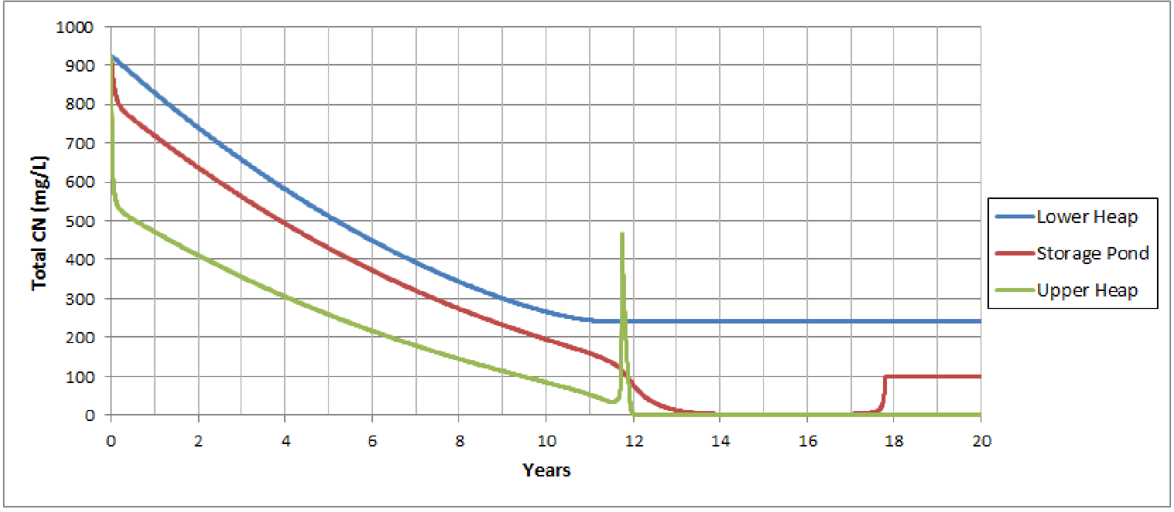

Figure **5**. The model conditions reflect the input conditions and degradation conditions.

The lowest Total Cyanide concentrations occur in the Upper Heap zone; this is because the waters have already experienced cyanide losses in the pond, and are then subjected to further losses due to the enhanced degradation rates applied to the spray irrigated water (with inherent aeration increasing cyanide losses).

The Storage Pond waters also show a more rapid reduction in the Total Cyanide concentration as volatilization losses remove HCN. The removal rates are moderately high, but there is a continual feed of higher cyanide waters entering the pond from the heap seepage.

The highest Total Cyanide concentrations occur in the Lower Heap zone. This comprises the vast majority of the cyanide reservoir at the end of operations. Cyanide is being removed in the seepage waters, and the cyanide added by irrigation is continuously decreasing. However, the overall quantity of water and cyanide retained within the main heap is such that it takes a significant length of time for cyanide levels to decrease, especially as no cyanide degradation is assumed to be active within the Lower Heap zone.

There is a change in behavior at around the 11-12 year stage, at the point when the draindown is less than the evaporation from the storage ponds. The pumping/irrigation to the top of the heap ceases, with the following effects:

- The cyanide concentration in the heap decreases at a much lower rate, as discharge from the heap is at a much lower rate than during the draindown phase and therefore the removal rate of cyanide decreases;
- Cyanide concentrations in the Storage Pond decrease more rapidly, as the residence time in the heap increases and there rate of inflow from the heap decreases. However, the Storage Pond volumes become limited after around 17 years, such that the cyanide concentrations within the reduced pond volume become more elevated (as the pond loses water more quickly than cyanide); and
- Cyanide concentrations in the Upper Heap rise sharply as the moisture content within the thin Upper Layer rapidly reduces once irrigation ceases. The cyanide concentration then reduces rapidly due to volatilization and that no further cyanide is added to the surface.

From an initial Total Cyanide concentration in excess of 900 mg cyanide/L, the modeled seepage concentration from the heap is predicted to be in excess of 800 mg/L after 1 year, over 700 mg/L after 2 years and still be in excess of 200 mg/L after 10 years. When run out for 20 years, the model predicts that seepage from the heap will contain over 200 mg/L Total Cyanide, as it assumes very low further losses over time and no cyanide degradation.

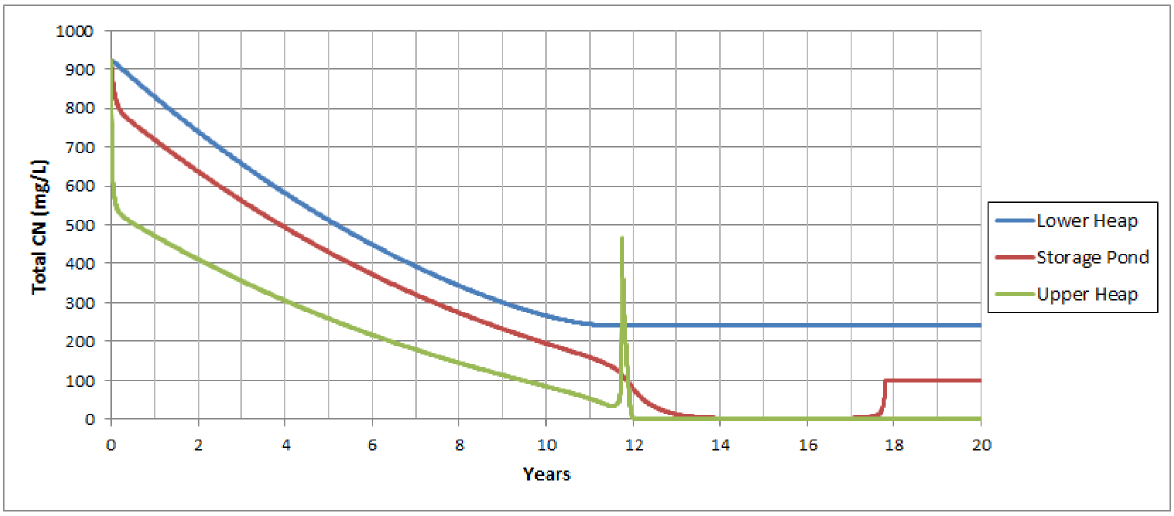

Figure 5 *: Base Case cyanide concentrations in the Heap Leach Pad and Storage Pond*

Conclusion

This study shows a certain cyanide distribution within the heap system due to both the degradation and the management strategy modeled here. Cyanide is shown to be present in lower concentrations in the upper part of the heap due to the volatilization and UV degradation while the main reservoir is the lower heap where the conditions prevent volatilization and UV degradation and consequently higher cyanide concentrations are observed.

From an initial Total cyanide concentration in excess of 900 mg CN/L at closure, the simulations predict cyanide concentration to remain above local discharge values for up to 10 years.

Based on the approach here, closure of this heap will require significant inventory reduction through evaporation or water usage or active treatment prior to environmental release.

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The effects of a plug of alkaline water in an acid stressed watershed

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Extended Abstract

Alkaline addition is a common strategy to treat acid mine drainage, adding sufficient alkaline material to buffer acid and reduce metal solubility. Alkaline addition aims to treat acid stressed environments. Previous work has suggested that it takes multiple years for a stream system to recover from short-term acidification (Kruse *et al*. 2012). This study aims to quantify the chemical and biological impacts of a pulse of alkaline water in a previously acid stressed stream.

Hewett Fork is a subwatershed of the heavily coal mined Raccoon Creek watershed in Southeastern Ohio. Three major acid sources, the Rice-Hocking Mine at Carbondale, Carbondale Creek, and Trace Run (Fig. 1) are treated by a lime doser located at the discharge from the Rice-Hocking Mine at the site labelled Carbondale Doser in Fig. 1, 11 mi (17.7 km) from the mouth of Hewett Fork. During typical operation, enough alkalinity is added by the Carbondale Doser to buffer the acidity from all three acid sources, allowing biological recovery further downstream. Typically, the alkalinity added by the doser is consumed by Waterloo and additional alkalinity enters the watershed from alkaline tributaries (Kruse *et al*. 2013).

After several months of inconsistent operation of the lime doser in Carbondale, Ohio, during the Spring of 2014 due to bridging of fine lime in the doser, the doser was manually unloaded to allow for delivery of coarser material. Approximately ten tons of lime were emptied into the stream channel over an eight-hour period at the site labelled Carbondale Doser in Fig. 1. Water quality was monitored 1.2 mi (2 km) downstream of the doser at site Route 56 (conductivity, temperature, water depth), 2.6 mi (4.3 km) downstream of the doser at site Waterloo (pH, conductivity, total dissolved solids, temperature, ORP), and 6.3 mi (10.1 km) downstream of the doser at site King Tunnel (pH, conductivity, total dissolved solids, temperature, ORP). Locations are shown in Figure 1. Water quality logging began two weeks before the doser was unloaded and continued for six weeks after. Macroinvertebrates were sampled six weeks after the doser was unloaded and used to calculate the multimetric index, MAIS (Macroinvertebrate Aggregated Index for Streams, Johnson 2007, Smith and Voshell 1997), used in Ohio to assess acid mine drainage stress.

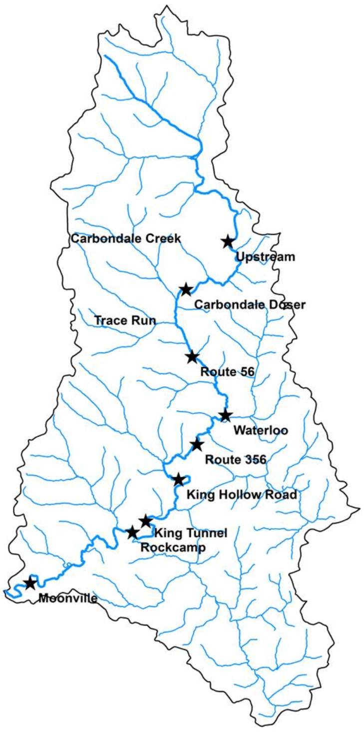

Figure 1 *Map of Hewett Fork Subwatershed located in Raccoon Creek Watershed in Southeastern Ohio. Long term sample locations are notated with black stars. The current study assesses the impact of an alkaline release from the Carbondale Doser site at Route 56, Waterloo, and King Tunnel sites.*

While in-stream chemistry in the day that followed the doser unloading did exceed ideal ranges for aquatic life both 1.2 mi (2 km) and 2.6 mi (4.3 km) downstream (pH > 11, conductivity > 3000 µS/cm), as shown in Fig. 2 and 3. The water quality impacts were much more moderate 6.3 mi (10.1 km) downstream, as shown in Fig. 4. The large alkaline pulse had a short extent, but had large water quality impacts in that zone; however, the section of stream that had the largest water quality changes was also the section of stream that had the poorest biological recovery (Fig. 5).

Before the alkaline pulse of water in this watershed, the biological community had improved from 6.3 mi (10.1 km) downstream of the doser to the mouth of the stream. The 2014 macroinvertebrate data shown in Fig. 5 suggests that the hyper-alkaline water did not significantly impact the biological community; there was no significant change from the previous year. One hypothesis of the mechanism for limited biological recovery is episodic pulses of poor water quality. This case suggests that this may be the case in a limited section of the stream and should be studied further.

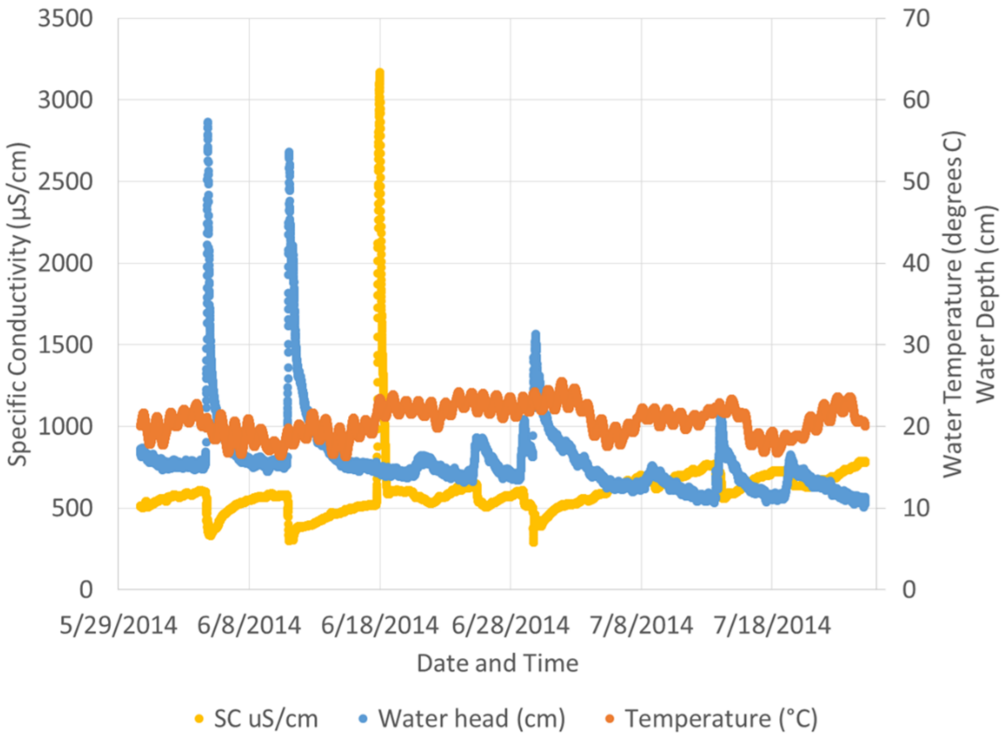

Figure 2 *Water quality at Route 56 shows the large increase in specific conductivity (SC) after the doser is unloaded on June 18, 2014. Other variations in SC at this site have a relationship with depth of water.*

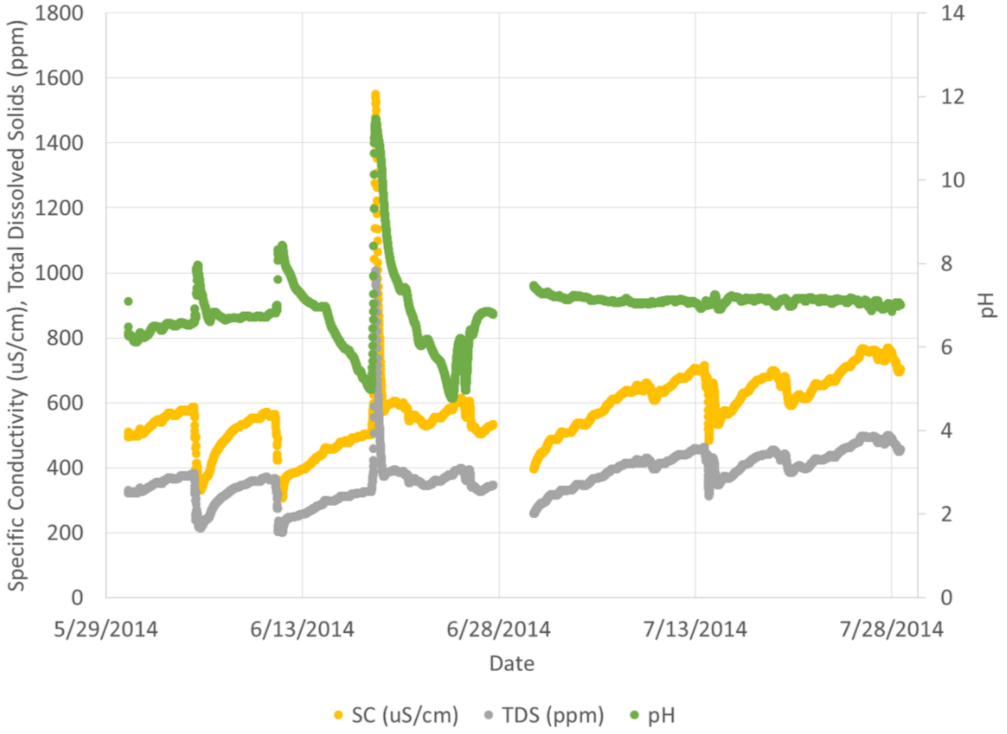

Figure 3 *Water quality at Waterloo shows a large increase in both specific conductivity (SC) and pH following unloading of the doser. The pH peaked at over 11 and SC peaked at over 1500 uS/cm.*

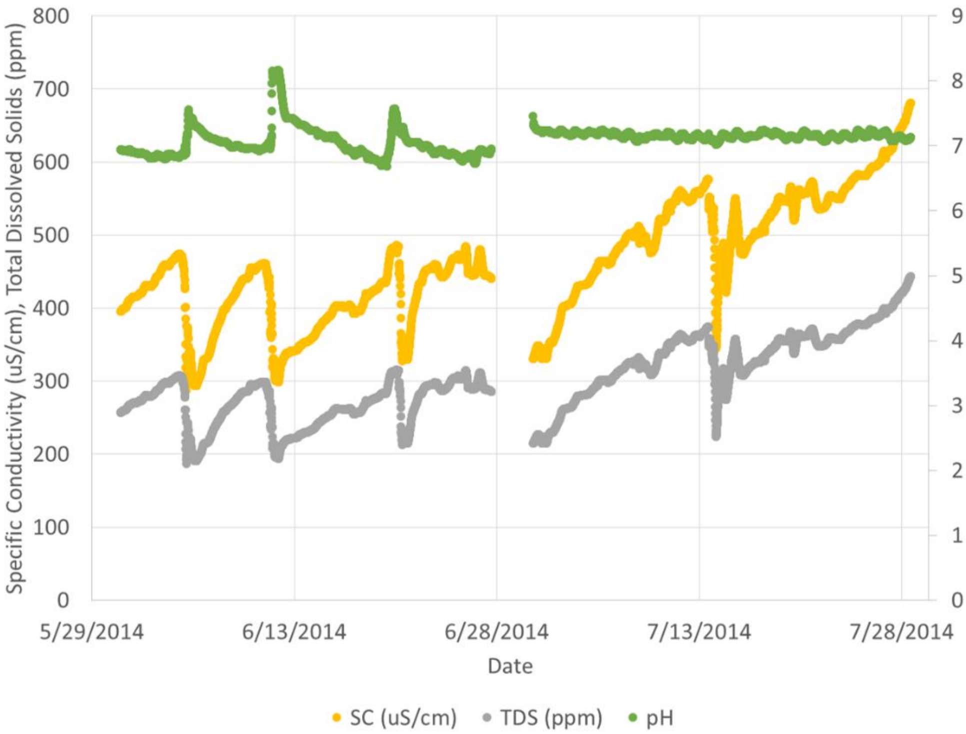

Figure 4 *Water quality at King Tunnel revealed that natural variation in pH was greater than the variation seen on June 18, 2014 due to the alkaline pulse. The pH peaked at less than 8.*

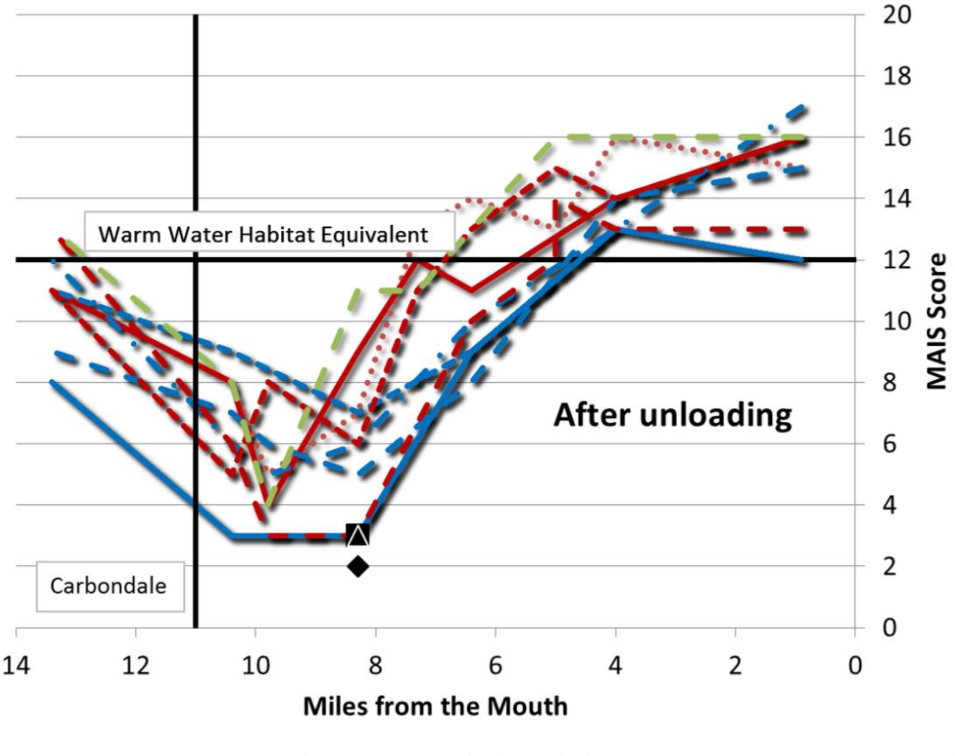

Figure 5 *MAIS scores in Hewett Fork since 2001. Black symbols represent pre-treatment scores, blue lines represent years 2004 – 2009, red lines represent years 2010 – 2013 showing the decrease in scores caused by 2 weeks of non-treatment at Carbondale as detailed in Kruse et al. 2012, the green line represents 2014 data. The lowest values are pre-treatment, scores from the 2007 drought year, and from 2010 after 2 weeks of non-treatment.*

While previous work (Kruse *et al.* 2012) suggests that short term acidification (~2 weeks) can impact the biological community for several years, a short term alkaline episode (~1 day) does not

significantly impact the biological community. This suggests that there may be a threshhold of duration of impact that macroinvertebrates can withstand or that alkaline tolerance may be greater than acid tolerance.

Key words: Mine water, hyper-alkaline, lime doser

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Assessment of the Influence of Coal Mining on Groundwater Quality: Case of Masisi Village in the Limpopo Province of South Africa

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Abstract

Coal mining in different coalfields in South Africa is known for decades (≈146 years) and its economic importance to the country has recently surpassed commodities such as gold. One of the Coalfield that is well known for coal production in the Limpopo province of South Africa is Pafuri Coalfield where Tshikondeni Colliery operated for 32 years before closure in 2014. In general, coal extraction has several environmental problems which include acid mine drainage that is now a serious problem currently confronting the government of South Africa. This therefore creates a need to proactively prevent or minimize potential groundwater impacts through long term monitoring of water quality meant for both domestic and commercial use. Assessment of borehole water quality at Masisi Village was vital due to its close proximity to Tshikondeni Coal mine.

Groundwater samples were collected from 22 active boreholes at Masisi Village and were analysed for a range of chemical constituents such as electrical conductivity, pH, total dissolved solids, turbidity, PO_4^{2-}, SO_4^{2-}, NO_3^{2-}, Mg, Zn, Cu, Cd, Cl^-, Cr, F^-,Fe, Mn, Ni, Se, Na, Mo, Ca, Pb, Sb, Ba, Al, Co, V, K, Al and As. Anions were analysed using the Ion Chromatography whilst, cations were determined using the Inductive Coupled Plasma Mass Spectroscopy technique. The physico-chemical parameters were compared with the Department of Water Affairs and Forestry (DWAF) and World Health Organization (WHO) standards for drinking water and public health. This was done in order to establish the quality of the groundwater resources in the study area.

Most parameters complied with the DWAF and WHO guideline values for drinking-water. However, TDS, EC, Cl^- , NO_3^{2-}, Mn, As, Cd, Cr, Pb, Mo, K, V, Sb, Ba and Mg exceeded WHO and DWAF permissible concentration with Pollution index >1 in all the boreholes. This gave an indication that groundwater resources at Masisi could be significantly contaminated. According to DWAF (1996) and Peplow and Admunds (2004). Long term exposure to polluted water can cause neurological disorders, cancer, renal damage and respiratory problems resulting in high mobirdity and mortality rates from water borne disease that lead to epidemics.

The study concluded that all boreholes at Masisi were contaminated and hence not suitable for human consumption. The outcome of this study may be used as baseline data for groundwater quality control for both domestic and commercial use by municipal authorities. A study of acid producing potentials of discard dumps at the mine was suggested in order to ascertain the source of the contaminants. Continuous monitoring of ground water quality within 10 km radius of Tshikondeni mine and making primary and secondary treatment mandatory before using it was also advised.

Key words: Coal mining, Groundwater quality, Pollution index, Permissible concentration

1. Introduction

Groundwater is an important commodity as an alternative source of water when surface water dries out. It can be used for various purposes such as agricultural, industrial, and domestic purposes. It is naturally replenished by surface water precipitation, streams and rivers when recharge reaches the water table (Todd, 1980). However, human activities such as mining impact on groundwater in terms of quality degradation and quantity depletion (Kuma, 2001; Dermietze and Christoph, 2001). Groundwater quality is intrinsically linked to the chemical properties of the aquifer's geology through which it flows (Aston, 2000). The oxidation of iron sulphides present within the discard dumps and stockpiles from coal mining may further influence the hydrochemistry, by generating acid mine drainage (MacDonald and Vermeulen, 2014). Acid mine drainage (AMD) and the release of toxic elements and transition metals, are possible due to mining operations (Ashton, *et al*., 2001; Ravengai *et al*., 2004). Acid and alkaline mine drainage alter pH and EC conditions hence the mobility of toxic elements and transition metals in the environment (Meck *et al*, 2006).

In South Africa, most rural communities in areas such Limpopo, Northern Cape and Northwest Provinces are currently experiencing water shortages. Though mining is not a major consumer of water in the Limpopo province, mining operations are widespread in the basin. One such mine is Tshikondeni Coal mine which operated for 32 years prior to its closure in 2014. The mine which was the main source of economic activity in the area prior its closure is located in the vicinity of villages such as Masisi, Tshikuya and Tshamavhudzi. It is also adjacent to the Kruger National Park. The geology of the area is typified by a succession of mudstone, sandstone, siltstone, and shale horizons of the Karoo sediment. The Karoo formations are overlain by a recent calcrete deposit with an interbedded alluvial boulder bed. The coal-bearing succession, consisting of the Madzaringwe and Mikambeni Formations of the Ecca Group, is approximately 250 m thick, with a basal zone, 25 to 34 m thick, consisting of shale and interbedded coal.

Salinisation in the water resources of the Limpopo are also attributed to mining activities (Chenje and Johnson, 1996; Warnick, 2003; Zilberman, 1999). In coal mines the pyrite in the coal is roughly three times as high as in the surrounding rock and this results in the generation of sulphate, heavy metals and acidity, and can have numerous environmental consequences (Usher *et al*, 2003). The assessment of water quality is of high importance because human health requires water that is both safe to drink and palatable (DWAF, 2006). Safe drinking water, as defined by the WHO (2003), is water which does not represent any significant risk to health over a lifetime of consumption. Drinking water must especially be low in metals, fluorides, nitrates and nitrites (WHO, 2004). In order to understand the impact of Coal mining on groundwater resource for communities in the vicinity of the mine, a study was proposed to assess the ground water quality at Masisi village in the vicinity of Tshikondeni Coal mine.

2. Site description, sampling, and methods

Masisi is the most populous village in the Mutale Municipality and is located about 8 km northwest of Tshikondeni mine in Limpopo province (Fig.1). The rapid expansion of this village has exacerbated demand for groundwater resource for domestic and agricultural needs. This water is accessed through numerous boreholes sunk by local authorities. The area has a semi-arid climate with 30-90 mm of precipitation annually between October and April. High precipitation is in February whilst July is the driest Month (S.A weather and climate, 2013). Mopani trees dominate in the area and it is also characterized by spaced thick grass cover such as Afromontane grassland. Its topography forms part of the Soutpansberg Mountain range, with a series of plateaus and low mountain lands.

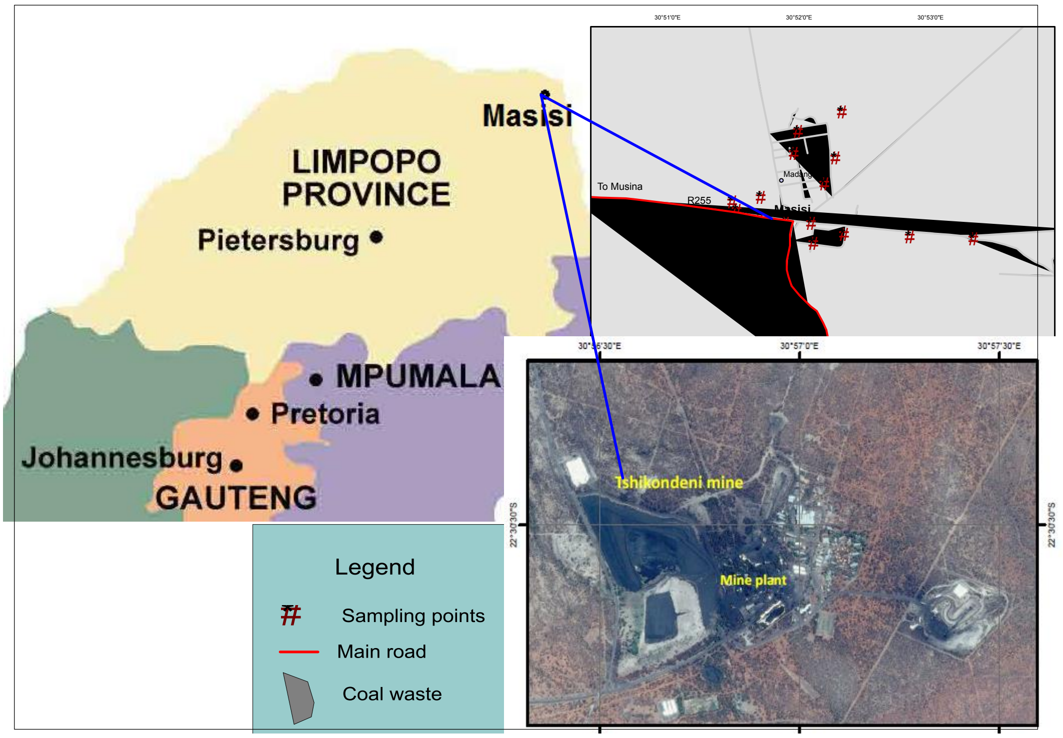

Figure 1 *Location map of the study area.*

Sampling was carried out during summer in 2014 and at least 22 samples were collected from communal boreholes around Masisi village for laboratory analysis. During sample collection, polypropylene bottles which were acid-washed, deionized water-rinsed were used to store the samples. All sample bottles were stored in a refrigerator at the University of Venda in an upright position to prevent water entering into or leaking from the container. Samples were subsequently pre-treated by filtering and preserved by adding 1% HNO_3 (Nitric cid). Consequently, major and minor cations (Mg, Zn, Cu, Cd, Cr, Fe, Mn, Ni, Se, Na, Mo, Ca, Pb, Sb, Ba, Al, Co, V, K, Al and As) were analyzed by Inductively Coupled Plasma-Mass Spectrophotometry (ICP-MS). Anions (NO_3^{2-}, Cl^- and F^-) were determined by Ion Chromatography (IC). Physical parameters such as electrical conductivity (EC), pH, total dissolved solids (TDS) were determined using Thermo Scientific Orion Star A215 pH/ Conductivity Bench top Meter after calibration with standards and buffers.

All the reagents used for analysis were AR grade and de-ionized water used for preparation of solutions. In order to ensure that the analytical results are accurate and precise, quality control measures were incorporated during sample analysis such as blank or spiked samples, and equipment decontamination. There was no detectable major and trace elements in the distilled water which served as the control. After sample analysis, the analytical data was evaluated and compared with the water quality guidelines of World Health Organization (WHO, 2003) as well as Department of Water Affairs and Forestry of South Africa (DWAF, 1996).

3. Results and Discussions

Physical parameters and major and trace elements for the 22 borehole water sample results are presented in Table 1. In general the concentration of cations increased in the orders Na>Mg>Ca>K>Al>As>Cr>Ba>V>Pb>Mn>Cu>Fe>Se>Sb and anions $NO_3^{2-}>Cl^->F^-$. The pH levels, Turbidity, F^-, Cu, Mn, Ca, Cr, Fe, Na, Zn, K, Mg and Sb were below the WHO (2003) and DWAF (1996) threshold concentration in all the boreholes. However, TDS ranged from 592-1506 ppm and exceeded WHO and DWAF threshold concentrations of 500 and 450 ppm respectively. Even though no direct health effects are known for TDS, certain components of TDS, such as chlorides, sulphates, magnesium, calcium, and carbonates, result in excessive scaling in household appliances and consequently the service life of these appliances (McQuillan and Spenst, 1976). Normally at a high TDS concentration, water becomes saline and water with a TDS above 500 ppm is not recommended for use as drinking water (USEPA, 2005). Since TDS can be regarded as a crude indicator of water quality for many purposes, it is related to the sum of all ionized solutes or total dissolved solid (TDS) content.

The conductivity of the groundwater ranged from 1082 - 2555 µS cm^{-1}. For groundwater, EC values greater than 500 µS cm^{-1} indicate that the water may be polluted, although values as high as 2000 µS cm^{-1} may be acceptable for irrigation water. Concentration of chloride was within WHO and DWAF permissible limit with only 5 boreholes indicating concentration > 250 ppm and these ranged from 267-439 ppm. Nitrate concentration exceeded the permissible limit by two folds with a range of 22-750 ppm.

Table 1 *Summary statistics for borehole geochemical data for Masisi village.*

Parameter	Unit	Max.	Min.	Mean	STD Dev.	Threshold (WHO, 2003)	Threshold (DWAF, 1996)
pH	-	7.99	7.05	7.58	0.26	6.5-8.5	6-9
TDS	ppm	1506	592	707	212.46	500	450
EC	µS/cm	2555	1082	1285	366.26	500-800	700
Turbidity	NTU	0.73	0.00	0.07	0.25	1	1
Cl^-	ppm	439	90	205	83.53	250	200
NO_3^{2-}	ppm	750	22	102	182.74	50	50
F^-	ppm	0.94	0.31	0.4	0.40	1.5	4
Cu	ppm	0.1	0.02	0.07	0.05	1	1
Mn	ppm	0.12	0.09	0.1	0.01	0.04	0.15
Ca	ppm	38.9	0.93	11	6.97	200	80
Cd	ppm	0.06	0.02	0.03	0.01	0.01	0.02
Cr	ppm	0.99	0.04	0.38	0.53	250	5
Fe	ppm	0.1	<0.01	0.09	0.01	0.3	0.3
Pb	ppm	0.15	0.09	0.12	0.02	0.1	0.05
Al	ppm	4.8	0.09	0.71	1.04	0.2	0.5
Na	ppm	160	66	111	28.05	200	200
Zn	ppm	0.17	0.02	0.08	0.05	5	10
K	ppm	5.9	3.5	5.18	0.70	10	50
Mg	ppm	133	74	84.95	12.43	150	400
As	ppb	1553	0.83	76.5	329.84	50	200
Se	ppb	16	1.16	6.55	4.60	10	50
V	ppb	243	18.9	44.6	49.31	200	200
Sb	ppb	0.23	0.02	0.05	0.05	5	-
Ba	ppb	406	7.6	256	129.66	50	-

Parameters that indicated elevated concentration were plotted on a box whisker plot to evaluate the geochemical data for the groundwater samples. Box plots are another convenient way of examining the distribution of a data set and for identifying variations caused by natural and human factors. Box plots of EC, Cl-, NO_3^{2-}, TDS, As, V and Ba content showed a significant difference between the median and maximum values with the median and mean values being near the lower quartile (Fig. 2). This suggested local contamination of the groundwater system with respect to these parameters. The wide range of EC (1082-2555 ppm), NO_3^{2-} (22-750 ppm), TDS (592-1506 ppm) and As (1-1553 ppm) may be a result of the lateral geological variations in the subsurface formation. The increase concentration of these parameters may also be attributed to different mechanisms such as water rock interaction processes.

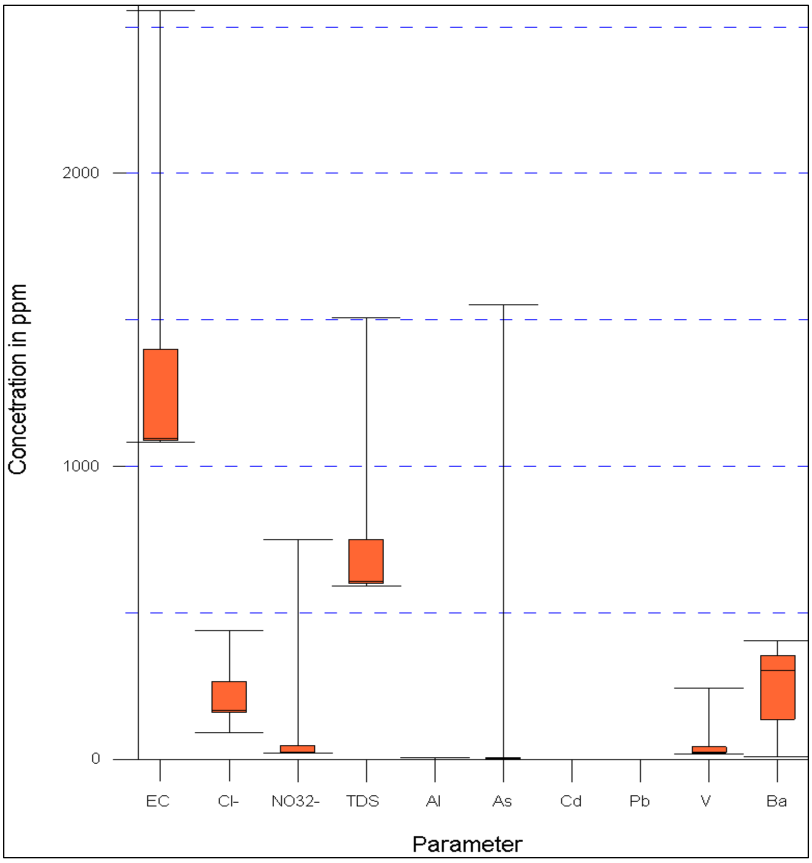

***Figure 1** Box and Whisker plot for parameters of groundwater samples.*

To examine the geochemical parameters, a correlation matrix was generated from the derived groundwater parameters (Table 1). The correlation matrix exhibited strong positive correlation among Ca^{2+}, Mg^{2+}, Cl^-, EC and TDS. A positive correlation observed between TDS and EC implies that conductivity increases as the concentration of all dissolved constituents/ions increases. Likewise, a strong correlation was also observed between Mg^{2+} and Ca^{+2} indicating most of the ions are involved in various physiochemical reactions, such as oxidation-reduction and ion exchange in the groundwater aquifer system (Udayalaxmi *et al*, 2010).

Significant correlation among TDS and V, As, Cd and Al also indicated that these metals were dominant in groundwater of the study area. On the other hand, fluoride was found to be negatively correlating with Ca^{2+} and with weak correlation against Mg^{2+} (correlation coefficient = 0.21 and -0.20 respectively). An inverse relationship among F^- and Na^+ was also observed. This might imply that Ca^{2+}might have been replaced by Na in cation exchange reactions as increasing concentration of sodium leads to increased solubility of fluorite in water (Kundu *et al*, 2001; Apambire *et al.*, 1997). The weak correlation between pH, Chloride, Calcium, Sodium and Magnesium, against fluoride may be due to the presence of low level fluoride in the rocks that can dissolve in the ground water. Moreover, the occurrence of low levels of fluoride in groundwater from this area may be due to either to the absence of fluoride bearing magmatic solutions or of fluoride containing minerals in the strata through which groundwater is circulating. It could also be attributed to too rapid fresh water exchange resulting in concentration through evaporation or evapotranspiration being not very effective in raising the fluoride content of the groundwater to high values. Similar phenomenon was observed by studies such as Sreedevi *et al. (*2006), Umar and Alam (2011).

Table 2 *Correlation coefficient between different hydro-geochemical parameters in the study area.*

	pH	EC	Cl-	NO32	F-	TDS	Turb	Al	As	Ca	Cd	Cr	Cu	Fe	Pb	Mn	Se	Na	Zn	K	Co	V	Sb	Ba	Mg
pH	1.00																								
EC	0.16	1.00																							
Cl-	-0.11	0.62	1.00																						
NO32	0.09	0.49	0.51	1.00																					
F-	-0.14	0.27	0.63	0.53	1.00																				
TDS	-0.18	0.48	0.86	0.72	0.84	1.00																			
Turb	-0.12	-0.02	0.43	0.22	0.60	0.62	1.00																		
Al	-0.46	0.04	0.50	0.29	0.69	0.74	0.67	1.00																	
As	-0.42	0.08	0.62	0.35	0.83	0.84	0.78	0.91	1.00																
Ca	0.21	0.56	0.39	0.54	-0.20	0.18	-0.31	-0.28	-0.32	1.00															
Cd	-0.42	0.08	0.63	0.35	0.83	0.84	0.78	0.91	1.00	-0.32	1.00														
Cr	-0.19	-0.13	-0.11	-0.11	-0.16	-0.13	-0.09	0.01	-0.06	-0.01	-0.05	1.00													
Cu	0.20	-0.04	0.08	-0.10	0.02	-0.04	-0.12	-0.09	-0.07	0.01	-0.07	-0.08	1.00												
Fe	0.09	0.33	0.41	0.26	0.23	0.31	0.13	0.02	0.16	0.14	0.17	-0.32	0.24	1.00											
Pb	0.27	0.04	-0.20	0.38	0.34	0.02	-0.08	-0.13	-0.04	-0.15	-0.05	-0.05	-0.07	0.17	1.00										
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00									
Se	0.10	0.43	0.63	-0.18	0.32	0.31	0.09	0.12	0.21	0.01	0.22	-0.14	0.23	0.38	-0.20	0.00	1.00								
Na	0.53	0.47	0.12	0.37	-0.08	0.05	-0.38	-0.26	-0.36	0.50	-0.35	0.04	0.11	0.21	0.31	0.00	0.17	1.00							
Zn	0.37	-0.09	-0.10	0.02	0.10	-0.09	-0.17	-0.16	-0.09	-0.08	-0.10	-0.11	0.17	0.33	0.33	0.00	0.01	0.18	1.00						
K	-0.23	-0.41	-0.15	-0.51	-0.24	-0.19	0.26	0.23	0.15	-0.41	0.16	0.08	-0.01	-0.34	-0.44	0.00	-0.07	-0.45	-0.30	1.00					
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00				
V	-0.18	0.29	0.64	0.64	0.91	0.92	0.68	0.82	0.90	-0.14	0.90	-0.12	-0.08	0.24	0.21	0.00	0.17	-0.03	-0.02	-0.16	0.00	1.00			
Sb	-0.50	-0.25	-0.06	-0.13	-0.01	0.01	0.11	0.37	0.20	-0.15	0.20	0.25	-0.20	-0.40	-0.14	0.00	-0.16	-0.19	-0.28	0.33	0.00	0.02	1.00		
Ba	-0.33	-0.35	-0.33	-0.75	-0.59	-0.59	-0.53	-0.26	-0.37	-0.19	-0.36	0.09	0.18	-0.07	-0.43	0.00	0.13	-0.14	0.07	0.35	0.00	-0.63	0.17	1.00	
Mg	0.18	0.62	0.65	0.76	0.21	0.57	-0.06	0.06	0.07	0.84	0.07	-0.04	0.08	0.30	-0.04	0.00	0.18	0.58	-0.05	-0.52	0.00	0.31	-0.26	-0.37	1.00

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4. Pollution Analysis using Pollution Index (*Pi*)

Pi was used to show the level of pollution of borehole water by each parameter. The critical value being 1.0 and values >1.0 indicating significant degree of pollution while values <1.0 showing no pollution/ danger of pollution (Akpoveta *et al.*, 2011). Pollution index (Pi) according to Akpoveta *et al.* (2011) is expressed as a function of the concentration of individual parameter values against the baseline standard (WHO permissible value). It is given as below in equation;

$$\text{Pollution index (Pi)} = \frac{\text{Concentration}}{\text{Standard}} \text{.......................................(i)}$$

For this study, the number of boreholes with Pi>1 were plotted and DWAF threshold concentration were used to derive Pi for the parameters (Fig. 3). The data indicated chemical parameters (Ni, Cu, Co, Al, Ca, Fe, Se, Zn, Na, Turbidity, pH and F^-) with *Pi*<1.0 and therefore implying that all the boreholes were free from contamination by these parameters. Parameters such as TDS, EC, Cl^- , NO_3^{2-}, Mn, As, Cd, Cr, Pb, Mo, K, V, Sb, Ba and Mg had *Pi*>1 in some of the boreholes and consequently indicating significant degree of contamination. Electrical conductivity had *Pi* ranging from 1.6-3 and Total Dissolved Solids Pi ranged from 1.3-3.4 in all the 22 boreholes, whilst Pb, K and Ba had *Pi*>1 in borehole number 21, 15 and 19 respectively.

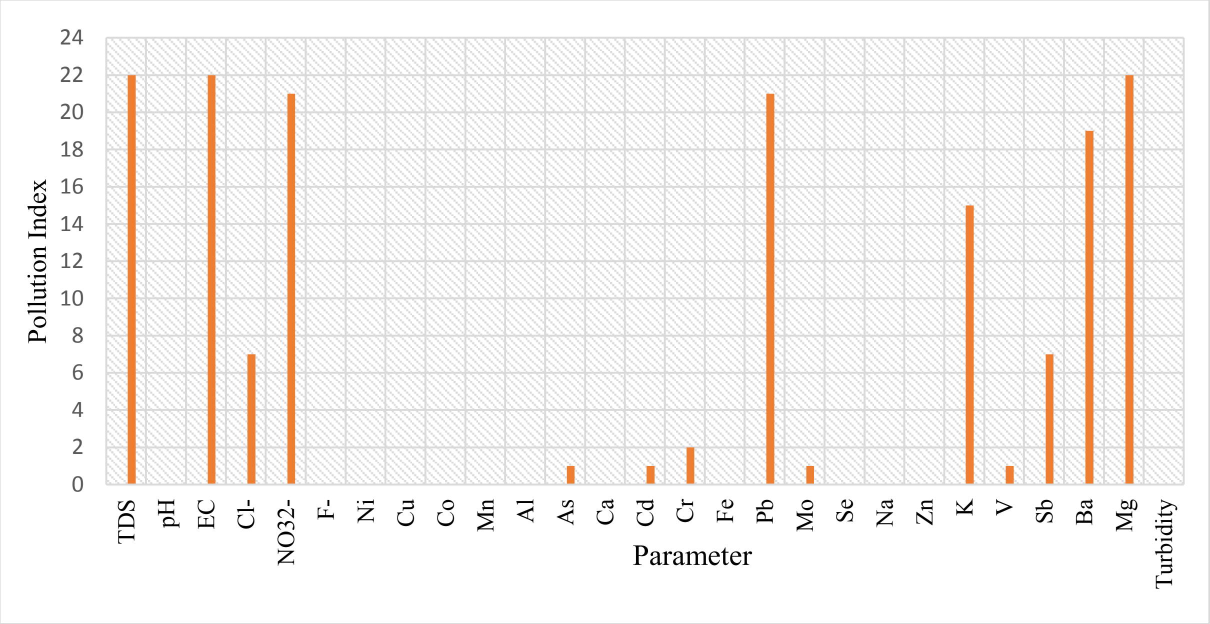

***Figure 3** Pollution Index of Boreholes based on WHO and DWAF threshold concentration.*

5. Conclusion

Overall quality of groundwater in 6 -10 km radius of Tshikondeni mine in the Limpopo Province is not pristine. Therefore, this groundwater should not recommend for its direct use for domestic and agricultural purpose. The water is hard in nature and has high total dissolved solids (TDS) which is not suitable for drinking purpose as described by WHO (2003) and DWAF (1996). Moreover, Pollution index were >1 in all the boreholes sampled which indicated significant pollution to the groundwater resource at Masisi village. Elevated TDS and EC values are indicative of inorganic dissolved solids such as chloride, nitrates and fluorides anions or sodium, calcium, magnesium, iron and aluminum cations derived various physiochemical reactions, such as oxidation-reduction and ion exchange. The increase in concentration of these parameters may also be attributed to different mechanisms such as water rock interaction in the subsurface formation or groundwater migration from point source pollution. Local authorities should look for alternative sources of water supply as these boreholes are polluted and communities are at risk of renal disease (Cd poisoning), blood pressure and kidney problems (Pb poisoning), kidney and liver damage (As poisoning), gastrointestinal disorders (Sb poisoning), cancer and mild neurological effects (V poisoning). Based on the findings of this study, continuous monitoring of ground water quality and water table within 10 km radium of Tshikondeni Coal mine is recommended. Primary and secondary treatment prior to domestic and agricultural use is also recommended.

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Contamination load in a river affected by AMD discharges: Odiel River (Huelva, Spain)

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Abstract

In the Odiel River can be observed how a clean river at its source, starts to decay as a consequence of various water mine discharges. The high concentrations of metals like iron, aluminum, copper or zinc provokes the acid mine drainage (AMD) contamination in the river. This work presents a theoretical contamination load estimate from the mixes river-mine discharges and it is compared with the observe contamination load obtained from a sampling campaign. In this way, there has been calculated the total and dissolve metals transported by the river and the behavior of each one has been analyzed. As long as the river keep the pH around 7, elevate portion of iron, copper and aluminum precipitate while cobalt and zinc remain mostly dissolved. When the pH falls down to 4, all metals turn to be conservative excepting iron.

Key words: AMD, Contamination Load, Odiel River

Introduction

The Odiel River is situated in the Iberian Pyrite Belt (SW Iberian Peninsula) and is heavily affected by acid mine drainage (AMD). The presence of many polymetallic massive sulfide deposits has generated intense mining activity in the past. The impact of AMD processes in the Odiel river basin have been thoroughly studied. For instance, Olias et al. (2006) determine that both the Odiel and Tinto rivers transport annually 7922 t of Fe, 5781 t of Al, 1721 t of Cu and 3475 t of Zn.

The Odiel headwaters show a good quality status, however the confluence of several mining discharges (i.e. Concepción, San Platón, Esperanza and Poderosa; Fig. 1) along a 7 km-long reach cause a water quality worsening. The deterioration of the Odiel river waters become irreversible with the confluence of the Agrio River, which drains the AMD highly contaminated from the Riotinto mines (Sanchez-España et al., 2006; Nieto et al., 2013). The aim of this work is to analyze the evolution of the dissolved metal load along the first AMD contaminated reach as well as to determine the different metal transport patterns.

Methods

A sampling was carried out in 14 points of this reach in February 2015 (Figure 1), when the river had average flow rates (1140 L/s). Water samples were taken in each AMD discharge and along the Odiel River. The samples were filtered and acidified to pH<2 in order to determine the dissolved concentration. The pH, oxidation-reduction potential (ORP), temperature and electric conductivity were measured in situ using an equipment CRISON model MM40+. Water samples were analyzed by ICP-OES and ICP-MS for major elements and trace elements respectively. The flow rate was measured in each AMD discharge by means of an electromagnetic flowmeter. On the other hand, the flow rate at the beginning of the studied reach was measured by a tracer injection test.

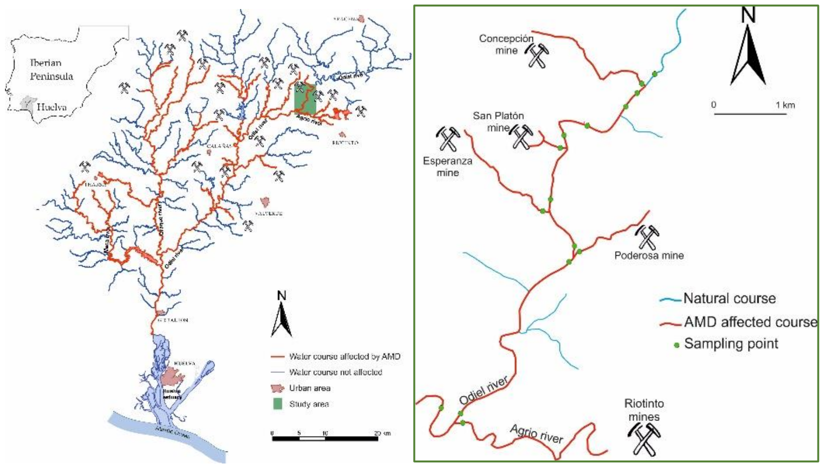

***Figure 1** Site and sampling points situation.*

Results and discussion

The observed contaminant load (OCL) was calculated from the flow rates and the analyzed concentrations. By far, the Agrio River constitutes the major metal contributor with up to 2292 kg/day of Fe, 4724 kg/day of Al, 643 kg/day of Zn, 579 kg/day of Mn, 279 kg/day of Cu and lesser amounts of Co, Ni or Pb. (Table 1). Concerning the rest of AMD discharges, Concepción transported between 4 and 16 times higher discharge than the others drainages, however only carried greater loads of Al, Mn, Co and Ni (Table 1). Especially lower loads were carried by Esperanza due to the implementation in December 2014 of a treatment plant that partially neutralizes AMD discharges. It is also striking the greater As contribution from San Platón (including the Agrio River) considering the low flow rate of this source. In spite of the confluence of these AMD discharges the pH in the Odiel River was close to 7.7 up to junction of the Agrio River when the alkalinity may be totally consumed and the pH dropped to 3.9.

***Table 1** Flow rate (L/s), pH values and observed contamination load (OCL) (kg/day) in the AMD discharges studied.*

Mine discharge	pH	Flow rate	Fe	Al	As	Pb	Cu	Zn	Mn	Co	Ni
Concepción	2.9	20	77	41	0.003	0.011	2.4	3.7	3.33	0.28	0.023
San Platón	2.8	1.2	146	23	0.078	0.003	1.4	12	0.92	0.068	0.008
Esperanza	3.5	2.0	7.0	4.7	0.0001	0.002	0.4	0.54	0.46	0.014	0.005
Poderosa	2.6	4.8	78	20	0.10	0.017	4.7	3.8	0.88	0.066	0.013
Agrio River	2.7	132	2292	4724	0.063	0.095	279	643	534	16	7.2

The theoretical contaminant load (TCL) along the reach was calculated considering conservative mixing of the Odiel River (Q_0, C_0) and the AMD discharges (Q_i, C_i). Before San Platón mines an increase in sulfates (600 kg/day), Zn (8 kg/day), Co (0.3 kg/day), Mn (2.6 kg/day) etc. was detected, related to diffuse discharges into the river, which were also considered for calculating the TCL:

$$TCL = Q_0 \cdot C_0 + \sum Q_i \cdot C_i$$

Figure 2 compares OCL and TCL for some selected metals in the Odiel River upstream the Agrio confluence. Differences between both dissolved loads may indicate a deviation from a conservative behavior and thus, a quantification of the precipitated mass which is deposited in the riverbed. It can be seen that most of the Fe and Cu dissolved may precipitate (300 kg/day of Fe and 8 kg/day of Cu) during mixing processes. In the same way, As, Al and Pb (not shown in Fig. 2) were present in all discharges (see Table 1), but were not detected in the river due to precipitation processes.

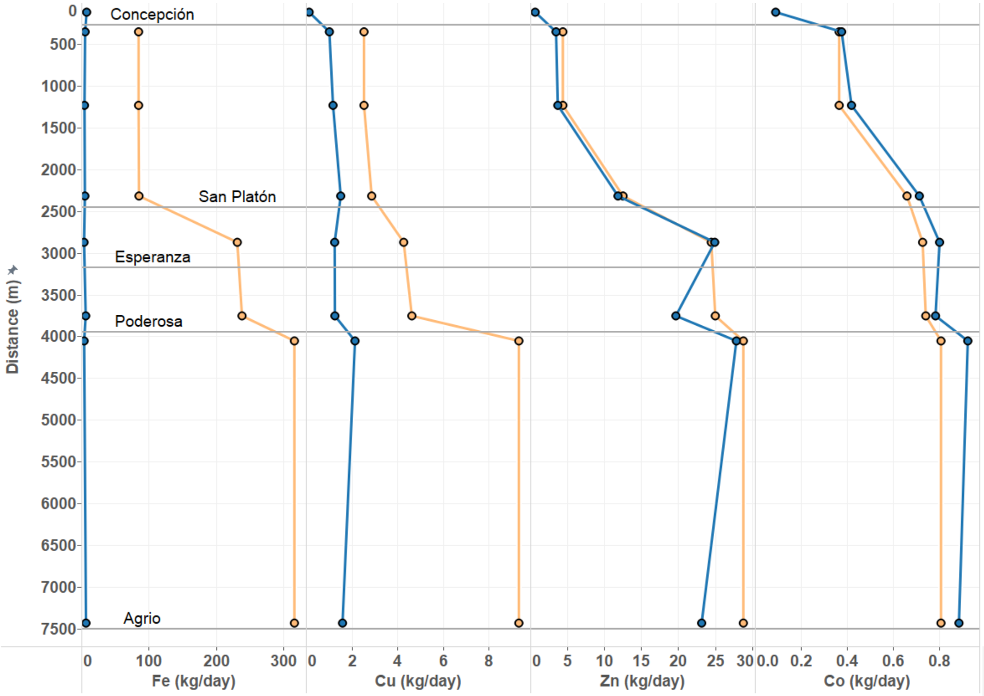

Figure 2 *Evolution of observed contamination load (OCL) vs theoretical contaminant load (TCL) along the Odiel River, upstream of the Agrio River confluence.*

Zn seems to behave initially almost conservatively, although after the Esperanza and Poderosa discharges precipitation along the river may occur (Fig. 1). The behaviour of dissolved Co and Mn (the last not shown in Fig. 2) also seem to be conservative. The small differences observed between OCL and TCL for Co must be due to the analytical uncertainty.

The metal transport pattern in the Odiel River change drastically after the Agrio confluence. The river pH decreases to 3.9 and Al become a conservative element increasing its dissolved load up to 5000 kg/day. In addition Co, Cu, Zn and Mn remain mostly in the aqueous phase during the rest of the Odiel course (18 kg/day, 376 kg/day, 843 kg/day and 630 kg/day of dissolved metal load, respectively). Most of Fe transported by the Agrio River (2292 kg/day) precipitates during mixing processes with the Odiel waters (pH 7.7), although a significant increase in Fe transport is observed after the confluence of the Agrio River (from 6 to 90 kg/day).

One important issue that emerges from these observations is that most of the precipitates remains in the river in form of poorly crystallized minerals (Fe and Al oxyhydroxysulfates). This was previously highlighted by Sánchez-España et al. (2006) and produces a relevant secondary contamination of the Odiel River due to high contents of particulate matter which accumulate in the sediments

Conclusions

The dissolved metal/loid load transported by the Odiel River along its first AMD contaminated reach has been quantified. The confluence of these mine discharges provokes the progressive deterioration of the river quality, causing the precipitation of some non-conservative elements (Fe, Al, Cu, As or Pb) while the most mobile elements (Mn, Co, Ni and Zn) remain in solution. The Agrio confluence produces an inflection point in the Odiel river water quality; the dissolved metal load increases significantly and the river become acidic (pH drop under 4) enhancing the solubility of Al which was entirely precipitated upstream. At this point, the Odiel River transports up to 5000 kg/day of Al, 843 kg/day of Zn and 376 kg/day of Cu.

Acknowledgements

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Reiche Zeche Mine Water Geochemistry

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Extended Abstract

Historical water quality sampling of the Reiche Zeche mine in Freiberg, Saxony, Germany, has been inconsistent and infrequent after a 2002 flood that destroyed underground sampling equipment. The need for a present day analysis of water quality is important to understand current leaching and quality conditions within the mine. Historical data analysis and comparison to present day sampling data shows that metal and ion concentrations have decreased over the last 15 years, leading to overall improvements in water quality across most sampling locations within the mine.

Underground mine water samples were taken in June 2015 and analyzed for metal content to determine what compounds are still present in the mine. In addition, sample metal levels were compared to federal surface and groundwater contaminant threshold allowances. Historical data was catalogued, and results of 2015 sampling were compared to historical levels to demonstrate that concentrations of metals and ions both within and coming out of the mine have decreased over time. This is perhaps due to an 'armoring' of pyrite surfaces within areas of the mine. As pyrite oxidation is the primary mechanism by which sulfides are released, and since no fresh surfaces have been exposed in nearly 50 years, previously exposed sulfide surfaces have likely been weathered enough that no more oxidation is occurring, leading to decreases in minerals leaching from the ore. Results show decreases in metals leaching from well documented areas, but high (average sum total metals > 1,000 mg/l) metal content in areas lacking historical data. Metal transformation was predominantly precipitation of secondary minerals and hydroxides, with some adsorption. Results also show an interesting correlation between electrical conductivity and total organic carbon, as well as zinc and cadmium concentrations.

Metal concentrations were predictably highest in the deepest parts of the mine where water flow was little to none. Greatest concentrations of Pb and Fe were measured on the third level below ground level, far from any previous mined veins. All sampled points were undersaturated for all modeled compounds, except for barite, bixbyite, anglesite, goethite, and quartz, which precipitated at certain locations. Highest SO_4^{2-} and Mg concentrations were observed in slow flow water leaving a main mined vein, seen in Fig. 1. Highest concentrations of Zn were also observed at the same location. All measured metals were below federal surface, ground, and drinking water contaminant thresholds by the points at which adit water left the mine, signifying adequate natural buffering or neutralization of metals.

Figure 1: *High SO_4^{2-} and Mg content water.*

This water quality assessment will enable planning of future projects at the Reiche Zeche to reference up to date water and geochemistry data. Information from this study will be useful for TU Bergakademie Freiberg, other parties associated with the mine, and regional authorities.

Key words: Mine water, geochemistry

Magnesium and aluminum sulfates in salt efflorescences from acid mine drainage in the Iberian Pyrite Belt (SW Spain)

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Abstract

The current study is focused on AMD-precipitates that compose the typical magnesium and aluminum sulfate assemblages in the Spanish sector of the Iberian Pyrite Belt (SW Spain). The main objectives are identify and describe the composition, morphology and paragenetic relationships of these sulfate phases.

From the methodological pint of view, sampling procedure covered the entire metallogenetic province, including five selected representative mines and eight river basins, which are the main receptors of the acid mine drainage discharges. The mineralogical analyses were performed by X-Ray diffraction and electron microscopy. The obtained results showed the extraordinary abundance of aluminum sulfates with acicular habit, from the series pickeringite-apjhonite-halotrichite. They form typical assemblages with other aluminum sulfates, such as alunogen and tamarugite, and with the Mg sulfates: epsomite and hexahydrite. Moreover, the paragenetic relationships indicate the late occurrence of acicular Al-sulfates from the halotrichite group.

Key words: Salt efflorescences, soluble salts, magnesium and aluminum sulfates, mineral assemblage

Introduction

Secondary soluble salts form ubiquitous assemblages in acid mine drainage (AMD) affected systems. They occur commonly as complex mixtures of very fine grained minerals, mainly sulfates. (e.g. Nordstrom and Alpers, 1999). The properties of the sulfate efflorescences, regarding morphology, chemistry and paragenesis, are important for understanding the environmental conditions of the affected systems as well as the evolution processes undergone by AMD (Valente et al., 2013). Therefore, the ability of the soluble sulfates to indicate the prevailing conditions in which they form contributes to their monitoring relevance. Moreover, environmental significance is enhanced by their role in controlling pollutants mobilized by acid mine drainage solutions.

The Iberian Pyrite Belt (IPB) is a paradigmatic metallogenic province, well-known by the magnitude of the AMD processes (Grande, 2013). In this region there are many works investigating various aspects of AMD-precipitates (e.g., Buckby et al, 2003; Valente et al., 2013). The present study is focused on the mineralogical assemblages dominated by aluminum and magnesium sulfates. It documents data from the entire metallogenic province, covering sampling sites in the most representative sulfide mines as well as in the receiving watercourses. The main objectives are (i) to identify the most common assemblages, (ii) to describe typical habits, occurrence modes and spatial distribution; (iii) to obtain chemical composition; and iii) to understand possible paragenetic relationships between the Mg and Al sulfate phases that compose some of the most common efflorescences.

The mineralogical highlighted the role of aluminum and magnesium sulfates in the Pyrite Belt river network. These minerals, especially from the groups of pickeringite-halotrichite and epsomite, are extraordinary abundant, mainly in distal positions. Mineralogical identification, chemical composition and morphological description also allowed some paragenetic interpretations, revealing the late occurrence of acicular aluminum sulfate phases.

Methods

Study area

The Iberian Pyrite Belt (IPB), located in the southwest of Iberian Peninsula, is well-known by the historic mining activity, especially for copper in volcanic-hosted massive sulfide deposits. It extends from north of Seville – in Spain – to southern of Portugal, being known for its large massive sulfide ore deposits within the Volcano-Sedimentary Complex. In general, the ore deposits are classic volcanic-hosted massive deposit (VHMS). Although with variable ore paragenesis, the most important deposits consist of ore lenses located in the lowermost volcanosedimentary complex overlying a thick siliclastic sequence from the Phyllite-Quartzite Group (Tornos et al., 2008; Mantero et al., 2011). The sulfides mineralization is mainly represented by massive pyrite, followed by chalcopyrite, sphalerite, and galena. Gangue minerals include abundant quartz and aluminum silicates (mainly chlorite), with minor amounts of carbonates.

The study area, located in the Huelva province, has a Mediterranean climate, which can be classified as semi-arid, due to low precipitation rates. Annual precipitation is about 630 mm/year, being mostly concentrated in the wet season from October to May. Monthly precipitation ranges from 3 to 121 mm, corresponding to June and December, respectively. Average annual temperature is 17.1 ºC, January being the coldest month (mean 9.8 ºC), while in the summer, July and August have the highest temperatures (mean 25.7 ºC) (Instituto Nacional de Meteorología; unpublished data). July also has higher evapotranspiration (162 mm) than January (19 mm). It should be noted that sampling for this study was performed in July, with temperature and relative humidity readings consistent with the typical mean annual values (temperature up 25ºC and relative humidity around 50%) (Instituto Nacional de Meteorología; unpublished data).

As a consequence of historic mining legacy, the IPB is characterized by strong environmental contamination by AMD. Nowadays, there are more than 4800 ha occupied by waste dumps, open pits, tailing dams, and mining facilities, corresponding to 88 sulfide mines (Grande et al. 2013). The present research was focused on the entire Spanish sector of the Iberian Pyrite Belt, covering different situations: abandoned mining sites, with their waste dumps and seepages, and the receiving river network. So, there are soluble salt samples from contaminated rivers and from selected representative mines, which locations are presented in Table I. The fallowing abandoned mines were selected in order to represent the diversity of the main sources of AMD. In turn, the receiving river network comprises eight major river basins: Trimpancho, Cobica, Meca, Oraque, Olivargas, Odiel, Tinto and Guadiamar (Table 1).

Sampling and analyses

The sampling campaign was performed under strong evaporation and low flow hydrological conditions (July 2015). The sampling network comprised two distinctive environments. One refers to waste-dumps, seepages and leachates in the abandoned mines. The other environment corresponds to the watercourses, which represent the receiving river network. For this, eight sampling areas were established, in order to represent the sub-basins defined in the IPB by Perez-Ostalé (2014) (Table 1). At each sampling area, the AMD-precipitates were collected in order to represent the field variability, given rise to approximately 200 complex samples. Air temperature and relative humidity were measured in the field.

Efflorescent salts and crusts were examined for morphology, photographed and sorted by binocular microscopy. Afterwards, samples were lightly ground in preparation for mineralogical analysis. The samples were analyzed by X-ray powder diffraction (XRD) with a Philips X'pert Pro-MPD difractometer, using Cu Ka radiation at 40 kV and 30 mA. Morphological and compositional features were analyzed by scanning electron microscopy with a LEICA S360 microscope, combined with an energy dispersive system (SEM–EDS, 15 keV). The samples were coated with platinum or Au/Pa, in order to allow high resolution images. The XRD data were processed with the X'pert Pro-MPD software, which help to identify the most probable phases. However, this type of sample poses particular problems, which imply the use of an iterative procedure to accomplish mineralogical identification. (Jerz and Rimstidt, 2003; Hammarstrom et al. 2005). Sample preparation procedures and the appropriate XRD and SEM conditions for dealing with fine grain size, high hydration states, and impurity have been described by Valente and Leal Gomes (2009).

Table 1 *Location of the study sites (rivers and mines)*

	River waters – Location (coordinates)
Tinto	N-37º 40’ 59”; W-06 32’ 56”
Meca	N-37º 29’ 10; W-7º 04’ 12”
Cobica	N-37º 38’ 50”; W-07º 16” 46”
Trimpancho	N-37º 42’ 40”; W-07º 26’ 52”
Oraque	N-37º 31’ 16” W-06º 59’ 40”
Odiel	N-37º 29’ 49”; W-03º 56’ 59”
Olivargas	N-37º 46’ 17”; W 06º 47’ 24”
Guadiamar	N-37º 41’ 06”; W-06º 22’ 35”
	Mine sites for AMD-precipitates
Herrerías mine	Waste-dumps N-37º 37’ 51”; W-07º 18’ 59”
Riotinto Mines	Waste dumps Seepages; surface drainages N-37º 40’ 54” ; W-06º 33’ 59
Lazunazo Mine	Mine pond N-37º 37’ 34”; W 07º 10’ 08”
Tharsis Mine	Waste dumps and AMD-emergences N-37º 35’ 13”; W-07º 06’ 27”
San Telmo Mine	Waste dumps and pit lake banks N-37º 48’ 50”; W-06º 58’ 55”

Results and discussion

Most of the samples occurred as powder or crusted efflorescences as shown in figure 1. The XRD data provided identification of several iron, copper, magnesium, calcium and aluminum sulfates. These efflorescences are mainly complex assemblages since pure minerals are rare.

Magnesium and aluminum sulfates occur mainly in the river network, hence with distal distribution regarding the mine waste dumps. Nevertheless, sometimes they may appear near the main focus of AMD (e.g., Herrerias, Tharsis and San Telmo mines). In these cases, they are often in association with copper and iron sulfates.

The mineralogical study by SEM has led to the chemistry of the secondary minerals and to the morphological characterization of the typical associations (Fig. 2). The study has revealed the extraordinary abundance of aluminum sulfates with acicular habit (mainly pickeringite and halotrichite) as well as magnesium sulfates (mainly epsomite and hexahydrite) (Figure 1) which had already been detected in XRD.

Figure 1 *Field images showing the occurrence modes of typical efflorescences, composed by aluminium and magnesium sulfates. a) General view of Meca River with white powder efflorescences; b) crustified efflorescences dominated by aluminocopiapite ; c) Orange plate efflorescences dominated by magnesium sulfates (epsomite); d) Blue-green globular efflorescences with magnesium sulfates (hexahydrite) and cooper sulfates (chalchantite).*

They form typical assemblages with other aluminum sulfates, such as alunogen and tamarugite, and sometimes with iron sulfates, such as copiapite and aluminocopiapite or copper sulfates (chalchantite and alpersite). The SEM images presented in fig. 2 show the morphology of some of the most typical assemblages, namely:

Epsomite+pickeringite

Epsomite+tamarugite

Hexahydrite+pickeringite

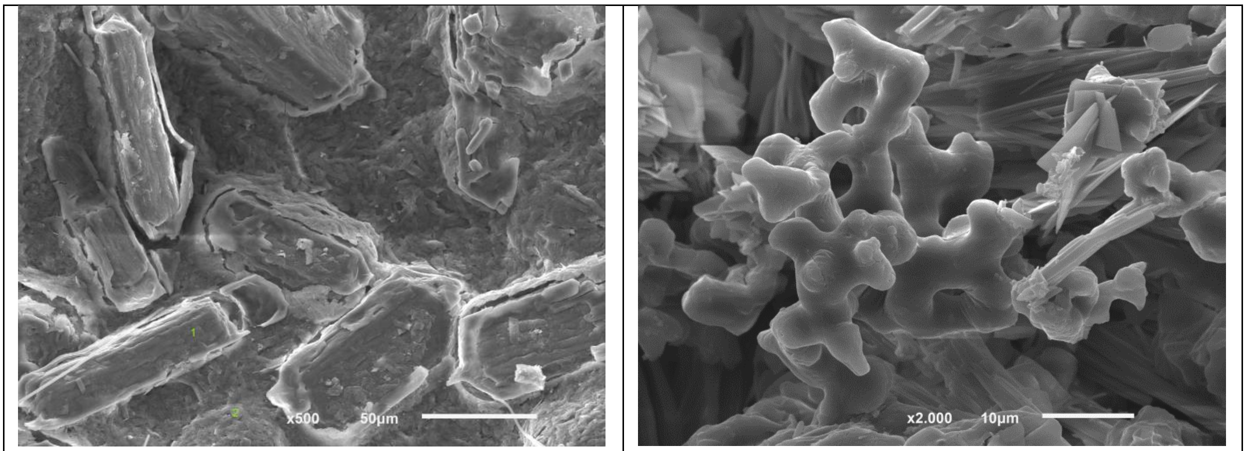
Tamarugite+pickeringite

Hexahydrite+alpersite+chalchantite

copiapite+Aluminocopiapite+Alunogen+Holotrichite

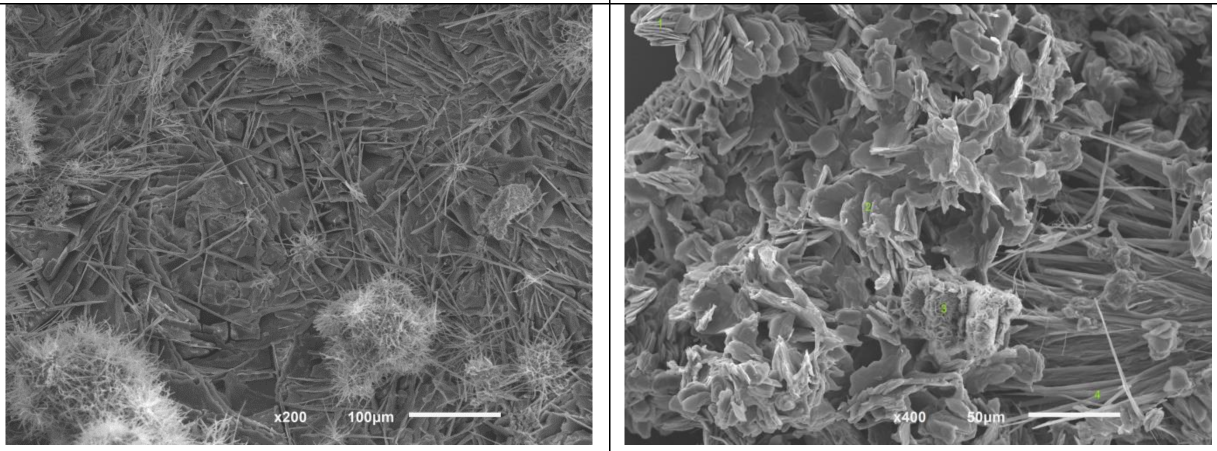
The morphological relationships suggest that aluminum sulfates have late occurrence. This paragenetic relatioship is evident in the SEM images presented in figs… The acicular aluminum sulfates, mainly pickeringite or halotrichite, are ubiquitous over epsomite or hexahydrite. Other aluminum sulfates, such as tamarugite, also occur often covering the crystals of epsomite, as shown in fig.

Epsomite and hexahydrite are the most abundant magnesium sulfates. They appear generally in different assemblages. Epsomite occurs more often nearest the water bodies, in accordance to its higher hydration state.



Epsomite ($MgSO_4$ $7H_2O$) covered by tamarugite ($NaAl(SO_4)_2$ $6H_2O$)

Hexahydrite ($MgSO_4$ $6H_2O$) with acicular pickeringite ($MgAl_2(SO_4)_4$ $22H_2O$)



Acicular pickeringite ($MgAl_2(SO_4)_4$ $22H_2O$) growing over plate tamarugite ($NaAl(SO_4)_2$ $6H_2O$) and epsomite ($MgSO_4$ $7H_2O$)

Mineral assemblage composed by plate copiapite alunogen (2), aluminiocopiapite (3, roses) and acicular halotrichite (4)

Figure 2 *SEM images showing morphology of typical mineralogical assemblages composed by aluminium and magnesium sulfates.*

Conclusions

The present study showed the extraordinary abundance of aluminum and magnesium sulfates in the AMD-precipitates from the Iberian Pyrite. These minerals dominate the mineralogical assemblages in the receiving environment, as a fingerprint of the abundant Mg and Al-silicates that compose the host rocks of the sulfide ores in the Iberian Pyrite Belt. The late occurrence of acicular aluminum sulfates from the halotrichite group is typically noticeable in the paragenetic relationships. Tamarugite and alunogen are other typical aluminum sulfates composing the mineralogical associations. Near the AMD sources, in the abandoned mines, the aluminum and magnesium sulfates occur more often in assemblage with iron and copper sulfates.

Acknowledgements

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Characteristic variation of precipitate in limestone layer

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Extended Abstract

In successive alkalinity-producing systems (SAPS), precipitate generated on limestone layer tends to be increased over time, deteriorating the permeability of SAPS and reducing the treatment efficiency of mine drainage as well as the life of SAPS. A flushing system, as the alternative to deal with it, has been emerged recently but the study on characteristics of precipitate that travels in pipe has still remained far behind. This study is intended to identify the characteristics of precipitate generated on limestone layer and thus, the growth test of precipitate was conducted and consequently, changes to the type of precipitate and physical & chemical properties were identified. Besides, minimum transport velocity of precipitate which is the major design factor in flushing system was estimated through the test.

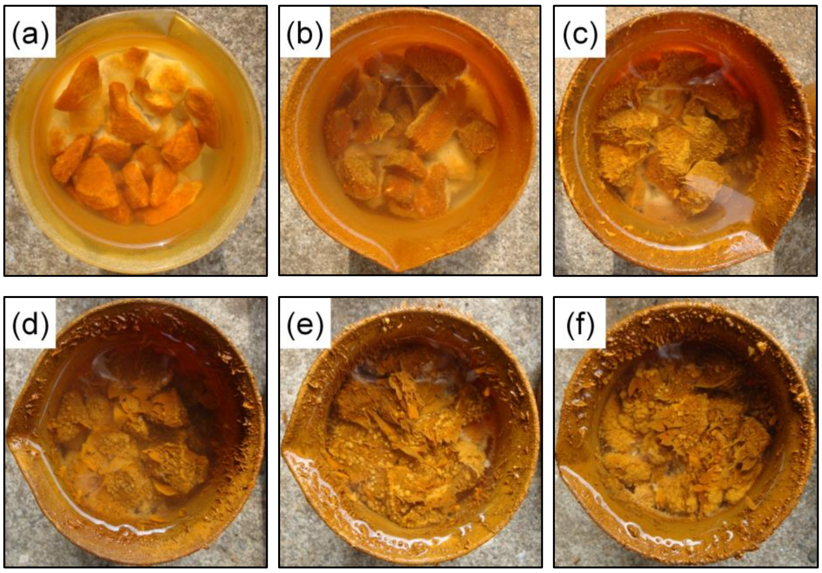

Figure 1 *Images of samples obtained from precipitation experiment during six months; showing each sample spending to one week (a), two weeks (b), three weeks (c), four weeks (d), five weeks (e), and six weeks (f).*

Table 1 *Minimum velocity for precipitate transportation of each precipitation type acquired by laboratory experiments.*

Precipitation type	Diameter (mm)	Critical velocity (m/sec)		
		Measured value	Oroskar and Turian (1980)	Thomas (1979)
Membrane	4.2	0.050	–	–
Botryoidal	2.5	0.063	0.063	0.074
Fine grain	0.2	0.120	0.120	0.540

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CHAPTER 6

Water related Mine Design and Mine Dewatering

Optimized Dewatering Wells for Open Pit Mining to Prevent Well Loss from Ochre Formation

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Extended Abstract

The lignite mining industry in the Rhenish district has to pump ca. 570 Mio. m^3 groundwater each year to facilitate open pit mining. Around 1,500 wells are in production and each year a cumulative length of 35,000 m or approx. 200 wells is newly drilled. Obviously, it is of high economic interest to push the yield of wells to an optimum, although dewatering wells have in general a much shorter lifetime than water supply wells. Well clogging by ochre formation is a common reason for well loss and increasing maintenance of e.g. the pumps. The paper reports about 5 years of research and experience in optimizing well design and well operation to prevent or at least minimize ochre formation.

We studied processes of ochre formation in an unscaled experimental rig to investigate kinetics of ochre formation and influences by e.g. filter pack or screen length [1]. This was compared with ochre observed in the wells and sampled from excavated wells inside the pits including studies about the microorganisms producing ochre inside the wells [2]. Understanding the leading processes, the well operation and well design was improved. The two most effective measures were operating the well with respect to certain water levels instead of discharge values and using the annular space for dewatering higher aquifers to avoid screens.

Sediments in the Rhenish district have a modest content of pyrite of 0.1 – 0.3 % pyrite-S, part of which is oxidized during the dewatering. Some aquifers have optimal conditions for ochre formation, i.e. 0.1 – 0.6 mg L^{-1} O_2, 2 – 4 mg L^{-1} Fe, and bacteria like Leptothrix ochracea were found. Yet, it was not possible to establish an aquifer specific water type susceptible to ochre formation to use this as a management tool. The most serious influence was by groundwater enriched in oxygen from the gas phase in the open casing section of the wells. The two measures mentioned above both have in common that intake of ground water into open casing sections is avoided.

Until recent years dewatering wells in the Rhenish district were installed with several screens. Due to high pumping rates upper screens often fell dry and allowed seepage getting enriched in oxygen in the open casing running down or splashing into the lower well sections. In an optimized well operation the drawdown of the well was set to the upper level of the highest screen as long as possible. To do so, a high number of wells got re-equipped with controllers to regulate the pumping rate.

Special dye tracer tests showed that the annular space and coarse filter pack were sufficient to enable dewatering of one aquifer by a screen installed in the next deeper one. Again, ground-water will not get into contact with the oxygen in the open casing. This has become the common design of wells drilled for open pit dewatering in the Rhenish district in recent years except for wells outside the mining field.

Key words: Open pit dewatering, ochre formation, well operation, well design

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Deploying Oil & Gas drilling techniques with Dewatering Well Placement technology (DWPt) in open pit and underground mines

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Abstract

Dewatering of mining operations brings many advantages including improved access, increased stability of pit slopes, reduced cost of ore haulage and more cost effective blasting. In many cases dewatering is achieved through the use of vertical in-mine wells. The presence of these wells within the pit can however cause operational issues, while space constraints often mean that the wells cannot be sited in the optimum location from which to achieve dewatering impacts. In order to overcome these issues SWS has developed Dewatering Well Placement technology (DWPt), which applies oilfield directional drilling and completion approaches to implement dewatering wells which can be drilled from outside the final pit footprint, and place the well in the optimum production zone based on the final pit floor. The ability of these wells to target key hydrogeological structures, together with their improved operational run times, means that improved drawdowns are achieved when compared to vertical in-mine wells. Engineering design of these wells requires a comprehensive technical evaluation and cost benefit analysis to be undertaken in order to determine whether DWPt is the appropriate dewatering approach for any mining operation. SWS has developed a comprehensive workflow for implementation of DWPt, and the application of this workflow at the Sishen iron ore mine, South Africa, is presented as a case study of the evaluation process.

Key words: Dewatering, Well Placement technology, well trajectory, rate of penetration

Introduction

The majority of large open pit and underground mines require dewatering as part of the mining operation. The dry mining conditions that dewatering is aiming to achieve provides a number of operational benefits (Figure 1) which include:

- Unrestricted access to mine benches
- Dry pit slopes have a reduced risk of failure
- Dry ore has a lower cost of haulage
- Dry blast holes enable the use of lower cost explosive and generally achieve enhanced fragmentation
- Dry conditions help reduce the health and safety risk.

Figure 1 *Operational impacts of wet mining conditions*

In most cases dewatering is achieved through the use of vertical in-mine wells which are pumped to reduce groundwater levels ahead of mining, thus creating the dry working conditions. However the use of in-mine vertical wells can face a number of challenges, including:

- Well infrastructure, including power supply lines and pipelines, may interfere with mining operations
- Access restrictions due to mining activities to the dewatering infrastructure can result in significant downtime when trying to schedule repairs
- Space constraints within the pit mean that it may not be possible to site dewatering wells in the optimum location from a hydrogeological perspective
- Dewatering wells may result in the sterilization of ore, or as more often occurs mining of that ore will result in the destruction of the dewatering well.

The impact of these operational constraints on dewatering programmes mean that:

- Dewatering wells are frequently mined out and new wells need to be drilled, and dewatering infrastructure (pumps and pipelines) is repeatedly moved around the operation
- Dewatering wells do not operate at their optimum efficiency and therefore the dewatering programme is not as effective as it could be, resulting in wet operating conditions
- The use of vertical wells means that vertical structures, which may be controlling groundwater flow, are not intersected thus reducing the effectiveness of the dewatering programme.

In order to address the issues highlighted above Schlumberger Water Services (SWS) has developed its Dewatering Well Placement technology (DWPt). The approach integrates Schlumberger technology and expertise in subsurface characterization and well placement, developed through its position as the world's leading service provider to the Oil and Gas industry, with SWSs industry recognized expertise in mine dewatering (McCartney and Anderson 2015). Dewatering Well Placement technology has been developed over a 5 year period, backed by both SWS and industry funding, and has taken the approach from pilot trials, through proof concept and into operational implementation.

Directional Well Placement technology

Although directional well placement is commonplace in the oil and gas industry, it has been little used in mining apart from some specific coal mine fluid management applications, general related to Coal Bed Methane extraction. Its application in the hard rock geologic environment associated with most ore deposits provides many new challenges which need to be addressed. Central to development of DWPt has been the evaluation of the applicability of different drilling, surveying, measurement and well completion technologies to the mechanical and hydraulic constraints of different ore deposit settings. In order to ensure that DWPt offers the best dewatering solution for a given mine, SWS has developed an evaluation workflow which is implemented prior to initiation of any drilling programme. The workflow includes:

- A hydrogeological assessment of the suitability of DWPt to dewater the mine. This assessment reviews:
    - Ability of DWPt to intersect the main water bearing horizons and/or structures. DWPt provides a hydrogeological advantage where either vertical structures or lithologies act as conduits for groundwater flow, or where groundwater is compartmentalized by low permeability barriers to flow, such as dykes or sealed faults
    - A key advantage of DWPt is that the dewatering well is placed outside the final pit shell. However the well must be able to dewater the current pit and therefore understanding the hydrogeological connection between the current mining level and the DWPt trajectory is vital
- The directional well trajectory is designed with the objective of attaining the best possible hydraulic contact between the well and the ore deposit and is based on review and analysis of permeable fracture distributions inferred from fracture frequency, RQD and water strike data for the mine (Figure 2)
- The technical feasibility and cost associated with drilling and completing different trajectories needs to be assessed:
    - The time required to drill the well is a key control on overall costs as it will determine the time that the drill rig, plus associated directional drilling equipment and key staff, are onsite. Selection of appropriate drill bits and motors to help maximize Rate of Penetration (ROP) is a key element of the design
    - The design build up rate (BUR) of the well trajectory needs to balances the requirement to intersect specific hydrogeological targets and/or achieve a specific Total Vertical Depth (TVD) against the ability to install the completion, particularly the Electrical Submersible Pump (ESP), within the well
    - Measurement while drilling (MWD) is key to the ability to steer the well and to ensure that it intersects the horizons/structures that have been identified as controlling groundwater movement in the pit and reaches the targeted position beneath the final pit
- A comprehensive cost benefit and risk analysis is undertaken comparing both CAPEX and OPEX of the traditional in-mine approach to DWPt, as well as the risks associated with implementing a new drilling and dewatering approach at a particular mine site.

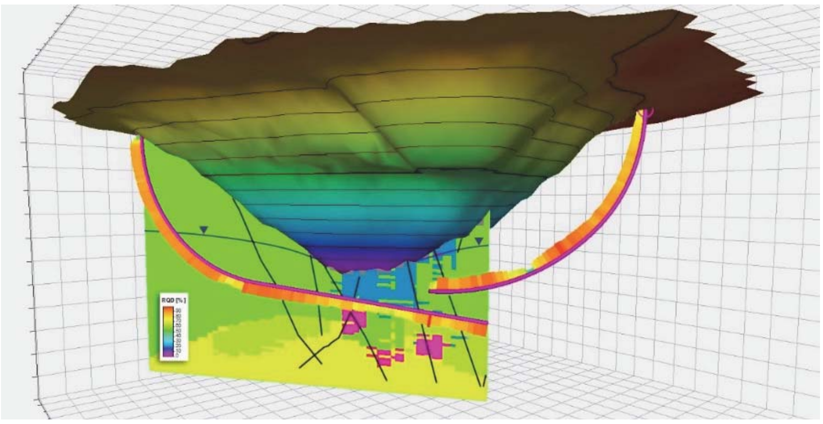

Figure 2 *Sub-surface geo-mechanical and fracture evaluation and simulation as part of dewatering well placement design process*

To date DWPt wells have been implemented at open pit mines in the USA and Mexico, while evaluation of its use is currently underway in a number of varying geological and geographical settings across the globe. Dewatering benefits that have already been reported from the first DWPt well include (Dowling and Rhys-Evans 2015):

- The well yield is five to ten times greater than previously installed in-mine wells
- The well was immediately commissioned into the active dewatering program and utilisation during its initial year was close to 100%
- The combination of its high production rate and year-long uninterrupted operation meant that it effectively produced two orders of magnitude more groundwater than any of the pre-existing in-mine vertical wells and it exceeded the combined groundwater production from the rest of the dewatering system, comprising six vertical production wells
- Drawdown of water levels was significantly enhanced in the pit area in response to operation of the DWPt well (Figure 3).

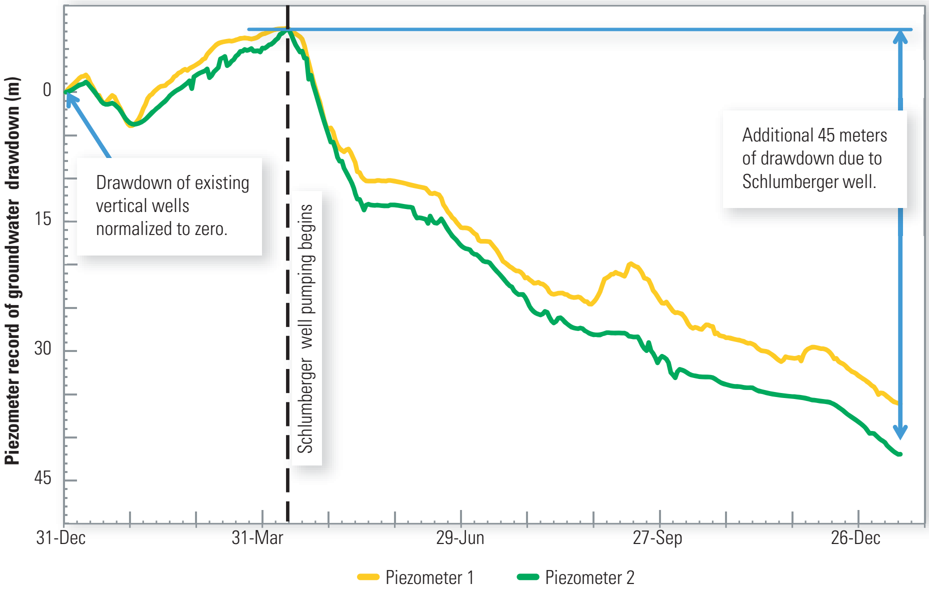

Figure 3 *Enhanced drawdown associated with implementation of a DWPt well at an open pit copper mine in North America*

Case study of DWPt evaluation: Sishen Mine, South Africa

GR35 project

The use of DWPt for dewatering the GR35 pit at Kumba Iron Ore's (KIO) Sishen Mine in the Northern Cape Province of South Africa was assessed from an initial pre-feasibility assessment of its hydrogeological benefits through to a fully costed design for implementation, with associated cost benefit and risk analysis. Application of the DWPt evaluation workflow to Sishen Mine allowed a number of aspects of the workflow to be further developed, including:

- The mine sites at which DWPt had been implemented in the USA and Mexico were located close to areas of O&G activity and therefore the service support required for implementation of DWPt was close at hand. The GR35 project tested the technical and cost risk associated with implementing DWPt in a mining area which is remote from O&G bases
- Specific "lessons learnt" from implementation of DWPt at other sites were evaluated within the Sishen project, in particular design elements around ROP/drill bit selection and borehole cleaning.

Background

Iron ore in the GR35 pit lies below the water table and is effectively sterilized without dewatering. Based on the mine plan the pit floor was to be lowered by 100m in approximately 15 months. The GR35 pit has been dewatered using vertical in-pit wells, however operational constraints meant that dewatering well utilization was approximately 60-80% (Nel 2015). The constrained nature of the pit also meant that wells are mined out quickly and there is limited space to site new wells, an issue which would become more prominent as the pit deepens and the pit floor area decreases.

An analysis of available hydrogeological data showed that:

- The size and frequency of water strikes was highly variable across the lithologies onsite
- Faults and diabase dykes result in compartmentalization of the groundwater system with stair stepping of water levels occurring across structures
- Major water strikes are associated with subvertical faults.

Dewatering wells target vertical faults but 2-4 dry wells were being drilled for each well that intersected a high yielding structure.

The aims for the DWPt well were:

- Placement of the wellhead on the pit rim and outside the final pit footprint
- Development of a DWPt trajectory that intersected permeable fractures beneath the final pit shell
- Placement of the pump at a depth below the final pit elevation such that water levels could be drawdown below the final pit floor.

Schlumberger's Petrel software was used to investigate the feasibility of different well trajectories for dewatering the GR35 pit. A hydro-geological conceptual model of the GR35 pit was developed in Petrel using:

- The Sishen geological block model
- The structural model for the GR35 pit, which showed the location of the main faults within/adjacent to the pit
- Water strike flow rate data; RQD data: An RQD block model, based on the same block size as the geological model, was developed for the GR35 pit using data from the Sishen geotechnical database.

A Petrel "plug in" allowed different well trajectories to be developed within the block model by varying the azimuth, inclination/BUR and metres drilled for different sections of the proposed borehole. The location for the wellhead, which was sited outside the final pit rim, was selected in consultation with the mine to optimise access to surface infrastructure including power and water pipelines. The well trajectory was then modified to review its feasibility with respect to a number of criteria, including:

- A maximum BUR of <6° per 30 m
- The production zone should extend below a final pit floor elevation of 862.5 masl
- The trajectory should avoid drilling along lithological contacts where possible as core data shows the rock quality to be poor along these boundaries
- Maximise drilling within the dolomite (DOL) units over the harder/more abrasive chert (MM/CH)/banded iron formation (BIF)/hematite (HEM) units
- Maximise the intersection of the well with zones of known or probable high groundwater flow, based on measured water strikes and RQD.

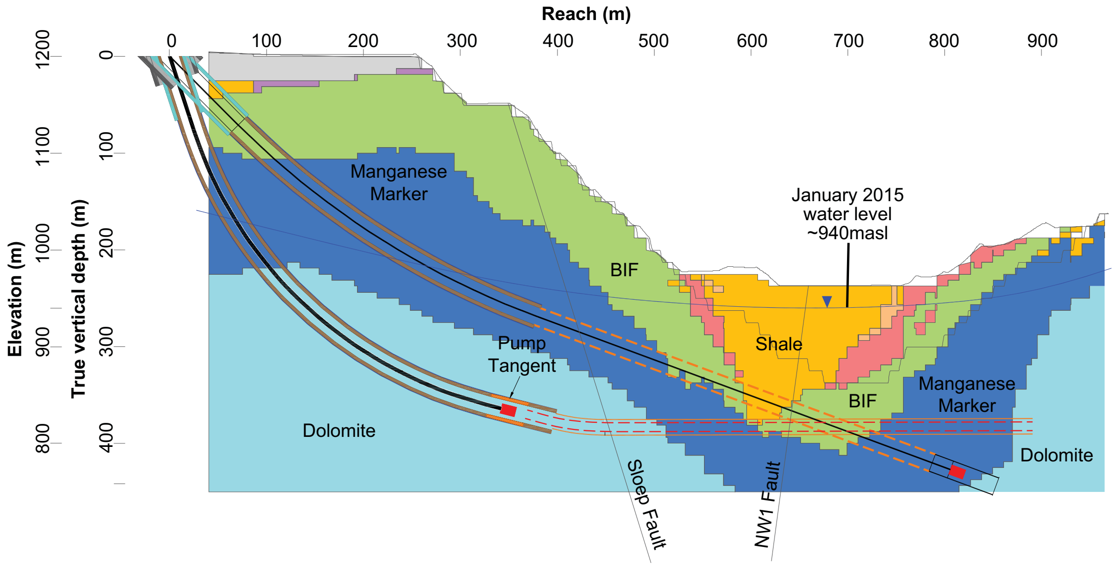

***Figure 4** DWPt well trajectories evaluated for dewatering of GR35 pit, Sishen Mine, South Africa*

The lithologies present at Sishen have UCS values which are significantly higher than those typically encountered during directional drilling in the oil and gas sector, or those encountered in previous DWPt projects executed in copper and gold mines in North America. As a result it was identified that selection of appropriate drill bits was a key project risk, as low Rates of Penetration (ROP) caused by use of inappropriate bits would significantly increase the time required to drill the well, and therefore the costs associated with rig and personnel hire.

In order to minimize the risk associated with this element of the programme the Smith IDEAS Laboratory in Houston, Texas was commissioned to carry out a series of tests on representative lithological samples from the Sishen mine in order to have site specific data available which could be used to evaluate the likely performance of different designs of drill bits. Samples of BIF, HEM, together with core samples of DOL and CH were sent to the testing laboratory (Figure 5). A series of tests were carried out to provide data on the effectiveness of standard Tungsten Carbide Inserts (TCI), commonly used on rollercone bits, and Grit Hot-pressed Insert (GHI) elements, commonly used on full-face Impreg bits. Drilling tests were carried out in the laboratory to assess the impact on ROP of varying the diamond size, concentration and substrate hardness in the GHI Insert.

Figure 5 *Laboratory drill bit testing of Sishen lithologies*

The laboratory test data were input to the Schlumberger Integrated Drillbit Design Platform (IDEAS) simulator to model ROP and select bits based on the lithologies and drilling diameters for the planned well trajectory. It should be noted that ROPs decrease by up to 70% during directional drilling (when building angle and sliding) and a correction factor is required to be applied for directional drilling sections when estimating total drilling time.

Cost benefit analysis

A cost benefit analysis was carried out to compare the cost associated with ongoing use of vertical in pit wells, and the cost associated with developing a dewatering programme based on implementing the DWPt well as designed for GR35. The cost benefit analysis compared both the Capex and Opex costs associated with implementation of the two different approaches, and also aimed to put a cost on the intangible benefits that will result from being able to implement the dewatering programme from outside the operational pit. The direct tangible costs compared for both approaches to include:

- Drilling costs associated with a DWPt well and the cost of drilling vertical wells which will provide the equivalent dewatering rate
- The cost of completing the two dewatering options, including the cost of casing the wells, installing pumps, connecting the pumps to both a power supply and into the water reticulation network
- Electricity costs for operation of both types of dewatering network
- Wet mining costs associated with ineffective dewatering based on site experience and data, including potential loss of revenue where benches cannot be mined.

Key intangible benefits which would result from implementing a DWPt approach to dewatering include:

- Reduction of interference to the mining operation and improvement of pit traffic movement due to removal of dewatering operations from the pit
- Improved in-pit operational conditions and ore recovery due to dewatering occurring in advance of mining
- Reduction in step outs, drilling pads and general space preparation and maintenance for in-pit dewatering infrastructure

- Simplified mine planning due to removal of the need to incorporate dewatering infrastructure and maintenance in pit
- Addition of 'ore body knowledge' gained from the information gained from the directional well trajectories, particularly with respect to the ore body beneath the current pit floor.

Although direct costs were easily compared, with those for the existing dewatering programme being available from the mines annual budget, and the costs for implementing the DWPt being compiled as part of evaluation workflow, intangible benefits are less easy to assign a cost saving to.

Conclusions

Implementation of DWPt at mines in the USA and Mexico has shown that these wells can provide a step change in dewatering impact through both increased yields from individual wells and utilization rates which approach 100%. The ability to site DWPt wells outside the final mine footprint, while at the same time placing the well production zone such that it can dewater the final pit shell, provides additional benefits in terms of reduced interference with mining from dewatering activities and development of dry conditions ahead of mine development.

The applicability of DWPt for dewatering the GR35 pit at Sishen iron ore mine, South Africa was evaluated using the workflow developed by SWS. The project provided the opportunity to assess the technical and financial challenges associated with implementing DWPt outside of North America, while specific aspects of the engineering design, including drill bit selection, were focused on based on "lessons learnt" from DWPt implementation at other sites.

Evaluation of DWPt showed it to be an appropriate approach for dewatering the GR35 pit, while the engineering design also demonstrated that it was technically feasible to complete the DWPt well within the high strength rocks present at Sishen. The risk analysis indicated that the mine location required significant contingency to be built-in to the availability of drilling equipment which had an associated impact on the cost of implementation. The cost benefit analysis indicated that the DWPt provided a viable alternative to the use of vertical in-mine wells. The cost benefit of DWPt was shown to increase the longer it operated, and was therefore considered to provide the greatest benefit where a greater Life of Mine remained.

Acknowledgements

Grateful thanks is given to Elaine Nel and Richard Carey for their introduction to the geology and hydrogeology of the Sishen Mine.

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Ghaghoo Mine Dewatering and Injection of Excess Water

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Abstract

Ghaghoo Mine is situated in the Central Kalahari Game Reserve in central Botswana. Ghaghoo is mining a Kimberlite pipe that vertically intruded into host sediments and basalts. The Kimberlite, sediments and basalts are overlain by 80m of unconsolidated and unsaturated aeolian Kalahari Sands. Regional groundwater level is 100m below surface in the fractured basaltic aquifer and the underlying dual porosity sedimentary aquifers.

In order to mine, Ghaghoo has to be dewater to a depth of 350m. The volumes from the dewatering exceed the mine water demand by 6500m^3/day and as a result the mine has an excess water balance. Ghaghoo is require to dispose of the excess water environmentally sustainable manor. The mine is situated 42km from the nearest settlement (outside the national park) and groundwater has a TDS of 7000mg/l making it unsuitable for domestic and agricultural purposes. The mine investigated a number of different options to manage the excess water and the most environmentally sustainable and economical option is to inject the water into the unsaturated Kalahari Sands. This paper discusses the hydrogeology of the dewatering operations and the injection of excess water.

Introduction

Botswana is world renowned for its diamonds with the majority being mined from large open cast pits in the vertical kimberlite pipes that have intruded into the host rock (Orapa, Jwaneng & Letlekane) These mines are significant contributors to the Botswana economy and provide employment and foreign revenue. A number of smaller kimberlites are now being developed in Botswana, including Ghaghoo being developed by Gem Diamonds. In the case of Ghaghoo, the kimberlite is overlain by 80m of unsaturated Kalahari Sands and as a result is an underground mine. The proposed Ghaghoo mining operations will extend below the regional groundwater level and as a result the mine has to be dewatered to ensure safe mining conditions. The volumes of groundwater from the dewatering operations exceed the mine requirements necessitating the handling of excess water.

Ghaghoo investigated a number of different options to dispose of excess water consisting of evaporation and forced evaporation, constructed wetlands, water treatment for agriculture and/or domestic supplies and game watering. The most economical and environmentally sustainable option, given Ghaghoo's location, is to inject the groundwater back into the unsaturated Kalahari Sands. Ghaghoo has been granted permission by the Botswana Ministry of Water to undertake a pilot study of the injection process.

The mine plans to mine to a depth of 350m below surface some 250m below regional groundwater level. The Kimberlite is 15ha in extent and consist of 2 lobes, an outer and the richer inner lobe which will be mined for 10 years at a rate of 60 000 ton/month. The mine will be required to dispose of 6500m^3/day over a 10 year life of mine with an estimated total volumes of 23,75 M m^3 of water.

The initial desk top investigation proved that the Kalahari's Sands have sufficient storage capacity for the dewatering volumes, without excessive recirculation and the water will gradually be released back into the underlying aquifer.

Location and Physiography

Ghaghoo is situated 40km west of the eastern boundary of the Central Kalahari Game Reserve (CKGR) in Central Botswana and about 360km north west of the capital city Gaborone (figure 1).The area is on average 1000 mamsl (ranging from 985to 1033mamsl) and is very flat, with minor changes in topography being related remnant dunes. There are no significant drainage systems due to the topography and the thick unsaturated sands. The area experiences summer rainfall and cold dry winters. Mean annual rainfall is 350 mm/annum and the potential evapotranspiration is 1 825mm/annum. Numerous studies have been undertaken to determine the rate of rainfall related recharge in the area (De Vries & Von Hoyer 1998).The studies conclude that very limited rainfall related recharge occurs in areas of excess unsaturated Kalahari sand cover.

The Ghaghoo mining lease area is 4400ha and is situated in the CKGR which is a national game reserve. Permit conditions stipulate that any mining associated activities have to be undertaken within the mining lease area. As a result the injection system must be within the mining lease area which necessitated the development of a preliminary groundwater model to determine potential recirculation of water back to the mine.

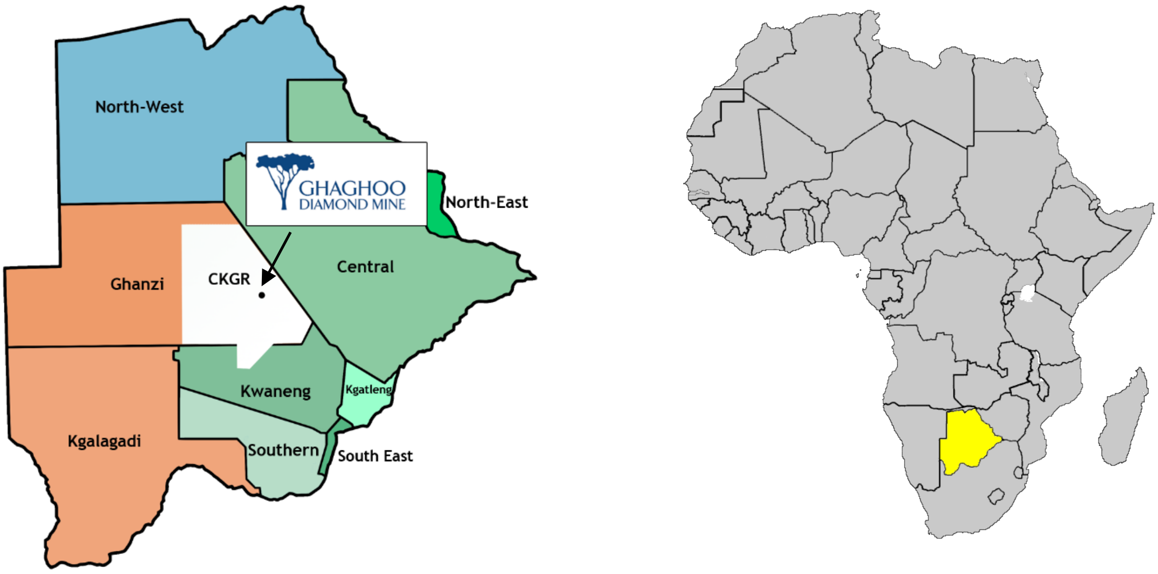


Figure 1: *Locality of Ghaghoo Mine in Botswana*

Hydrogeology

The hydrogeology of Ghaghoo consists of unconsolidated and unsaturated Kalahari sediments to a depth of 80 m below surface, which are underlain by saturated fractured basalt from 80 to 260m below surface and which is in turn underlain by sediments of the dual porosity confined Ntane formation from 260 to 340m below surface. The lithostratigraphy of the Ghaghoo area is shown in Table 1. The exact recharge mechanism in the Central Kalahari has been studied by De Vries JJ & Von Hoyer M (1988) and the general consensus is that very little recharge occurs due to the climatic conditions and the thickness of sand cover. The Kalahari sand cover increases in thickness from east to west. Groundwater gradients and an increase in the salinity of the groundwater occurs from east to west, further supporting the theory that the majority of recharge occurs in the outcrop areas in the east.

The Stormberg basalt is a typical fractured rock aquifer with zones of secondary permeability and storage being associated with fractures, faults and geological contacts. The Ntane aquifer is an important aquifer in Botswana and supports a number of wellfields. The Ntane aquifer at Ghaghoo is confined and has dual porosity, with the primary porosity being associated with the poorly cemented aeolian sand and the secondary porosity being associated with post deposition faults and fractures and contact zones of kimberlite or dolerite intrusions.

Table 1: *Lithostratigraphy of Ghaghoo Area.*

Supergroup	Group	Formation	Lithological Description
-	Kalahari	Kalahari Beds	Loose sands, calcrete layers, calcareous sandstone and mudstone
Karoo	Stormberg	Ramoselwana Volcanics	Crystalline, massive amygdaloidal basalts
	Lebung	Ntane	Fine to medium grained, clean, friable sandstone. Often calcretised in zones
		Mosolotsane	Red/brown greenish mudstones and siltstones with fine to medium, occasionally coarse intercalated sandstone. Basal conglomerate in places.
	Ecca	Marakwena	Conglomerate and sandstone intercalated with silty mudstone
		Tale	Fine-grained meta-arkoses, shale and minor sandstone
Damara	-	Kgwebe	Porphyry, felsite's, diabase and tuffaceous sandstone
		Ghanzi	Sandstone, siltstones quartzite's and minor carbonates

The ambient groundwater quality at Ghaghoo has a TDS of 7000 mg/l and can be classed as a sodium chloride water. The raw water is used in the processing plant and for domestic consumption after being purified by means of reverse osmosis. The ambient groundwater quality is shown in Table 2.

Table 2: *Ghaghoo Ambient Groundwater Quality*

Parameters		Unit	Value
- pH	pH	pH unit	7.62
- Electrical Conductivity	EC	mS/m	1104
- Total Dissolved Solids	TDS	mg/L	7006
- Total Alkalinity	T-Alk	mg $CaCO_3$/L	64
- Bicarbonate	HCO_3	mg/L	78.1
- Carbonate	•CO_3	mg/L	0
- Total Hardness	T-Hard	mg $CaCO_3$/L	1170
- Calcium Hardness	Ca-Hard	mg $CaCO_3$/L	1110
- Calcium	Ca	mg/L	444
- Magnesium	Mg	mg/L	14.6
- Potassium	K	mg/L	10.5
- Sodium	Na	mg/L	2182
- Sulphate	SO_4	mg/L	810.55
- Chloride	Cl	mg/L	3249.3
- Fluoride	F	mg/L	0.598
- Orthophosphophate	PO_4 as P	mg/L	0.003
- Iron	Fe	mg/L	3.45
- Manganese	Mn	mg/L	0.36
- Nitrate as NO_3	NO_3 as NO_3	mg/L	0.638

Dewatering and Injection

Dewatering will occur from the confined Ntane Sandstone from a series of bores which will terminate in the relatively impermeable Mosolotsane formation. The Ntane will be targeted for the dewatering bores due to the high yield of bores in this aquifer. As the Ntane is depressurized water levels in the overlying basalt will decline. Boreholes will be sited to intersect post deposition fracture zones both in the basalt and the underlying sandstone. These bores will pump to a central reservoir from where the water will be pumped to the injection wells downgradient of the mining area. This is graphically presented in Figure 2.

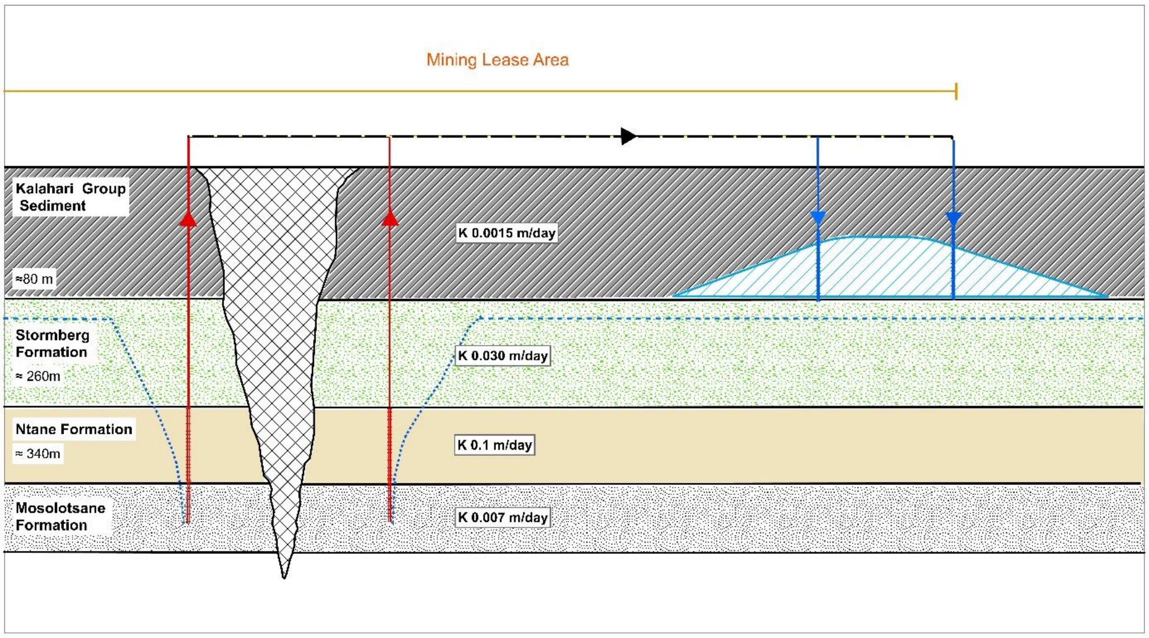


Figure 2: *Schematic of the Dewatering and Injection System*

The unsaturated Kalahari Sands has an average storage of capacity of 20% and is some 3 orders of magnitude greater that the confined Ntane Sandstone (s= 0.0001). This will result in substantially less volume of Kalahari sands being statured for the same volumes of dewatering of the Ntane and basalt aquifers.

In order to determine the potential recirculation of water and to comply with the mining permit conditions, preliminary groundwater model simulations were undertaken with the injection wells downgradient, and along the western boundary of the mine lease area in two configurations as shown in Figure 4. The simulations were run for a period of 10 years to determine the mound and the potential for recirculation into the mine dewatering bores. The mathematical simulations indicate that very limited volumes of water will be recirculated via the Kalahari Sands. The dewatering operations are however going to dewater the basalts around the mine and future investigations will have focus on the leakage through the basalt into the Ntane aquifer and recirculation into the mine dewatering system.

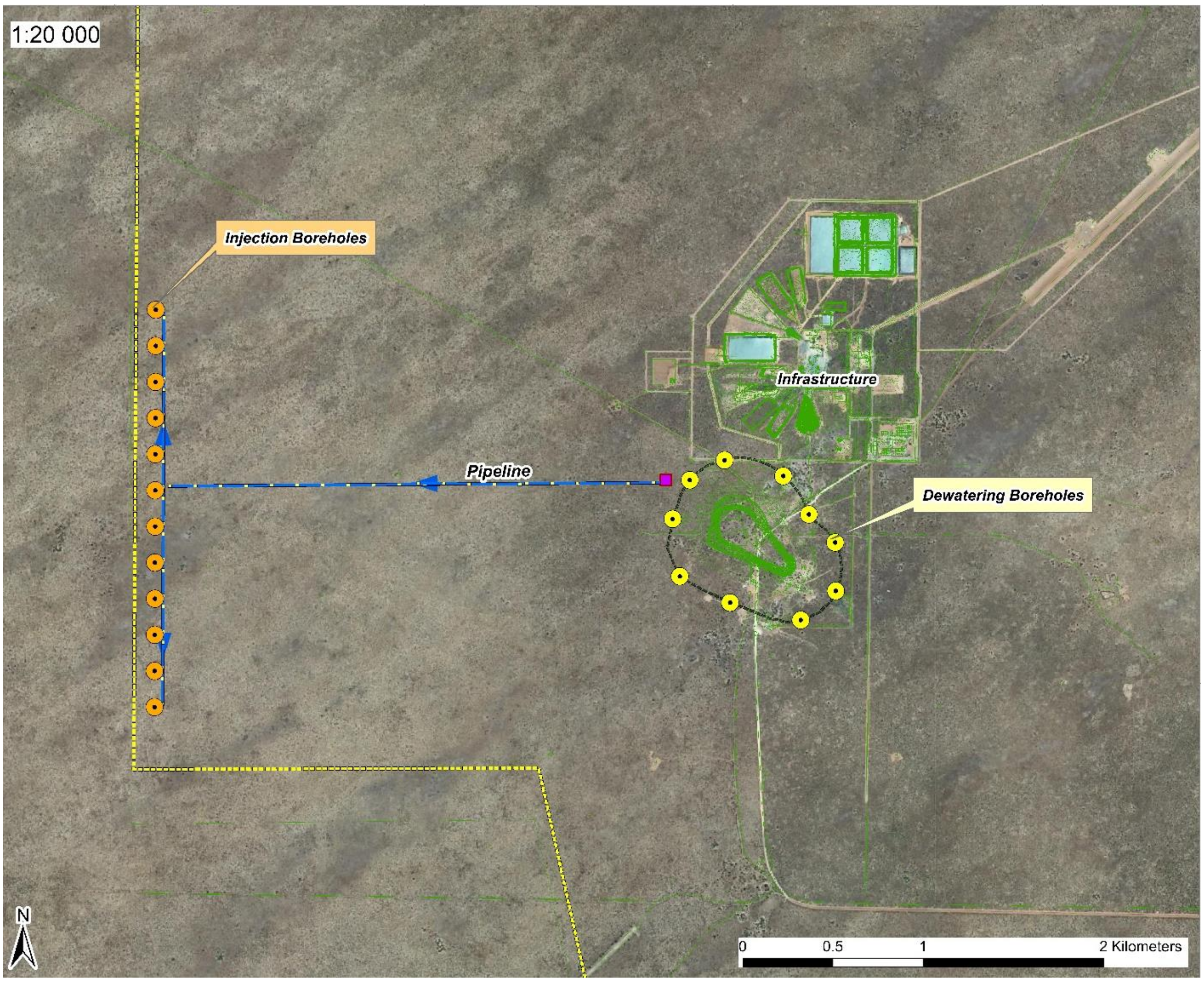
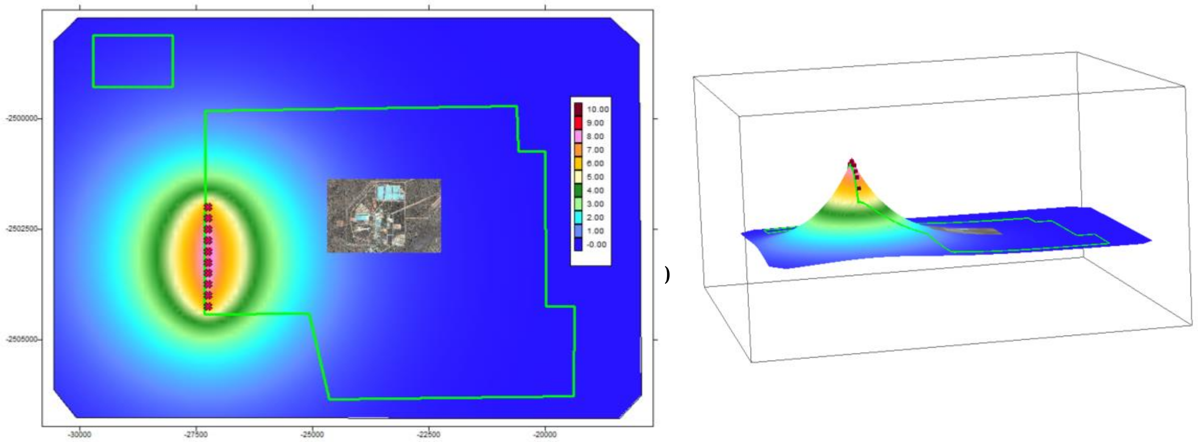


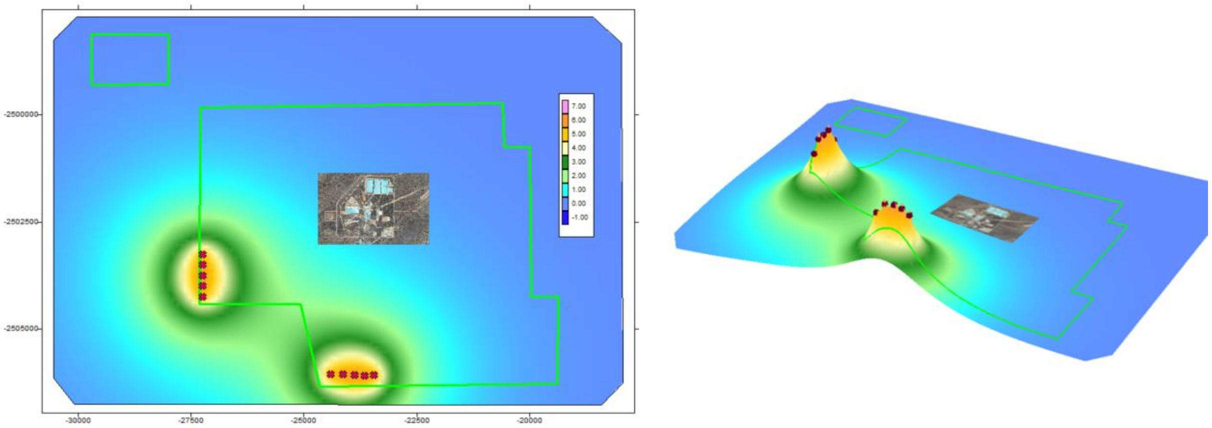
Figure 3: *Schematic layout Dewatering and Injection Systems*

The mathematical simulations of the mounding were undertaken using the Theis equation. Aquifer hydraulic properties were taken from previous groundwater investigations and geotechnical studies (figure 4).The pilot injection study will consist of a number of injection wells and monitoring piezometers to determine the injections rates at different pressures. This will provide additional information relating injections rates, number of bores required to dispose of the excess water. In addition the pilot test will allow for the determination of geometry of the groundwater mound.

The dewatering rates required to ensure dry mining will be determined by groundwater model and the mine plan. This data will then be combined with the mine plan and associated dewatering requirements.



Scenario 1: Single injection system after 10 years



Scenario 2: Western and Southern Injection System

***Figure 4:** Simulated Groundwater Mounds*

Conclusions

Ghaghoo mine must dewater to allow for mining and safe mining conditions. The most economical and environmentally sustainable method of disposing of the excess water is to pump directly from the dewatering wells into an injection system in the unsaturated Kalahari Sands. The sands have sufficient capacity to store and then release the groundwater from the dewatering operation back into the aquifer over time.

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Cut-off Wall Technologies in Mining

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Abstract

Cut-off wall technologies are widely used in civil engineering, in dam and dike construction, for temporary and permanent groundwater barriers. Innovative construction methods and cut-off wall equipment have been developed over the last 40 years and grow the application of cut-off walls to a large variety of construction sites with vastly different constraints and subsurface conditions, both in civil and in mining related projects. Also in environmental cases cut-off walls are used to enclose contaminated areas or to direct contaminated ground water to a central water treatment facility.

During the construction of deep foundations in groundwater bearing strata or for the construction of e.g. concrete dams with powerhouses in river beds, temporary cut-off walls in coffer dams are commonly used to minimize dewatering efforts during the construction phase. Permanent cut-off walls form a seepage barrier in or underneath new built dams, but also in existing dams which needs to be remediated against seepage through the dam itself or through the foundation under the dam and the consequences of such seepage. Permanent cut-off walls are also used in dikes where temporary flood events with high seepage and underflow, risk the overall dike stability.

In mining, such systems are more and more applied due to their proven, long term reliability and due to the increase in mine safety regulations. Cut-off systems minimize the influx of ground water or surface water into open-pit mines, allow the development of open-pit mines extending from onshore into nearby lakes or even oceans. Since more and more low grade deposits are mined with higher volumes of tailings and higher grades of toxic materials in the treated tailings, cut-off walls in tailings dams become necessary to mitigate the risk of mine water to contaminate nearby ground water systems and surface waters and minimize the amount of seepage water to be treated before release to the environment. Cut-off walls may also help to achieve better acceptance of tailings ponds from the authorities and the public which are very critical towards mining and its tailings dams after various collapses of tailing dams in recent history.

Key words: cut-off wall, mining, tailings dam, ground water flow, seepage

1. Water Dams versus Mine Tailing Dams

Tailings dams and water dams are designed for fundamental differences from construction til closure.

* Tailings dam must safely contain tailings and process water with various contaminants. Water dams contain water only.
* Active operational life time of a tailings dam is for about 10 to 30 years. Water dams are designed for about 100 years and more
* After Mine closure, tailings ponds still have to safely contain the tailings for perpetuity. After the closure of water dams, the water is released without any further safety concerns.
* Construction of tailings dams happens normally in stages over the life of a mine. Construction of water dams is in one construction phase.

2. Classification of risks for tailings dams

Tailings dams are exposed to risks which can cause severe consequences to the environment, not only in the case of failure, but also in case of uncontrolled seepage or Acid Mine Drainage AMD.

* Internal instability due to design mistakes, improper construction or unsuitable materials used in construction
* Long term erosion of the dam body by seepage with piping effect
* Instability by overloading with tailings and mine water
* Instability caused by flooding and overflow
* Instability caused by leakage through the foundation of the dam with piping effect
* Instability caused by settlements of the foundation
* Instability caused by seismic events
* Instability due to chemical reaction between the cutoff medium and the contaminants

To minimize most of the risks listed above, a positive tailor made cut-off wall in relation to erosion stability, chemical stability, permeability and flexibility is the solution of choice.

3. Cut-off wall systems

Depending on the soil formations encountered, the design depth of the wall as well as the requirements for erosion stability a selection of different cut-off wall systems is available. Key to any successful, economic cut-off system is the optimum installation performance including the successful key-in at the bottom of the wall into a low-permeability soil or rock formation. The COW mix design can be tailor made to achieve the required permeability which normally is in the order of 10-8 m/sec. Cut of walls can also be designed as flexible walls to accommodate expected dike settlements and the like.

Excavation equipment	**Long reach excavator**	**Soil Mixing Systems**	**Hydraulic grab**	**Trench cutter**
Cut-off system	Soil Bentonite Wall	Soil Bentonite Wall	Soil Bentonite Wall	Soil Bentonite Wall
		Soil Cement Bentonite Wall		
			Cement Bentonite Wall	
			2-Phase COW	2-Phase COW
Depth	25 m	60 m	80 m	150 m
Soil strength UCS	0-10 MPa	0-30 MPa	0-25 MPa	0-100 MPa
Boulders / Obstructions	small	small	medium	all
Rock socketing	no	yes	no, only with chisel	yes

Figure 1 *Cut-off wall systems*

3.1. Soil Bentonite Cut-off Wall

In soft formations and for shallow Cut-off walls (COW) with low hydraulic gradients soil bentonite walls are very cost effective and therefor frequently installed. Up to a depth of about 25 m, back-hoe excavators with a long reach boom are used for digging. For greater depth and when obstructions or hard layers are encountered, mechanical or hydraulic grabs are very effective. Under normal conditions the thickness of the wall is between 30 and 100 cm. Excavation takes place by simultaneously back filling of bentonite slurry properly mixed ideally with the excavated material into the trench. The excavated soil is dumped on the ground next to the trench, sprayed with bentonite slurry, homogenized by a dozer walking across and then pushed back into the trench. Other mixing methods may provide an even better result. The low permeability of the cutoff results primarily from the native clay and the bentonite in the backfill mixture. Secondarily, low permeability results from the development of a bentonite "filter cake" on each wall of the trench and from slurry entering the voids of the formation adjacent to the trench.

A key factor in selecting the Soil Bentonite cutoff is economics, especially when the excavated material can be used to backfill the trench. This avoids trucking and only a small amount of bentonite needs to be added. Soil bentonite walls have proven to be effective seepage barriers on various projects.

Soil-Bentonite Cut-off wall for lignite mine, Vattenfall, Welzow, Germany

The mining of the lignite started almost 200 years ago. To enable open pit mining, a suitable dewatering system was required. At first, wells and drainage system were used. With the increasing demand to go deeper to enable full use of the existing resources a decision taken back in the 60th of the last century, the amount of water which had to be pumped increased dramatically. In peak times, approx. 1.2 billion m³/year had to be pumped. This led to a lowering of the groundwater level for up to 70 m, impacting the regional lake landscape. In order to reduce the influence on the water balance, and bring the water level back to pre1970th, a first development took place to implement the use of specific COW system to depth of about 45m. Nowadays the surrounding ground water level can be kept unchanged with the use of such COW.

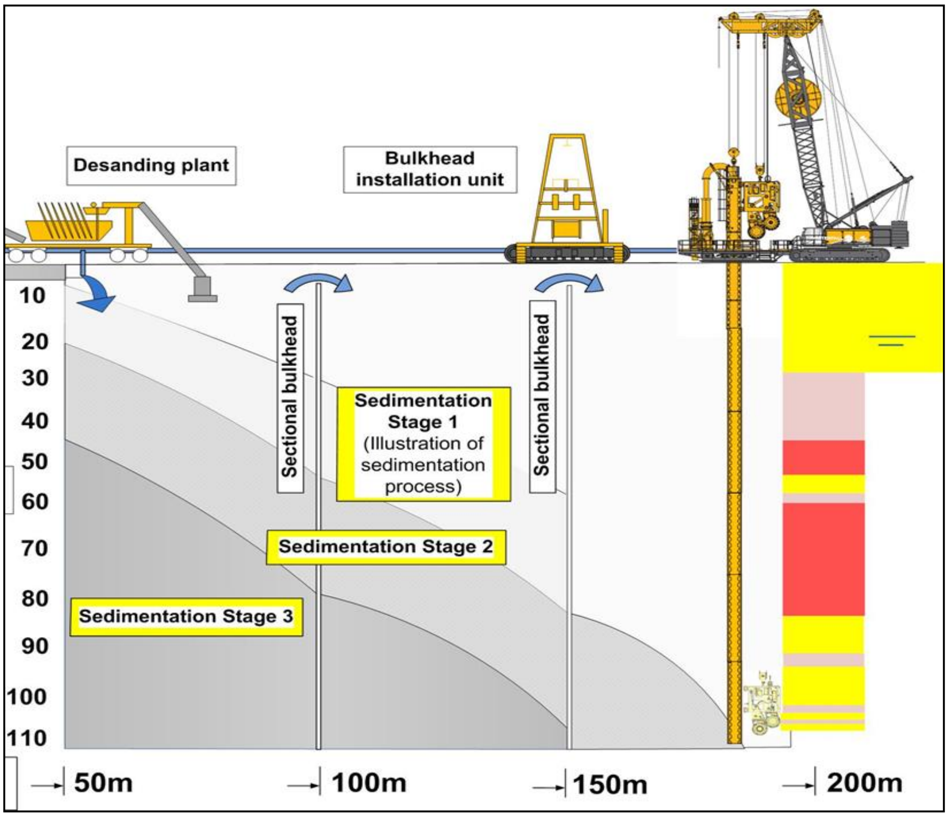

Figure 2: *Pile guided Trench Cutter Cut-off wall systems*

The pile-guided trench cutting system is a worldwide unique technique, originally developed by the engineers of the mining companies themselves. It guarantees a continuous, joint free, COW during a continuous installation process. At this specific site in Welzow, this technique has been pushed to new limits in order to address the local lake region. Depth capability has been designed to about 130m at a constant trench width of 1000 mm. This project has an approximately 11 km long COW, scheduled to be completed in a construction period of 12 years.

The system flushes special clay which forms a filter crust at the inner surface of the trench. Only natural clay resources are used, in order to achieve the cut-off effect. The effectiveness of the continuous COW construction process is based on the formation of a filter cake on both sides of the trench. Continuously, a mixture of natural clay, so called "Friedländer Blauton", and water are pumped into the fresh excavated trench. The slurry initially stabilizes the open trench according to the demands of the trench stability calculation.

Figure 3: *BAUER BCV 40 – 130 on MC 128*

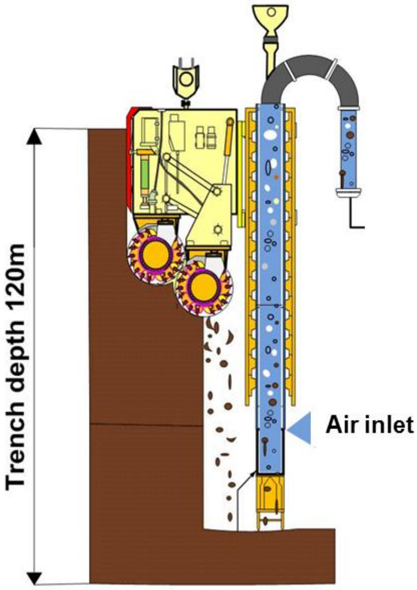

Figure 4: *Guide pile and Cutter BCV 40*

Depending on the geology met, the density varies in a range of 1.1 – 1.2 g/cm³. At the same time the slurry penetrates into the pores and the clay particles adsorbs at the trench wall surface. Already after a few minutes the filter cake then starts to grow, and a 2.5 – 5 cm thick filter cake, which is nearly impermeable, is formed after approximately three hours. The full process takes about 20 hours. Thereafter the trench will be backfilled with the screened excavation material, partially displacing the slurry in the trench over the bulk heads.

3.2. Cement Bentonite Cut-off wall

For projects with higher hydraulic gradients, erosion in soil bentonite walls may occur, leading to piping effects and instability of the dike. In such cases a cement bentonite wall, excavated by an hydraulic grab, is a suitable solution. Premixed bentonite slurry is mixed with cement and then pumped to the excavation, where it stabilizes the trench and then forms an erosion resistant membrane. Excavation by grab is performed in primary and overlapping secondary panels wet-in wet, which guaranties integrity of the of the cut off system. For harder soils, sometimes with boulders, hydraulic grabs are preferred over mechanical grab to securely achieve the required penetration depth and socketing into the specified impermeable layer. After completion of the excavation, the cement causes the slurry to harden to a strength comparable to that of a stiff clay. The cement-bentonite slurry contains no aggregate other than some suspended soil particles from the excavation process, Strength and plasticity of the hardened cement-bentonite slurry will vary, depending mostly on the cement/water ratio and the type of cement, with higher strengths having lower plasticity. The permeability of C-B cutoff walls depends on the proportions of bentonite, cement and sometimes filler used in the mix.

Cement-Attapulgite Cut-off wall, Namdeb, Pocket beaches, Namibia

The on-shore pocket beaches along the shore line of Namibia between Oranjemund and Luederitz, the so-called Sperrgebiet, are mined by DeBeers and later on Namdeb since first discovery of diamonds in 1908. Meanwhile most of the onshore alluvial deposits are mined out.

Figure 5: *Pocket beach mining area*

Figure 6: *Bogenfels*

The beach is pushed out further and further into the Atlantic ocean to allow open pit mining behind so called seawalls in dewatered pits even in areas which had been under water till now. The system however reaches its limits with the increasing water depth behind the seawall.

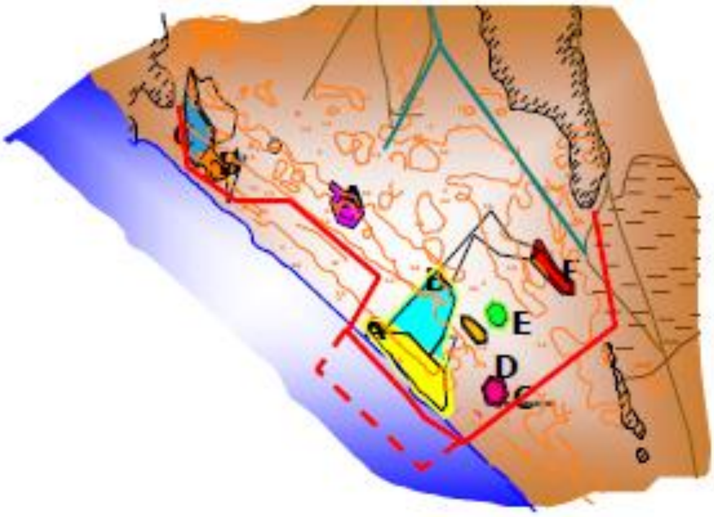

Figure 7: *Mining area with hot spots and cut-off walls*

To allow open pit mining in the dry of the diamond rich pocket beaches in vicinity of the Bogenfels, the mining area and the seawalls had to be sealed with a bentonite-cement cut-off wall to a depth of 25 m.

The design asked for a 400 mm wide cut-off wall and a slurry mix consisting of

2 x 40 kg Attapulgite
50 kg Cement
3 x 50 kg Slagment
900 kg Seawater

Since no fresh water was available in this very remote arid area, seawater directly pumped from the Atlantic had been used for the slurry mix. To achieve the required properties Attapulgite had to be used instead of bentonite, which also forms gel structures when mixed with salt water. The fresh slurry finally had a density of around 1,20 kg/dm³ and reached a compressive strength of 1,2 N/mm² after 35 days. Excavation of sections of the completed wall showed a final wall thickness of around 45 cm.

Figure 8: *Cut-off wall installation BAUER GB 60*

Figure 9: *Excavated cut-off wall*

In total approximately 54.600 m² Attapulgite-bentonite cut-off wall had been installed over a length of approximately 3000 m to allow for the safe mining of the diamond hot-spots in the Bogenfels area over a period of 2 years, including waiting periods when moving the dredger from one mining spot to the next.

3.3. Soil Mixing Wall

To minimize or even prevent disposal of excavated material during cut-off wall construction and to minimize the amount of self-hardening slurry used, active soil mixing systems are nowadays state of the art technology. Best results in quality and performance can be achieved in uniform soil formations. Limitations of the systems are in difficult, mixed soils with boulders and hard soils and rocks.

The BAUER Cutter Soil Mixing (CSM) system is technologically the most advanced system, using a modified trench cutter technique for constructing a cut-off wall. Deep Auger Mixing Systems are also frequently used but face various limitations compared to CSM.

The two counter rotating CSM cutter wheels penetrate into the ground at a continuous rate. The soil matrix is broken up by the cutting wheels and at the same time a fluid is pumped to the nozzles set between the cutting wheels, where it is mixed thoroughly with the loosened soil. Adding a compressed air stream can improve the breaking and mixing process in the down stream phase. The rotating cutter wheels cutter teeth push the soil particles through vertically mounted shear plates with the effect of a compulsory mixer. The penetration speed of the cutter and the volume of fluid pumped in are adjusted by the operator to create a homogeneous, plastic soil mass which permits easy penetration and extraction of the machine.

Having reached the design depth, the soil mixing cutter is slowly extracted while cement slurry is continuously added. Homogenization of the liquefied soil mixture is ensured by the rotation of the cutter wheels. A continuous wall is formed in a series of overlapping primary and secondary panels. Overcutting into fresh adjacent panels is called «fresh-in fresh method», but also the «hard-in-hard method» is possible, whereby the panel is cut into already hardened primary panels

For greater depth a two-phase system is recommended with bentonite only slurry introduced during lowering the cutter and cement slurry is added and mixed with the soil cuttings during retrieval of the cutter.

CSM wall, Herbert Hoover Dike, Lake Okeechobee, Florida, USA

The Herbert Hoover Dike (HHD) is a 143-mile earth dam that surrounds Lake Okeechobee, the heart of the Kissimmee-Okeechobee-Everglades system. The dam was built after several devastating hurricanes with flooding in the period from 1930 to 1937.

Figure 10: *Hurricane 1928*

The project reduces impacts from flooding as a result of high lake levels for a large area of south Florida. Since 2007, the Army Corps of Engineers has made a significant investment of over $500 million, in projects designed to reduce the risk of catastrophic failure of the aging structure. Actions taken include the installing of a partial cutoff wall in several dike sections which helps reduce the risk of failure by eliminating existing piping and preventing additional internal erosion through the dike and foundation. The rehabilitation is still ongoing in several sections and is planned to be completed in 2021.

Prior to the installation of the soil mixing wall bigger lenses with peat in the upper half of the wall had to be predrilled and the peat removed since the organic ingredients of the peat prevent the cement in the slurry from hardening and thus having a cut-off wall with open windows.

Figure 11: *CSM installation with RG 25 S*

Figure 12: *BCM 5 CSM Cutter wheel assembly*

Installation of 5,6 km, 640 mm wide cut-off wall was executed with two BAUER BCM 5 on base carrier BAUER BG 28 and on RTG RG 25 S, a cutter with 5 tom torque on each cutter wheel 2013 and 2014 to a maximum depth of 17 m. The slurry introduced consisted of a mix of slagment and bentonite with a compressive strength between 0,7 and 3,5 MPa and a permeability of 1 x 10-8 m/sec.

3.4. Two-phase Cut-off Wall

For great depth and difficult soil and rock conditions, the two phase cut-off wall is recommended, where excavation takes place under bentonite slurry to final trench depth and replacing the slurry in tremie method by a lean concrete mixed to special properties for each project in regards to permeability, erosion stability and plasticity.

Depending on depth and also on the soil conditions, which may constitute a risk to verticality, the width of the Cut-off wall can be selected from 800 mm to 2000 mm. Modern cutter systems can be equipped with hose winding systems which can reach down up to 250 m. Trench cutter can be fitted with various type teeth to penetrate different soils as well as boulder and rock and are best suited to achieve a proper seal at the bottom of the wall penetrating sufficiently into pre-determined low permeable layers. The over-cut joint system between primary and secondary panels is an excellent system to minimize leakage through the joints even for extremely deep cut-off walls.

Two-Phase Cut-off wall, Teck Cominco, Red Dog Zinc Mine, Alaska

To extend the life of the Red Dog Mine for another 20 years by mining the so called Aqqaluk Deposit also the capacity of the tailings pond needed to be heightened by about 10 m and forced by tightened mine regulations seepage through the foundation minimized.

Figure 13: *Red Dog Mine, Alaska*

Due to the arctic conditions on site and the limited access by sea and road for only 100 days a year, three arctic summers were needed to execute 53.300 m² cut-off wall in hard rock conditions over a length of 1500 m, with a wall thickness of 800 mm. Due to the ph value of 3,5 of the mine water in the pond, with high concentrations of heavy minerals and other chemicals, seating into the shale rock base was mandatory. Also to avoid any seepage, even in case of melting of the permafrost, the wall had to be socketed in competent rock, which was specified as 1 m core length with maximum one visible crack, to a depth of 48 m and UCS of more than 150 MPa. In consequence quite a number of panels had to be seated 25 m deep into fairly hard rock.

Grouting was no options, since the voids and cracks are filled with frozen water in permafrost which cannot be replaced by grout.

Figure 14: *Cut-off wall installation with cutter BC 40*

3.5. Sheet-pile walls

Due to their easy and fast installation, but limited depth reach to about 30 m, sheet piles are often used as temporary barrier during construction in water like harbor and bridge foundation construction, but can be re-used several times. In areas with limited space, sheet pile walls are quite common for flood water protection in dikes or instead of dikes.

Figure 15: *Construction of a ship lock near Quitzöbel, Germany.*
Sheet pile installation with RTG RG 19T and Top Vibrator MR 105 V

Sheet pile wall, Waikaia Alluvial Gold Mine, Northern Southland, New Zealand

In rare cases sheet piles are used also in mining applications to allow for easier dewatering or minimizing water influx into mining cells.
The Waikaia Gold mine in New Zealand sits in a environmentally very sensitive tourist area with very high ground water table along the Waikaia river which is also famous for trout fishing and gold panning. The Waikaia valley was first panned for gold in the early 1860s and up to eight dredges operated by the early-1900s.
Sited in mining cells a few hundred meters from the Waikaia River, a recovery plant floats in a pit up to 16m deep, surrounded by vertical sheet piles up to 19 m deep, installed by RTG RG 19T with top vibrator MR 100 to minimize ground water seepage and protect from flooding. The floating plant is fed with ore by an excavator and the tailings are fed back ashore. The pit water is pumped to settling ponds, to remove solids, before going into the Waikaia river.

Figure 16: *Sheet pile installation with RG 19T*

Figure 17: *Mining area with settling ponds*

5 million cubic meters of gold bearing gravels and 17 million cubic meters of overburden will be mined by Waikaia Gold Ltd over the 7.5 year mine life producing approximately 145,000 oz of gold. After annually removing 2 million to 3 million cubic meters of topsoil and gravel, which is then used as backfill as the pit is dug and sheet piled further up the mining cell, about 700,000 cu m will be

processed through the floating plant every year. Once the mining cell is backfilled, the sheet piles are recovered with the same rig as for installation and used for construction of the next mining cell again.

Figure18: *Floating recovery plant*

Over the seven to eight-year mine-life, the mine site will work its way about 5km upstream, then be shifted across the road to an adjacent stream, and might be shifted back downstream on the other side of the Waikaia River.

Conclusions

To achieve best results to minimize seepage into and out of mines and tailings ponds, cut-off walls are the best systems available to protect the mines and the environment. With various systems shown, the cut-off wall design can be optimized to every single mine in regard to seepage control and cost-efficiency.

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Wellbore Skin in Mine Dewatering and Drinking Water Supply: Field Observation, Mineralogy and Hydraulic Effect

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Abstract

When it comes to well loss and efficiency, the occurrence of wellbore skin layers is one of the strongest influencing factors. Besides difficulties to remove the skin layer that is necessary during the drilling process, it is also not easily possible to determine if a skin layer is present in a well and whether or not it imposes a certain degree of well loss.

With this work, three types of skin layers are presented (surface cake, deep-bed filtration, layered cake in the aquifer), that have been observed at dewatering wells excavated in open-pits of the Rhenish lignite mining district in western Germany. Disturbed and undisturbed samples were analyzed for their geochemical and mineralogical composition in order to better understand the formation of the skin layer types and their fate during well operation.

Geochemical analysis revealed the skin layer to be mainly composed of quartz (≈ 40 wt-%), kaolinite/illite (≈ 30 wt-%), organic material (5-15 %) and secondary gypsum precipitates (up to 12.5 wt-%). Despite the high quartz contents, the granulometry yields high fractions of clay and silt (75-85 %). However, preferential flow paths, transecting the skin layer are created by micro-cracks and erosion-pathways which will cause a higher hydraulic conductivity than could be expected from the granulometry.

Key words: Wellbore Skin Layer, Well Loss, Drilling Mud Cake, Well Efficiency Optimisation, Mechanical Clogging, Particle Filtration, Formation Damage

Introduction

As several authors have concluded in recent literature, wellbore skin is a phenomenon that profoundly affects head losses of a well (Klauder 2010, Houben 2015a, b). Wellbore skin forms during water well drilling, when the drilling fluid infiltrates into the aquifer. Fine particles of the drilling mud (additives like bentonite or fines taken up from the penetrated layers) that cannot enter the pores of the aquifer are retained on the borehole wall. During the drilling process, especially in unconsolidated rocks, the formation of this thin but barely permeable layer is necessary to prevent major losses of drilling fluid into the aquifer and to ensure stability of the borehole. During the later well operation, however, the pressure loss resulting from a skin layer can easily reach values as high as the one of the surrounding aquifer itself (Houben 2015a, b).

It is thus all the more surprising, how little information can be found in the literature on the composition, hydraulic properties and mineralogy of such skin layers, based on actual field measurements or observations. Yeh and Chen (2007) even claim that direct measurements of skin thickness or other parameters are not possible at all. Most of the sparse experimental data available originates from drilling operations in the petroleum industry, which works under different p-T-conditions and generally applies several kinds of additives (Durand et al. 1996, Salehi et al. 2014) so these results are of limited comparability to water well applications.

This study now focuses on descriptions and (undisturbed) sampling of skin layers, observed in water wells for open-pit dewatering as well as drinking water supply, where different types of skin layers should be expected. As wells for drinking water supply are generally constructed to last as long as possible – with service lives of up to 50 years – huge efforts are invested in a proper (hydromechanical) well development, in order to remove the drilling mud cake after well installation. In contrast, for mine dewatering in the Rhenish lignite district in Germany, a huge number of wells are needed to enable dry surface mining and to ensure slope stability of the open-pits. As the open-pit progresses, following the directions of the resource, dewatering wells in the pre-field eventually are excavated after design service-lives of 5 to 10 years or less. Thus, not much effort is put into well development, as the wells are generally operated at maximum capacity from the beginning anyway. Lately, for mine dewatering applications, the concept of intermittent abstraction (van Beek et al. 2010) has been found to be a successful alternative to conventional well development (Reich & Menz 2015). But also no chemical or particular additives (but only water) are used in the drilling fluid. Still, the tremendous hydraulic effect of the skin layer legitimates considerations about its formation and composition. Especially, when a large number of wells are needed to facilitate secure mining of natural resources or sustainable supply of high quality drinking water, there is a huge potential for cost reduction and energy savings through optimisation of well yield and efficiency.

Thus, within this work we present a direct observation, microscopic investigation and geochemical-mineralogic analyses of wellbore skin samples at five excavated open-pit dewatering wells in the Rhenish lignite district in W Germany and at one drinking water supply well in NW Germany, accessed by inclined core drilling (Tab. 1).

***Table 1** Wells included in the investigation (ststw: stainless steel wire screen, ppfg: prepacked fiber glass rod screen; ac: asbestos cement; Cu: copper; *): sample taken in cased section; hz.: regional geologic horizon; hz. 6B/D: shallow marine anoxic loose fine to medium sand; hz. 7: shallow marine anoxic loose medium sand; hz. 8: terrestrial, fluvial oxic terrace loose fine to medium gravel; quaternary: terrestrial medium to fine sand, light grey; P: Photo; M: electron and polarizing microscope; X: XRD and XRF; CT: computer tomography).*

Well	Location	Service life [yrs]	Sample [m bgl]	Screen [m bgl]	Screen type	Lithology	Analytics
WS5015	Garzweiler	< 10	≈ 100	93-108	ststw	hz. 6D	P, M, X, CT
WS5315	Garzweiler	< 5	≈ 100	102-108	ppfgr*	hz. 6D	P, X
WS3151	Garzweiler	< 10	140	133,5-142,5	ststw	hz. 6B	P
HS41	Hambach	> 20	230	229-242	ac	hz. 7	P, CT
HS1059	Hambach	< 10	267	297-309	ppfgr*	hz. 7/8	P
Well 31	Großenkneten	> 40	34.5	29-59	Cu	quaternary	P

Methods

At all six wells, photo documentations were conducted to compare the macroscopic characteristics of different skin-layer types. At three wells, disturbed and undisturbed samples were taken to allow for microscopic and/or mineralogical analysis by cored drilling (Fig. 1, center), core cutter rings (Fig. 1, left), and epoxy resin impregnation (Fig. 2).

For sample stabilization and preparation of thin sections and test pieces for SEM and CT analyses, the samples were impregnated with the epoxy compound Araldite® 2020 (XW 396/XW 397; density = 1,1 kg/m^3, viscosity = 150 mPa). Transmitted light microscopy analysis was applied to evaluate petrography on covered thin sections with a Zeiss Axioplan polarising microscope, supported by Zeiss Axiovision Software. An Environmental Electron Scanning Microscope (ESEM) of the type FEI Sirion D1625 (low vacuum, 0.6 mbar) was used to investigate samples of the borehole wall. Porosity determination and 3D-imaging was accomplished with a nanotom S 180µ-CT (GE Sensing & Inspection Technologies GmbH,Wunstorf, Germany) (tube characteristics: 180 kV, 500 mA). The 3D image data were processed with the AVIZO Fire software suite (Visualization Sciences Group). Measurements of hydraulic conductivity were taken from experimental data core cutter ring samples by Houben (2015a, b).

X-ray diffraction (XRD) was conducted with a PANalytical X'Pert PRO MPD Θ-Θ diffractometer (Cu-Kα) with variable divergence slit, soller collimators, and Scientific X´Celerator position sensitive detector (active length 0.59°). Samples of 28 mm diameter were investigated from 2° to 85° 2Θ (step size: 0.0167°; counting time: 10 s). Overnight treatment with ethylene glycol vapor was applied to investigate swelling clay minerals qualitatively by comparative XRD patterns (oriented aggregate mound, fraction < 2 µm).

Figure 1 *Inclined drilling into the annulus of a decommissioned water supply well in Großenkneten (centre) and undisturbed sampling at excavated open-pit dewatering wells in the lignite open-pits Garzweiler and Hambach (left and right).*

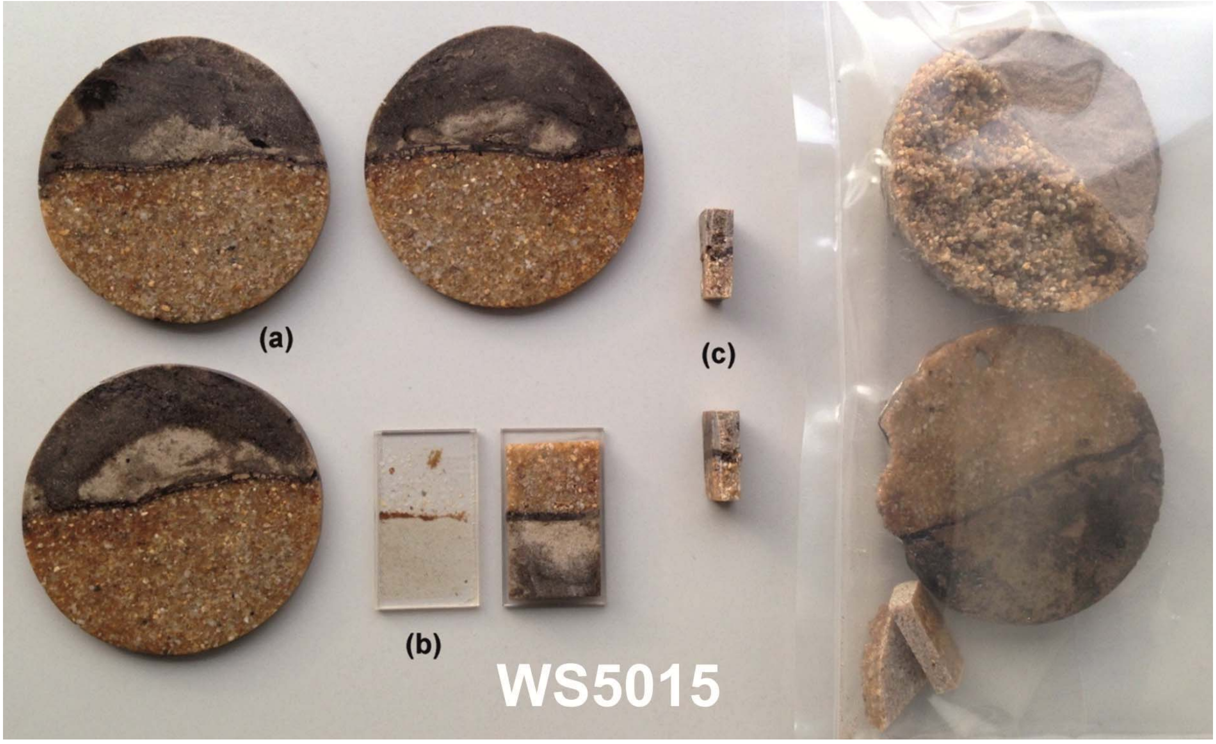

Figure 2 *Prepared specimens of an undisturbed sample from Well WS5015: core cutter ring sample, impregnated with epoxy and cut into slices (a) for thin section preparation (b), ESEM and CT inspection (c).*

Loss on ignition (LOI) was determined by heating 1 g of sample material to 1030°C for 10 min and subsequent weighing. Powdered samples were mixed with lithium metaborate (Spectroflux, Alfa Aesar) as flux material for subsequent glass conversion within 20 min at 1200°C. Wavelength dispersive X-Ray Fluorescence spectrometry (WD-XRF) was then applied to determine chemical composition with a PANalytical Axios and a PW2400 spectrometer.

For total carbon and sulphur contents, 170-180 mg of air-dried sample material were grinded and heated to 1800-2000°C in an oxygen atmosphere in order to expel carbon and sulphur as CO_2 and SO_2 gas which was then detected with an infrared detector of a LECO CS-444-Analyser. The procedure was repeated with a sample, pre-treated with hydrochloric acid at 80 °C until inorganic carbon contents were expelled (no further gas evolution) in order to determine the organic carbon content (C_{org}). Inorganic carbon (C_{inorg}) was then derived as the difference between total and organic carbon.

Results

Within the six samples, three different types of skin layers could be distinguished. A wellbore surface cake could be observed in three cases (Fig. 3.A), deep bed filtration occurred in one case (Fig. 3.B) and in another case the fines had invaded the aquifer material to be deposited at about 1 cm from the borehole wall (Fig. 3.C). In the case of the drinking water supply well, no skin layer was observed (Fig. 3.D).

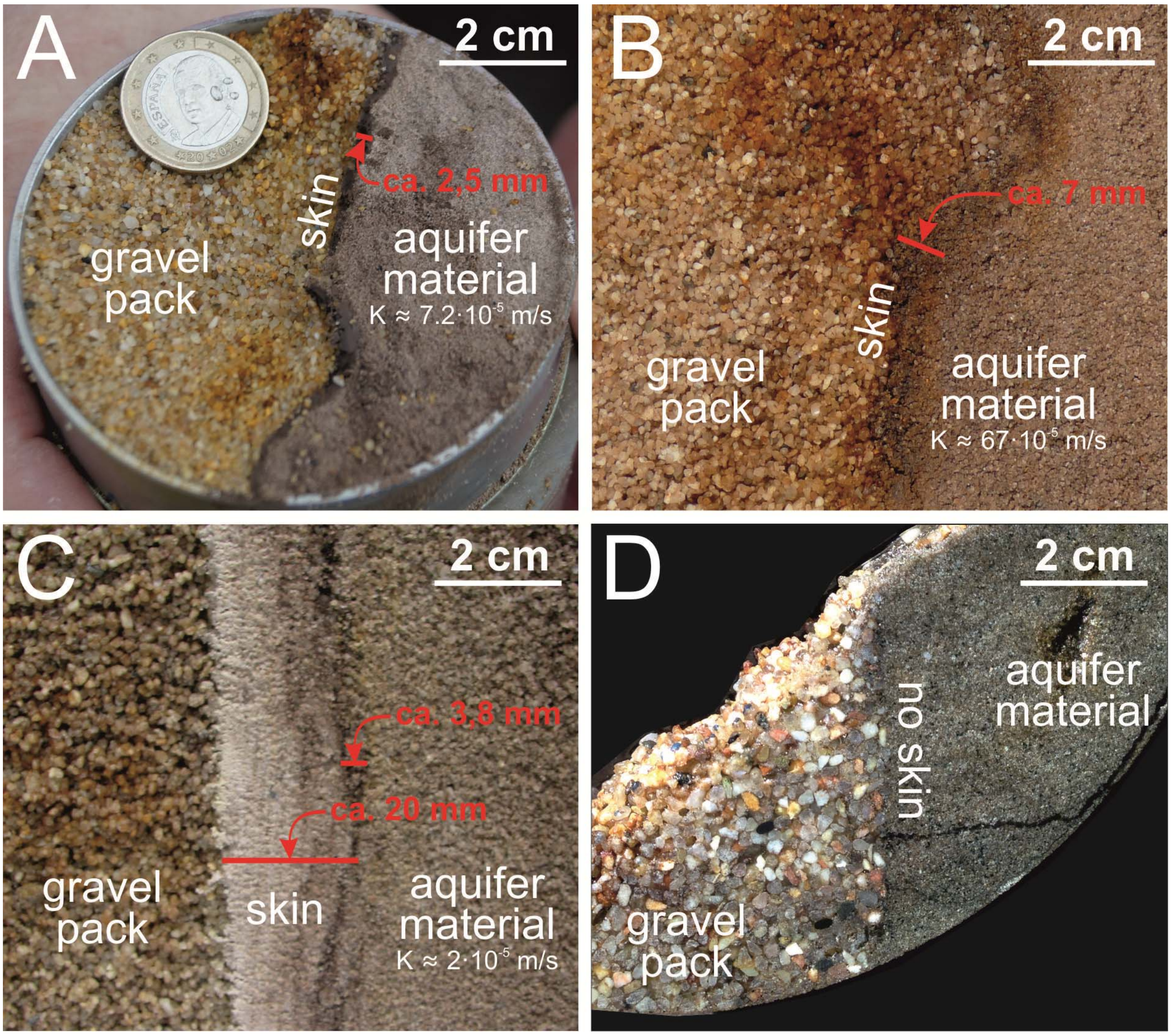

Figure 3 *Types of skin layers observed. A: wellbore surface cake (well WS5015, open-pit Garzweiler, RWE Power AG), B: deep-bed filtration (well HS41, open-pit Hambach, RWE Power AG), C: outer filter cake (well HS1059, open-pit Hambach, RWE Power AG), D: no skin (well 31, Großenkneten, OOWV).*

Polarizing microscopy of the thin section of sample WS5015 (Fig. 4) revealed the skin layer to be a densely packed brownish surface cake layer of up to 2 mm in thickness in between the finely sandy aquifer and the fine gravel pack materials. Within the skin layer, no singular mineral grains, but several micro-cracks could be identified. Detailed ESEM imagery of the skin layer (Fig. 5) showed an intricate assemblage of angular grains (mostly quartz) and platy clay and silt minerals. Electron microscopy, XRD and XRF revealed the skin layer of the surface cake samples WS5015 and WS5315 to be mainly composed of quartz with accessory components of kaolinite and muscovite/illite withtraces of feldspars, carbonate, chlorite, and organic matter as well as secondarily formed gypsum. No significant contents of expansive clays, e.g. smectite could be identified (Tab. 2-4).

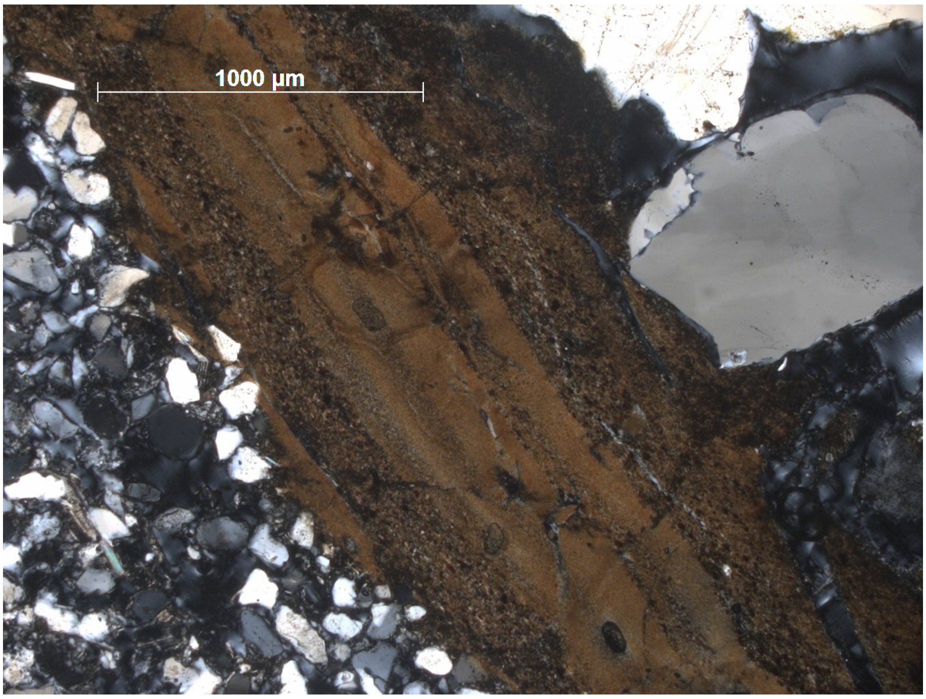

Figure 4 *Detail image of thin section of the former borehole wall of well Garzweiler WS5015 (screened well section; polarized light). The coarse rounded grains in the upper right corner represent the gravel pack, the smaller, more angular grains to the left represent the fine sand aquifer. The skin layer is visible in between as a brown laminated layer with varying grain sizes and microscopic cracks in different directions.*

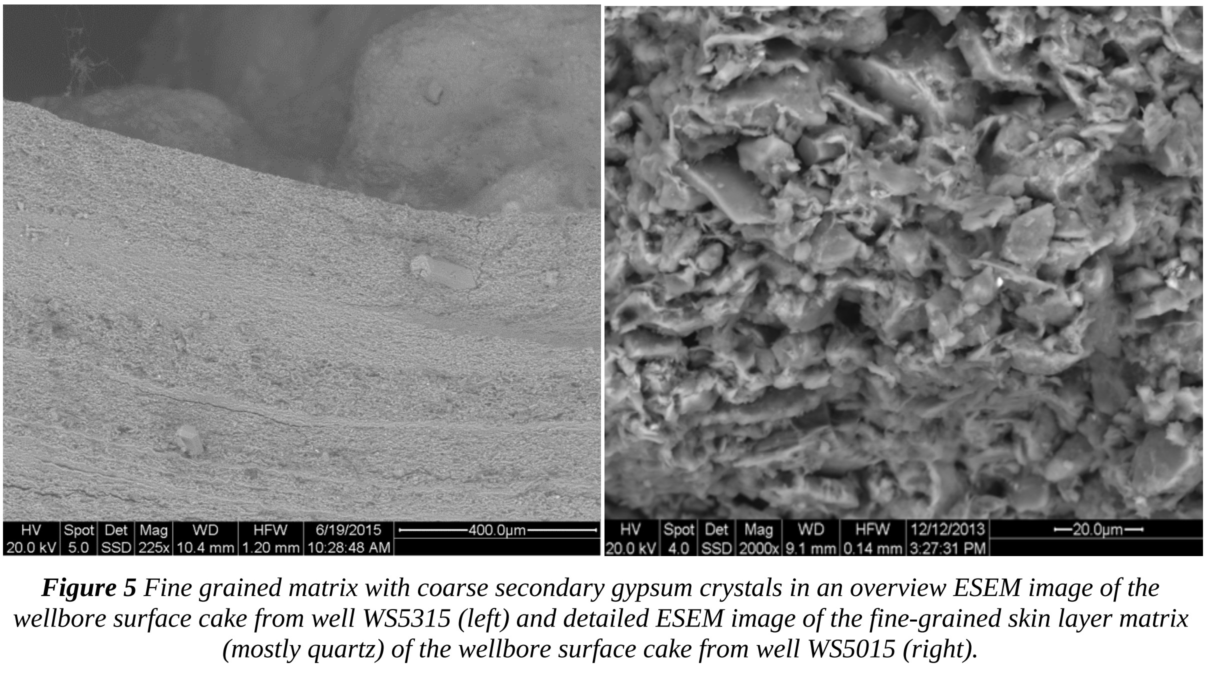

Figure 5 *Fine grained matrix with coarse secondary gypsum crystals in an overview ESEM image of the wellbore surface cake from well WS5315 (left) and detailed ESEM image of the fine-grained skin layer matrix (mostly quartz) of the wellbore surface cake from well WS5015 (right).*

Contrary to the WS5015 specimen, no distinct skin layer can be identified in the 2D CT cross section of sample HS41 (Fig. 6). Instead, fine particles have migrated into the aquifer material (Fig. 6, top) and form a deep-bed filtration layer. Within this layer, open and connected pores can be found (dark grey to black areas), showing that both aquifer and gravel pack, are hydraulically connected. Nevertheless, the hydraulic conductivity of the particle-invaded aquifer presumably is significantly lower than the conductivity of the undisturbed aquifer material. Digital image analysis (pore distribution and visualization) could not be performed, due to the overlapping grey values (i.e. similar absorption coefficients of the materials) of the resin and of the fine particles present in the pore spaces of the aquifer which had been possible for the WS5015 sample (Houben et al. 2016). The CT images of HS41 do not give information on when and from where the particles invaded. They could have accumulated during the drilling process (invasion of particles suspended in drilling fluid), as their color indicates but also through a later migration of aquifer fines towards the well during operation ("secondary filtration" or "mechanical wellbore clogging", cf. van Beek et al. 2010 and Reich & Menz 2015).

Table 2 *Mineralogy of skin samples, determined by qualitative XRD analysis*

Sample	Main components	Accessory components
WS5015	quartz	muscovite-illite, kaolinite, sodium feldspar, smectite/mixed layer
WS5315	quartz	gypsum, muscovite-illite, kaolinite/chlorite, potassium feldspar
HS41	quartz	microcline, orthoclase

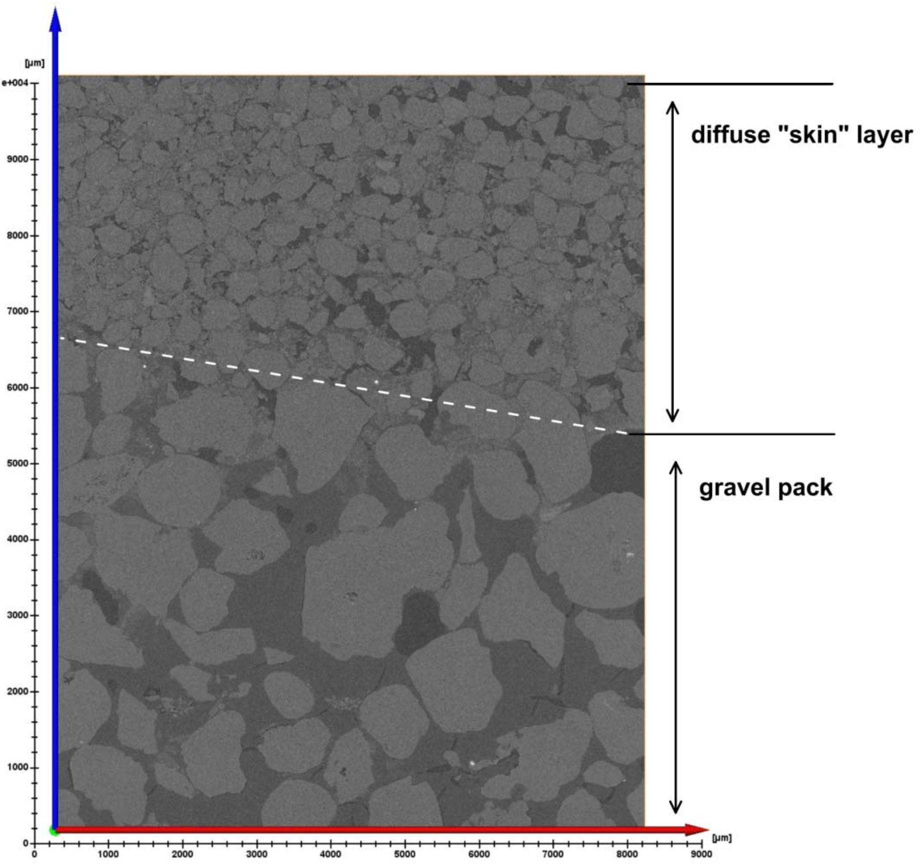

Figure 6 *2D CT cross section of sample HS41 (z-y plane: 9.94 x 7.85 mm). Contrary to sample WS5015, no distinct skin layer can be found. Instead, an invasion of fine particles into the pore space of the aquifer is visible in the upper part.*

From the XRF results, the mineralogical composition can be estimated from a simplified nominal mineralogy of only quartz and kaolinite. Stoichiometrically incorporating all aluminum into kaolinite ($Al_2[(OH)_4Si_2O_5]$), the remaining silicon is consumed for quartz (SiO_2). Other elements form iron/manganese oxides, sulfates/sulfides, carbonates and organics. Nominal compositions yield 7.72 mol/kg quartz (or 46.4 wt.-%) and 1.36 mol/kg kaolinite (or 35.1 wt.-%) in sample WS5015 and 6.85 mol/kg quartz (or 41.2 wt.-%) and 1.13 mol/kg kaolinite (or 29.1 wt.-%) in sample WS5315. The concentrations of inorganic carbon indicate a minor importance of carbonates in both samples (Tab. 3). A noticeable content of sulphur is present in WS5315 which, according to XRD and electron microscopy, appears as gypsum (12.6 wt.-% of $CaSO_4 \cdot 2H_2O$). Assuming a nominal composition of CH_2O, organic carbon corresponds to 4.65 and 14.5 wt.-%, in the samples WS5015 and WS5315, respectively, and is probably responsible for the brown color. The higher loss on ignition for sample WS5315 indicates higher contents of thermally instable phases such as gypsum and organic matter.

Table 3 *Geochemistry of skin samples WS501 and WS5315 as well as aquifer material samples HS41_u (unaltered aquifer material) and HS41+p (aquifer material invaded by fine particles) (LOI: loss on ignition)*

[wt.-%]	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	C_{inorg}	C_{org}	S	LOI
WS5015	62.7	0.78	13.9	6.22	0.017	1.06	0.84	0.39	2.34	0.04	1.86	0.19	11.3
WS5315	54.7	0.62	11.5	5.67	0.029	0.76	0.85	0.22	1.83	0.09	5.79	2.35	23.0
HS41_u	95.9	0.04	2.1	0.10	0.001	0.03	0.05	0.14	1.05	0.01	0.06	0.02	0.50
HS41+p	95.2	0.07	2.3	0.24	0.001	0.02	0.08	0.15	1.11	0.01	0.14	0.03	0.79

For the deep-bed filtration case of well HS41, the chemical composition of the unaltered aquifer and the aquifer affected by particle invasion were compared (Tab. 4). The XRD analysis of both samples indicated quartz as main phase, with traces of potassium feldspar. Only slight increases in LOI and C_{org} adumbrate a barely measurable invasion of organic particles. But the majority of invading particles therefore must be chiefly quartz as well.

In comparison to these mineralogical results, granulometric analyses and permeameter tests by Houben et al. (2016) resulted in high contents of clay and silt of about 75 % in the skin layer and a low measured hydraulic conductivity of $6.2 \cdot 10^{-6}$ m/s (WS5015). Still, this conductivity is significantly higher than should be expected from a poorly sorted silt and clay-rich sample, which is probably due to conductive micro-cracks transecting the skin layer and therefore creating preferential flow paths through the layer.

Conclusions

In conclusion, the typology of skin layers was found to vary significantly, even in a small number of samples. Even though very fine granulometries were measured by Houben et al. (2016), with > 40 wt-% quartz is the main component of the skin layer, accompanied by around 30 % of kaolinite/illite. Despite the overall lignitic environment, organic carbon contents appear to play only a minor role (5 to 15 %). Secondary gypsum precipitation can occur in the environment of pyrite oxidation and later neutralization by calcite.

With evaluation of the CT results, calculations of the pressure field and concentration of flow lines throughout the pore space are planned for the near future followed by calculation of the filtration process and buildup of the mud cake itself. Even an experimental reconstruction of mudcake buildup and its removal by (intermittent) backflow (normal abstraction, well development) is thinkable. Such investigations could help to understand the field observations by RWE Power AG of well efficiencies increasing by more than 10 % as a result of intermittent abstraction (Reich & Menz 2015).

Even very thin skin layers were found to cause a significant reduction of hydraulic conductivity of the whole system, though distinct structural properties like micro-cracks or skin erosion can possibly help to maintain a high well yield. Altogether, significant improvements should be expected from further studies on the effectivity of measures to remove the drilling mud cake (like well development) or to prevent its formation in the first place.

Acknowledgements

Thanks go to the Oldenburgisch-Ostfriesischer Wasserverband (OOWV) and RWE Power AG for the opportunity to take borehole wall samples from the aquifer/gravelpack-interface by well overcoring and access to the open-pits. Constructive suggestions of the reviewers were very much appreciated.

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Progressive Sinkhole Occurrence Induced By Dewatering Activities in a Large Lignite Mine (SE Turkey)

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Abstract

Following two successive massive landslides in 2011with a total of 10 casualties at the Çöllolar open pit lignite mine located in southeast Turkey, an extensive dewatering program was initiated as a preventive measure against further slope stability problems. Based upon a series of studies on hydrogeological conceptualization and characterization, two major hydrostratigraphic units have been identified as target zones for dewatering. Failure in lowering groundwater in the Neogene sequence is has thus been attributed to the excessive inflow from karst aquifer. Therefore, a second dewatering program targeting the karst aquifer was scheduled and initiated in February 2015. Four sinkholes were developed progressively as a consequence of sudden collapse in a period of about 120 days after karst dewatering has started. Occurrence of sinkholes is restricted to an area of about 0.7 km^2 between the pit and the limestone outcrop. Progressive occurrence and development of sinkholes posed a serious risk for not only mining operations but also the settlements close to the sinkhole area. This study was conducted to explain the mechanism of sinkhole occurrence in the area and thereupon to suggest a solution to this hazardous risk. All information were put in a conceptual model that explains the most plausible mechanism of sinkhole occurrence which required a detailed comparative study of morphological, hydrographical, geological and hydrogeological characteristics of the sinkhole field and its near vicinity.

Key words: dewatering, open pit, karst, sinkhole, Afsin

Introduction

Mining operations have hydrologic and hydrogeological impacts on the environment by altering the surface landscape, surface water and groundwater systems. Hydrogeological conditions may require intensive dewatering of the groundwater system to secure safe and feasible mining operations. Subsidence is one of the most common consequences of such intensive dewatering activities. A gradual development of subsidence is easier to predict, control and remediate. However, sudden subsidence or collapse producing large and deep sinkholes are less predictable and difficult to control. This type of occurrences may be hazardous and dangerous. Therefore, understanding the mechanism of sinkhole occurrences is an important issue of mining hydrogeology (Blodgett and Kuipres 2002; LaMoreaux et al. 2008; Commonwealth of Australia 2015).

In 2011, two successive massive landslides in 2011 killed a total of 10 persons at the Çöllolar open pit lignite mine located in southeast Turkey (fig. 1). Analyses of the landslides have suggested that occurrence of excessive pore water pressure in the overburden was the major factor responsible for these occurrences. Consequently, an extensive dewatering program was initiated as a preventive measure against further slope stability problems. Four sinkholes were developed by sudden collapse successively in the vicinity of the open pit (fig. 1) in a period of 4 months following an extensive dewatering. Progressive occurrence and development of sinkholes posed a serious risk for not only mining operations but also the settlements close to the sinkhole area. Authorities have expressed their concern about the role of dewatering. Dewatering might have a double but contradicting effects: enhances slope stability in the pit but triggers sudden collapses in the vicinity. This paper aims at suggesting a model to explain the mechanism of sinkhole occurrence in the area and thereupon to suggest a solution to this hazardous risk.

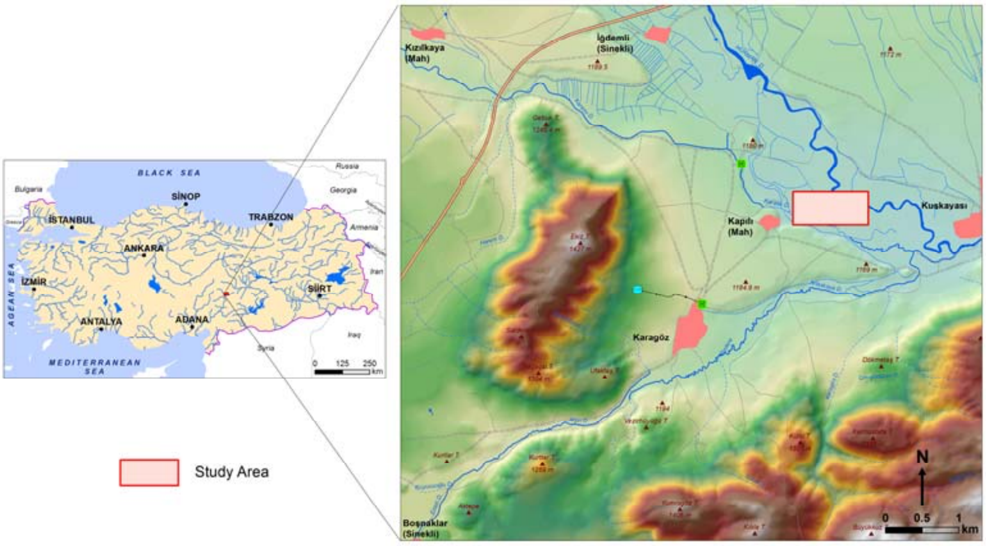


Figure 1 *Location Map of the Study Area.*

The technical approach applied in this study included a detailed desktop study on geological setting and analysis of hydrogeological data, followed by field work to characterize the sinkholes. Hydrographic, morphologic characteristics and hydrological conditions were analyzed to define the type of the sinkholes in accordance with the classification suggested by Waltham et al (2008). Once the type of the sinkholes were defined, the mechanism of development was hypothesized based upon the pre-mining hydrogeological conditions and the role and impact of dewatering on the occurrence.

Location and Basic Characteristics of Sinkholes

The four sinkholes occurred successively at the foothill of one of the metamorphic rock hills, 350 to 600 m to south-southeast of the Çöllolar pit (fig.2). The sinkhole area is covered by slope-wash material, colluvium and alluvium of Hurman stream which runs close to the periphery of the pit. The occurrence history and basic characteristics of the sinkholes are briefed below. The first sinkhole was developed at the end of February 2015 about 350 m distant from the southeast perimeter dewatering wells. The perpendicular distance to Hurman stream is measured as 152 m. This sinkhole is the smaller one with a diameter of 2.5 m and 1.5 m apparent depth.

Figure 2 *Location of the Sinkholes in Relation to the Open Pit.*

The second sinkhole was developed in April 2015, at the same area but closer (about 255 m).to the open pit. Development of this sinkhole was progressive. Diameter of this sinkhole continued to enlarge after its first development from 14 m to 16.5 m. Its depth was measured as 14 m. The third sinkhole occurred in May 2015 at a location between the first and second sinkholes. It progressively deepened from 4.5 m to 6 m in 15 days whereas its diameter remained the same at 7.5 m. The fourth and the last sinkhole was developed very close to the periphery of the open pit. This is the deepest sinkhole with a diameter of 9 m and depth of 18.60 m. All of the sinkholes are cylindrical in shape with steep walls (fig. 3).

Classification of sinkholes in karstic areas by Waltham et al (2005) suggests that sinkholes may also develop in overburden of karst systems through different mechanisms. Based on the morphological and geological characteristics of the studied sinkholes it can be postulated that they may be defined as suffosion or dropout type. The degree of cohesion of the overburden material determines which type will develop: suffosion in non-cohesive, dropout in cohesive overburden. Alteration of hydrological/hydrogeological is another basic factor underlying the mechanism that may produce these types of sinkhole.

Third sinkhole

First sinkhole

Fourth sinkhole

Figure 3 *Views From the Sinkholes Developed in the Study Area*

Geological Setting

A detailed study of regional geology by Bedi et al (2008) together with core log descriptions from a large number of boreholes at the site were utilized to describe geological setting at regional and local scale. The Çöllolar mine site is located within a large tectonic depression known as ion of the Afşin-Elbistan lignite basin. The depression is surrounded by high rock masses made of meta-carbonates and meta-clastics of Paleozoic-Mesozoic age. The depression is filled with Tertiary units. Miocene unconformably overlies the bedrock and is represented by alternation of mainly lacustrine siltstone, mudstone, sandstone, marl and limestone. Plio-Quaternary sequence is characterized by lacustrine units starting with clay and silt containing thick lignite horizons and a thick gyttja. The uppermost alluvial cover is composed of unconsolidated coarse and fine sediments. Figure 4 depicts the general geological setting in the region including the study area.

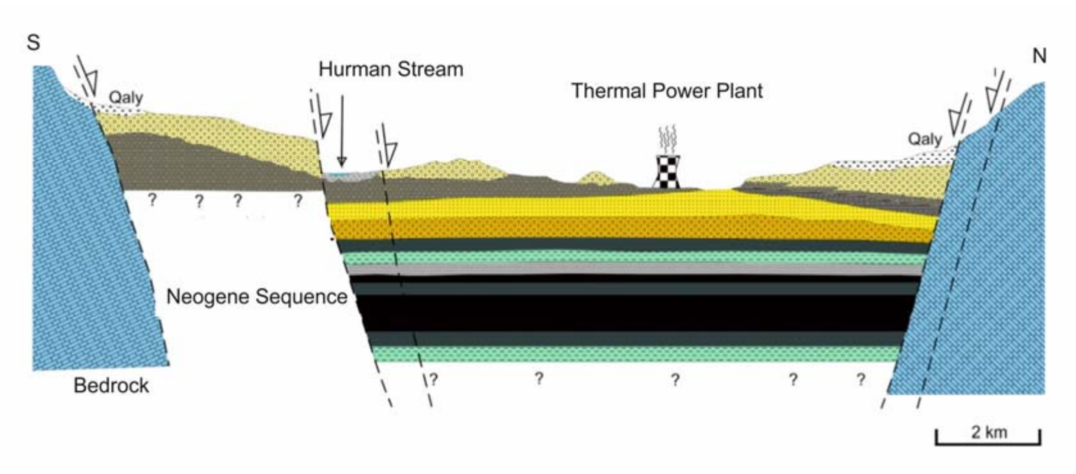
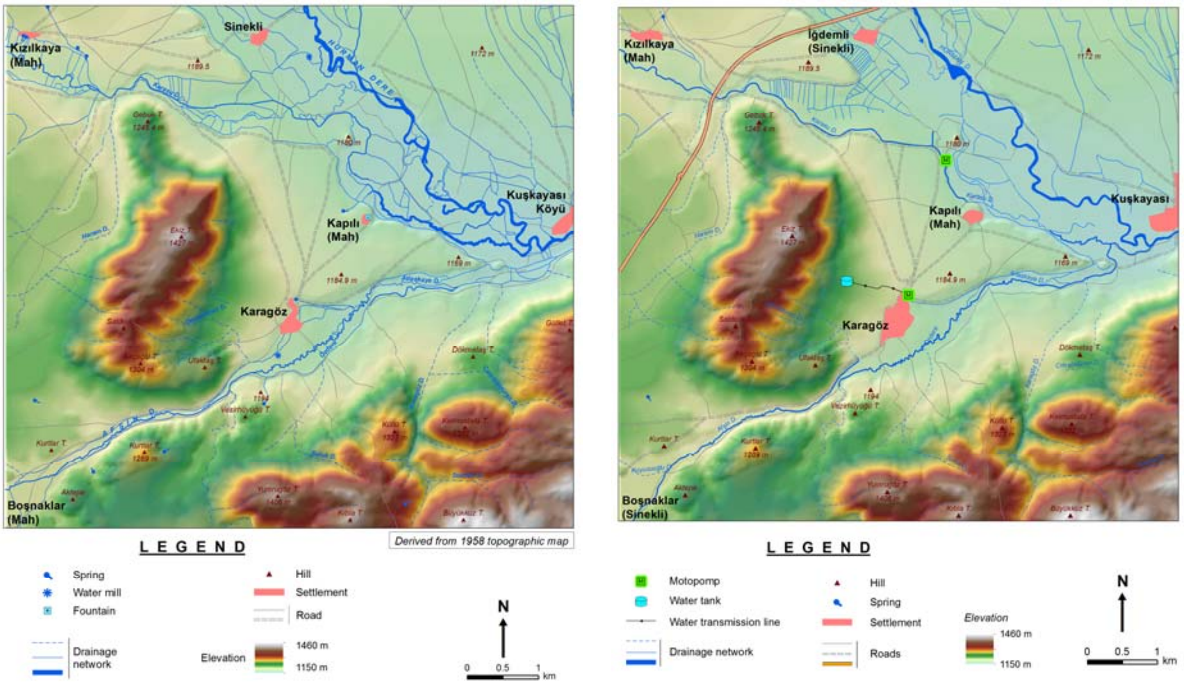


Figure 4 *Geological cross-section of the Afşin-Elbistan Lignite Basin (after Bedi et al 2009).*

Comparison of Pre and Post Mining Hydrographic Layout

Pre-mining hydrographic layout in the area of sinkhole development was derived from topographic map dated 1958 while the present conditions were reproduced from more recent topographic map and the GoogleEarth™ image. The hydrographic layout shows that the region was rich with respect to surface waters such as springs, streams and wetlands before the mining operation (fig.5a). Water mills suggests that the flow rate of springs and streams was high. Apparently, the mining operations have impacted the surface water occurrences in the area. Wetlands and springs have disappeared and streams have either dried up or their flow has been significantly reduced (fig. 5b). Alteration of the hydrographic setting in the vicinity of the pit was regarded as a consequence of dewatering and as indication of interaction of surface water-groundwater.



a b

Figure 5 *Hydrographic Setting of the Area. a) Pre-mining b) Post-Mining conditions*

The sinkhole area is also characterized with some closed crypto-depressions where the surface runoff is disappeared (fig. 6). These crypto-depressions are evaluated as indications of localized seepage in the alluvium. This information was used in developing a representative hydrogeological conceptual model of the site.

***Figure 6** Hydrographic Setting of the Area. a) Pre-mining b) Post-Mining conditions*

Hydrogeological Setting Under Natural Conditions

Based on detailed analyses of geology, borehole data, hydrochemistry and stable isotope data the pre-mining hydrogeological setting was conceptualized as illustrated in Figure 7. The paleogeographic development has suggested that karstification of pre-Neogene carbonate rocks was interrupted and karstic features were choked by the lacustrine sediments in Neogene. The karstic bedrock forms an extensive aquifer in the region. However, the groundwater flow through the aquifer is slow and the phreatic part contains almost stagnant groundwater due to the much less permeable Neogene sediments. The springs that issue at the foothill of the carbonate rock are of overflow or depression type. The foothill is consisted of coarser and therefore higher permeability slope-wash and fan material. Toward the plain, finer material dominates the alluvial deposits, thus reducing its permeability. The rich surface water occurrence before mining operations is thus explained by the groundwater overflow due to the shallow water table.

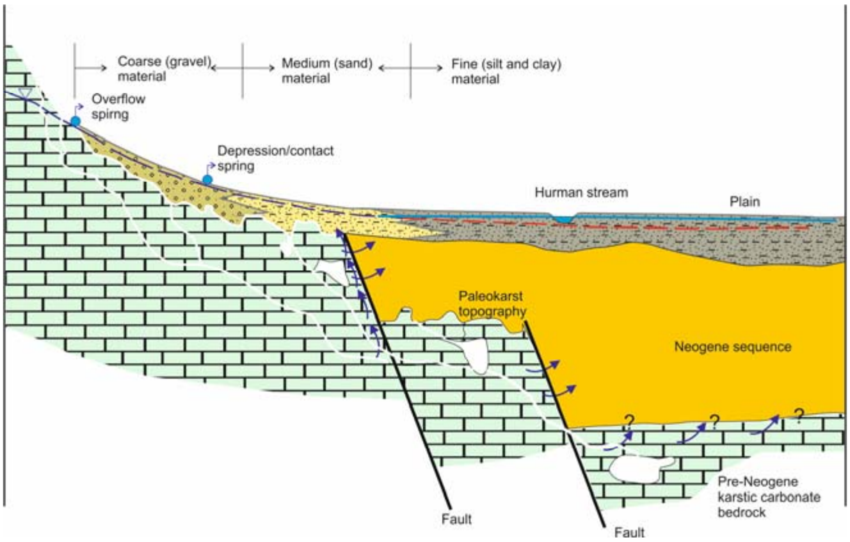


***Figure 7** Schematic Cross-sections Illustrating Natural Hydrogeological Conditions (not to scale)*

Pit Dewatering and Its Hydrogeological Impacts

Two major hydrostratigraphic units have been identified as target zones for dewatering as a result of a series of studies on hydrogeological conceptualization and characterization. The upper zone is composed of a sequence of clastic material with various grain sizes and organic material content of Neogene age. Gyttja having a thickness up to 70 m within the Neogene sequence is given a special importance in dewatering due to the fact that this material was defined to be sensitive to mass wasting. The lignite seam is seated on extensive clayey layer at the bottom of this sequence. Beneath the Neogene sequence there extends a thick limestone of Mesozoic age. It is well karstified and forms a high yield aquifer with confined groundwater to be depressurized and dewatered. Dewatering the Neogene sequence (upper unit) has increased to a total of abstraction rate of $2.5x10^4$ m^3/day in 2012 immediately after the landslides. Dewatering of this unit was found to be ineffective in lowering the groundwater to the targeted level which is the bottom of the pit. This was mainly due to the low transmissivity of the gyttja. According to the hydrogeological conceptual model described for the site, the karstic limestone aquifer is in contact with the Neogene sequence at the southern edge of the basin where karst groundwater feeds the gyttja and other layers of Neogene sequence.

The hydrogeological impact of dewatering of the Neogene sequence on the regional hydrodynamics has not been significant due to the low transmissivity of the sequence. The radius of influence remained limited and did not expand (fig. 8). Failure in lowering groundwater in the Neogene sequence has thus been attributed to the excessive inflow from karst aquifer. Therefore, a second dewatering program targeting the karst aquifer was scheduled and initiated in February 2015. As a first phase of dewatering of karst aquifer 5 boreholes have been drilled close to the southern edge of the pit where the karstic limestone crops out at only a few hundreds of meters from the pit wall. The boreholes have been screened only at the limestone and pumped with an average rate of 40 L/s (a total of 200 L/s). The sudden increase of pumping rate from karst aquifer had a significant impact on the hydrodynamics which altered the hydraulic interactions in the area. The first sinkhole was developed only after about three weeks following the massive dewatering of karst aquifer (fig.9). The impact of this dewatering on the hydrogeological behaviour is depicted in Figure 10.

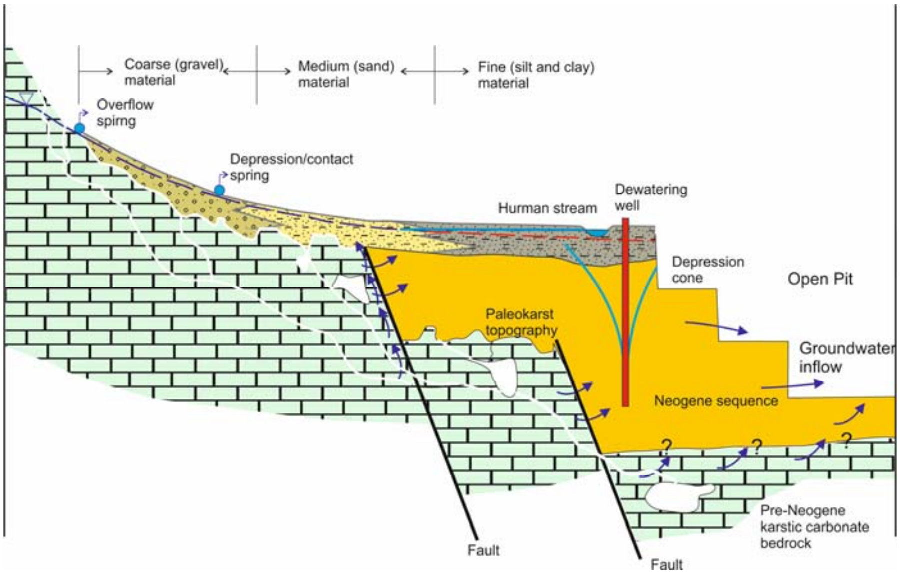


Figure 8 *Schematic Cross-sections Illustrating Hydrogeological Conditions Under Dewatering the Neogene Sequence (not to scale)*

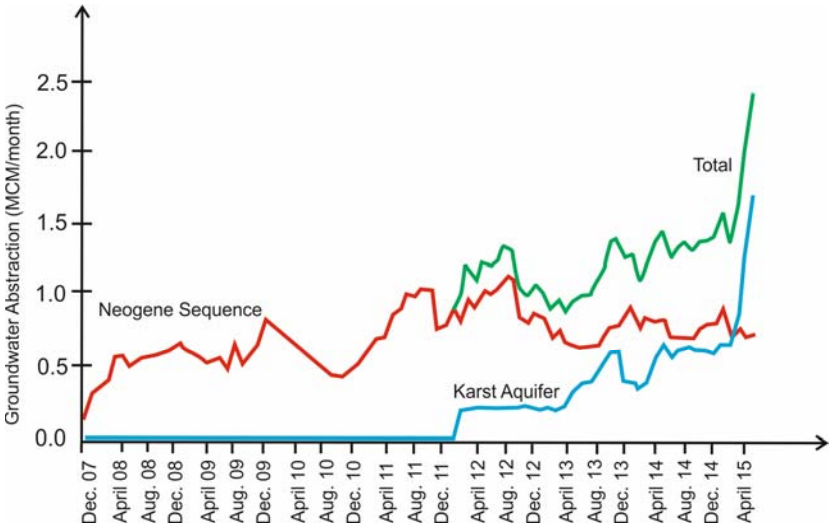


Figure 9 *Groundwater Abstraction For Dewatering Karst Aquifer and Neogene Sequence (in millioncubicmeter per month)*

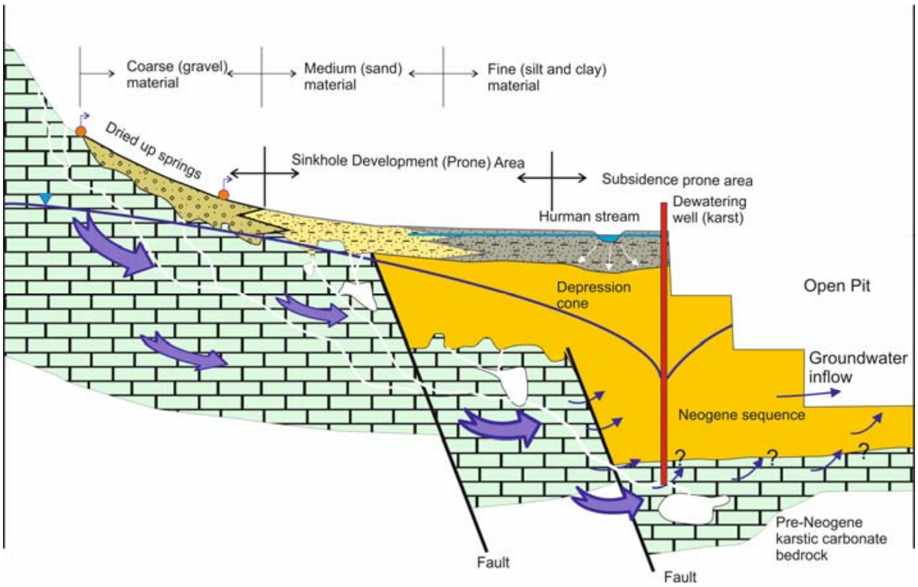


Figure 10 *Schematic Cross-sections Illustrating Hydrogeological Conditions Under Dewatering the Karst Aquifer (not to scale)*

Mechanism of Progressive Development of Sinkholes

The results of data analyses and observations in the field allowed us to suggest a plausible mechanism explaining the progressive development of the sinkholes. The area where sinkholes developed is located at the foothill of a carbonate rock outcrop. The overburden is made of unconsolidated alluvial and colluvial deposits. Toward the pit, the deposit becomes thicker, and composed of finer and more cohesive whereas close to the foothill it is thin, coarser and less cohesive. The sinkholes are developed within the overburden and all characteristics indicates that there has been no collapse in the bedrock. This has suggested that the sinkholes are of either suffusion type or dropout type, classified according to Waltham et al (2008). Those developed close to the foothill (the first and third sinkholes) are of suffusion type while those close to the pit (second and fourth sinkholes) are of dropout type.

Under natural hydrogeological conditions (before dewatering the karst aquifer), the groundwater in the karst aquifer is almost stagnant and the overburden is saturated. Groundwater in karst aquifer discharges through overflow springs and as base flow to the streams. After mining operations has started, the Neogene sequence only was dewatered. Dewatering the low permeability Neogene sequence had no significant effect on the hydrogeological setting in the area because of the limited extension of the drawdown cone (see fig. 8). However, following the destructive landslides, the karst aquifer was started to be dewatered. Dewatering of this high yield aquifer required massive and extensive pumping. Groundwater abstraction has had significant consequences on the hydrodynamics resulted in sinkhole development. Firstly, pumping has accelerated the groundwater movement and the groundwater was forced to move toward the pit with high velocity. Secondly, the high transmissivity caused a very rapid expansion of the drawdown cone, which reached the foothill in a timeframe less than a month. Drawdown in the non-cohesive material triggered suffusion of the finer particles in the coarser material. The first sinkhole has developed close to the foothill because the overburden is thin and as soon as the drawdown reached this area, suffusion has initiated. The drawdown was much greater close to the pit. However, the material is cohesive and thick. Therefore, there had been a time lag between the drawdown and the development of cavities in the contact zone between the carbonate bedrock and the overburden. After about four months, the cavities were large enough to cause dropout of the cohesive material, which resulted in formation of the second and fourth sinkholes.

Conclusions

A model explaining the plausible mechanism of the progressive sinkhole development in a large open pit was proposed based on geological, morphological, hydrographic and hydrogeological conditions. Massive dewatering of the karstic bedrock aquifer was found to trigger suffosion in thin, non-cohesive overburden at a distance of radius of influence of the pumping wells. Closer to the pit, the thick cohesive soil was affected from dewatering with a time lag and the sinkholes occurred in this section are of drop-out type. Based on the model, it was possible to delineate a sinkhole-prone area.

The study has shown that consequences of dewatering can be hazardous and may appear short after the dewatering program commences. Therefore, it is of great importance to predict also the consequences of the suggested dewatering program in mining areas. This can be achieved by integrating the results of groundwater flow models with geotechnical models of subsidence and collapse.

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Hydrogeological exploration and field tests on vacuum wells in overburden sediments for determination and modelling of process parameters and dewatering construction

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Abstract

To develop a further opencast mining area of MIBRAG´s Profen Mine it is necessary to excavate a former dump of overburden sediments including ashes and coal residues of an old coal power plant, which have been purged in between 1930 and 1990 over an area of about 0.3 km² and a thickness of 40 m.

Due to the planned excavation these sediments must be characterized problematic from geotechnical and hydrogeological point of view.

Several investigations have been used to reconstruct the composition of the complex dump and to estimate hydrogeological and soil mechanical properties of the consisting substrates.

Within this study typical exploration drill holes with substrate sampling and geotechnical sounding for soil properties and geoelectrical measurements to determine spatial water saturation were carried out accompanied by groundwater monitoring.

With reference to the determined data a spatial block model for relevant substrate properties of the complex dump is set up.

Hence the areas with a high amount of water saturation in association with small hydraulic conductivities could be worked out. In addition to that multi-step-outflow lab experiments with overburden samples suggest that vacuum dewatering is the most promising technology for an effective drainage.

With two testing sites the feasibility and impact of vacuum wells could be proved. For the whole complex dump dewatering an amount of about 120 vacuum wells will be drilled during the next months. The disposal of the required arrays of vacuum wells is based on hydrodynamic calculations. It is continuously adjusted on the latest monitoring and exploration data.

This paper shows possibility and limitations of exploration, modeling and subsequent planning of an opencast mining area by taking the example of a vacuum dewatering system on complex overburden sediments. At the end hydraulic and geotechnical conditions shall be enhanced whereby a save, efficient and economical excavation can be executed.

Key words: Exploration, Parameter Estimation, Spatial Modeling, Process simulation, Vacuum wells, Dewatering

1. Introduction

By developing the new mining field Domsen the mining company MIBRAG needs to excavate the Bösau dump amongst others within several former basins of ash and coal residual sediments which have been purged in. The further mining area is part of opencast mine Profen at the central German mining district in the southwest of Leipzig. The dump arises from a former mine which partly is designated for further exploitation of the underlaying coal seam. It is suited at the edge of the actual opencast mine with its bedrock 30 m beyond the bottom of the adjacent hollow pattern. It is surrounded in one third by a typical dump with mixed substrates of overburden sediments and in two thirds by bedrock. Whereby the fringe to the actual opencast mine is formed by a narrow bedrock pillar of 500 m width. The structure of the hydraulic dump system is visualized on **fig. 1.** The design of an appropriate technology for excavation of this dump requires a more detailed knowledge base of spatial extent and especially of its geotechnical characteristics and the related geohydraulic conditions. After primary investigations on about 40 exploratory drillings an approximate view of the situation was given. A highly water saturated and pasty sludge as main component of the overburden dump with an area of approximately 0.3 km^2 and an average thickness of 40 m have been first crucial insights. Due to these subsequent questions had to be answered: In which way according to the common used technics the exploitation of this area is possible? Is it possible to drain the substrates and how long does it take? How much water can be extracted from these sediments in a reasonable and effective way? To answer these questions a secondary exploration campaign including a historical inquiry, more detailed surveying methods and a testing site for vacuum wells was started.

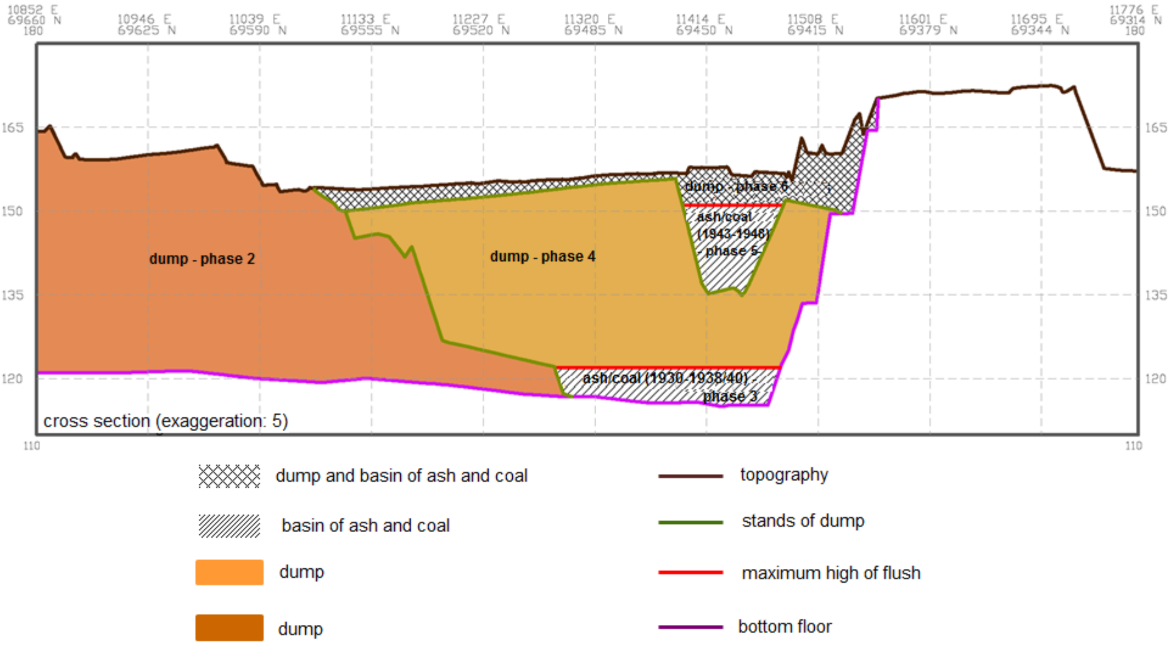


Figure 1: *Cross section through the Bösau dump system*

2. Methods

Exploration

The primary exploration campaign was realized with the objective to clarify basic geological structure of the Bösau dump system. Considering later recovery technology in detail the exploration focused on following aspects:

- geotechnical properties of border zone surrounding the dump system to be able to create a border slope for recovery
- completion of some parts of the Bösau dump system with insufficient amount of available geological data
- verification of historical data on structures that may have occurred during construction of the dump and that might be important for planning the recovery technology

During primary exploration campaign already 40 exploration holes have been drilled, 16 monitoring wells have been erected, 19 slug-and-bail-tests as well as 15 cone penetration tests have been realized.

At the end of this the knowledge of quantity and quality of the masses sedimented in the Bösau dump system could be improved. According to this the material deposited in the dump system, which needs to be recovered using special technology, has an overall volume of 6 Mill. m³. Although the structure of the dump turned out to be extremely heterogeneous, the material can be classified into 3 types:

- conventional overburden dump
- flushing dump consisting of ash- and coal-sludge residuals
- mixture of both

The sediments of the Bösau dump system can be identified as predominantly cohesive. Consistency varies significantly depending on water content. While in vadose zone solid to semi-solid material occurs, in the saturated zone dominates muddy material, settled irregularly.

But especially the mixture between conventional overburden and ash- and coal sludge, which makes around 30 – 60 % of the whole dump volume, are highly saturated. It is foreseeable, that slopes and working levels will show insufficient stability (highly problematical due to mine safety) unless measures are realized to improve soil quality.

Figure 2 shows drill core with dump material (from muddy on the left to semi-solid on the right).

Figure 2: *Drill core with muddy (left) to semi-solid (right) material from Bösau dump.*

Hydraulic conductivity k_f, derived from hydraulic tests (slug and bail) ranges from $1\cdot10^{-6}$ to $1\cdot10^{-8}$ m/s. The materials have very low conductivity and are hardly drainable. The inhomogeneity made it impossible to stratify the hydraulic characteristics.

As a result of the first exploration campaign with respect to the later recovery of the dump two resulting problems determined the next steps:

- In which way the Bösau dump system can be drained in an effective manner to improve mineability and transportability of the material?
- Is there some possibility in spite of heterogeneity of the dump to verify spatial distribution of geomechanical characteristics in order to improve extraction planning?

Answers of these two questions should be found with an additional exploration program on drainability and geomechanical characteristics.

As mentioned, after primary exploration hydrological characteristics could be named as low conductive and hardly drainable. Insofar to design an effective dewatering system special technology such as deep vacuum wells must be taken into account (Herth and Arndts (1994), Strzodka et al. (1975), Tudeshki (2014)). Therefore field tests were planned and realized.

With the objective of improving validity of geological, hydrological and geotechnical data exploration work continued with drilling 27 additional exploration holes, erection of 13 additional observation wells, realisation of about 40 cone penetration tests and soundings for determination of shear strength, cohesion and consistency and realisation of geoelectric measurements (deep electrical well logging) for interpretation of registered electrical resistances due to water saturation of the dump.

The plurality of exploration methods and the plurality of exploration objectives (determination of dump composition and its geological, hydrological and geomechanical characteristics) applied with this spatially limited problem, differ significantly from those, who are commonly used with the operational deposit reconnaissance.

For this reason the exploration results are not analysed using the regular geological model, but special modeling turned out to be necessary. While the mine operator regularly runs stratigraphic models for its lignite operations, the dump and flushing dump system had to be modelled using block modeling. This, amongst others, commonly used for modeling impregnated ore deposits, required data preparation in a special database as well, which enables to integrate all the different exploration data in the analysis.

Blockmodel

Lignite deposits, mined in German open cast mines, are typically in its stratigraphic characteristics. To set up the geological model the lignite seams and corresponding overburden materials like sands and clays and the lithology information from drilling are correlated using stratigraphic codes for equal units. Between the drill holes these intervals are interpolated by empiric algorithm. This results in a quite accurate model prediction of the deposit. An abstract on geology of German lignite deposits can be found at Stoll et al. (2009).

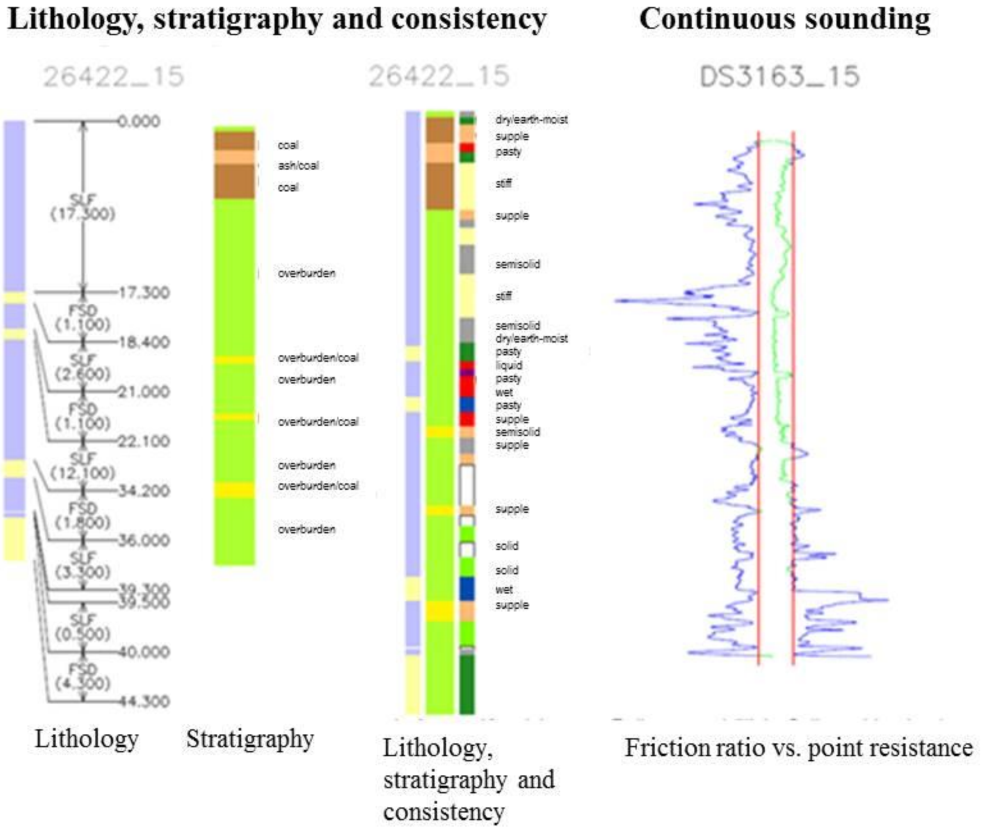
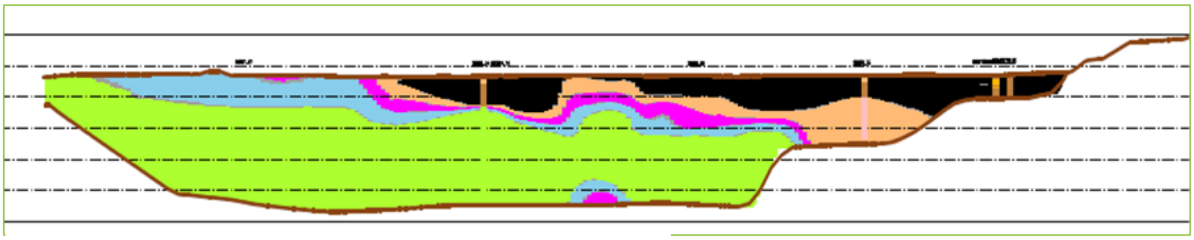


Figure 3: *Examples of exploration results*

However, stratigraphic models are not appropriate to reconstruct the lithology of old dumping sites, especially landfills with alternating emplacement and unknown origin of material. In case of the Bösau dump different sediments have been dumped and purged in over several years. To rebuild this heterogeneous unit of sediments a block model for soil mechanic, hydrological and mine planning decisions had to be set up. All different exploration results collected during different exploration phases were supposed to be addressed by the model and a prediction between the boreholes was aspired.

Fig. 3 shows an example of different types of information acquired by drilling, analyzing or probing to describe lithology, texture, consistency and ground stability. Whereas regular dump material was spoiled from west, ash and coal residual sediments were purged in from east, partially at the same time, which caused locally a random mixture of materials. A high proportion of ash and coal residual sediments will cause more problems during mining because of its critical geomechanical properties. Therefore one main parameter of the block model is the ratio between expected regular dump material and ash/coal residual sediments and its spatial distribution of the Bösau dump. Vertical sections through the model are shown in fig. 4.

Vertical cross section E-W



Vertical cross section N-S

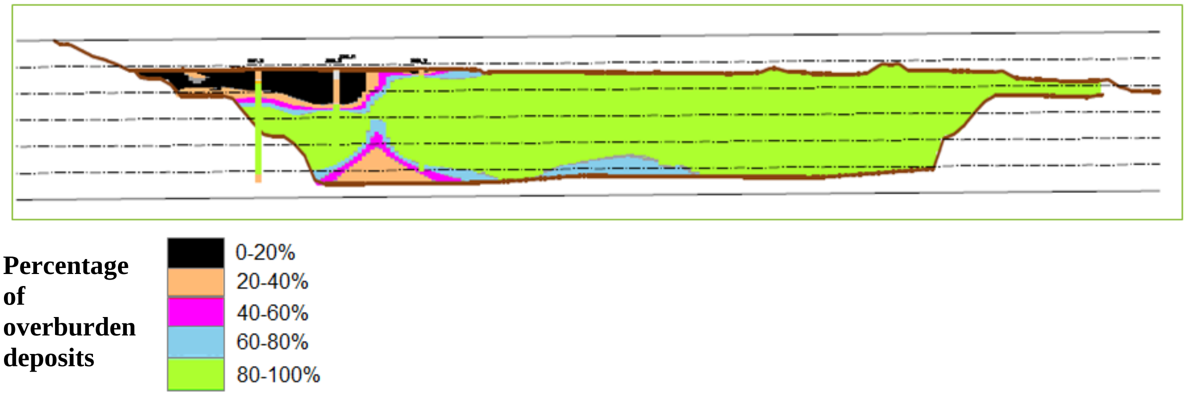


Figure 4: *Cross Sections of Bösau dump showing the percentage of regular dumped material.*

Hydrology and Vacuum Well Tests

Due to the maximum thickness of Bösau dump up to 45 m and an extent of 800 m North to South and 650 m East to West the hydrological situation is set by the adjacent dump and bedrock aquifers as well as groundwater recharge from precipitation at the area of about 0.3 km², the surface of the dump complex is on +155 to +158 m a.s.l. The bottom of the dump is on +110 m a.s.l. hence the groundwater levels of the underlaying aquifer complexes GWLK 5 (< +100 m a.s.l.) and GWLK 6 (< +95 m a.s.l.) are not recharging the dump. Rather a deep drainage can be assumed on discontinuities of the underlaying clay.

East of the Bösau dump the unexploited bedrock pile contains the groundwater complex GWLK 3 with groundwater levels up to +140 m a.s.l. Given that there is no inflow to GWLK 3 at this remnant the only recharge is given by precipitation and effluent from surface water. Within the range of local depression zones the saturated thickness is about 15 m.

The groundwater levels at the dump Wählitz II west of Bösau dump are on 145 m a.s.l. Due to the heterogeneous distribution of overburden substrates with different soil physics a discontinuous groundwater level can be assumed there. At this area groundwater recharge comes basically from precipitation.

The same can be supposed for the complex Bösau dump. The investigations on soil physics show highly cohesive soils by the majority with water contents up to 50 % Vol. The saturated thickness of the dump is up to 35 m or 5 to 10 m below ground level. Southbound the water level is slightly decreasing.

As a result of the high saturated substrates within the Bösau dump any additional hydraulic potential takes effect on large distances, too. For this reason recharge by precipitation or adjacent aquifers does not evoke a high amount of groundwater inflow. Rather on local depressions of groundwater levels inside the Bösau dump in case of dewatering the hydraulic gradient will effect a continuous subsequent delivery of groundwater from the outside aquifers with higher groundwater levels and higher hydraulic conductivities, too. Thus groundwater levels at the surrounding areas have to be lowered to comparable or subordinate levels.

Monitoring

In March 2015 four vacuum wells were drilled on two different places to investigate the feasibility and influence of dewatering the cohesive substrates with negative pressure. Laboratory multi step outflow experiments on the dump substrates showed a significant higher drainage on increasing pressure compared to free drainage. On each site one well was drilled to the bottom of the dump, circa 40 m deep and one well was drilled as a shallow one, circa 25 m deep each with a 10 m screen above the well sump.

The adopted method for drilling and mounting the wells ensured a continuous pressure of -0.9 bar for the three month test phase at each of the four wells. On the very high cohesive substrates which were drilled the achieved discharge flow at the wells was between 0.5 and 2.0 L/min with a drawdown up to 10 m nearby the wells.

One well had a discharge flow between 100 and 120 L/min. It caused a drawdown of about 3 m on a diameter >30 m. Compared to the other experimental wells this one had a significant higher discharge flow. The reason for this is a sandy seam with a thickness between 4 and 10 m which shows the inhomogeneity of the dump (see figs. 5 and 6).

The following essential results were made on the experimental wells: The maximum vacuum could be achieved with levels from 0.9 to 0.92 bar. This was ensured by setting up the bentonite seal underneath the groundwater level. At both experimental sites the drilled substrates were typical inhomogeneous dump substrates by the majority. At the site in the north fine sandy medium clay and aquiferous fine sands (thickness up to 10 m) were detected. At the site in the south the substrates were almost the same, more silty and without the sandy seam. The thickness of the bentonite seals at the wells is about 10 m, generally. Therefore the wells do not discharge coal and ash slurry which are lying in the upper zones of the Bösau dump.

The silty dump substrates show hydraulic conductivities between 1.1 · 10-6 and 2.0 · 10-8 m/s. Significant higher values from 1.4 · 10-5 to 2.9 · 10-5 m/s are possessed from the fine sands in the lower part of the dump. According to this the wells screened in silty seams had lower discharge rates than the ones in the fine sands. The radius cones of influence were calculated between 5 m for the shallow ones and between 40 and 200 m for the ones drilled to the bottom of the dump. With continuous flow rates the pumped water contained no turbidity or sediments.

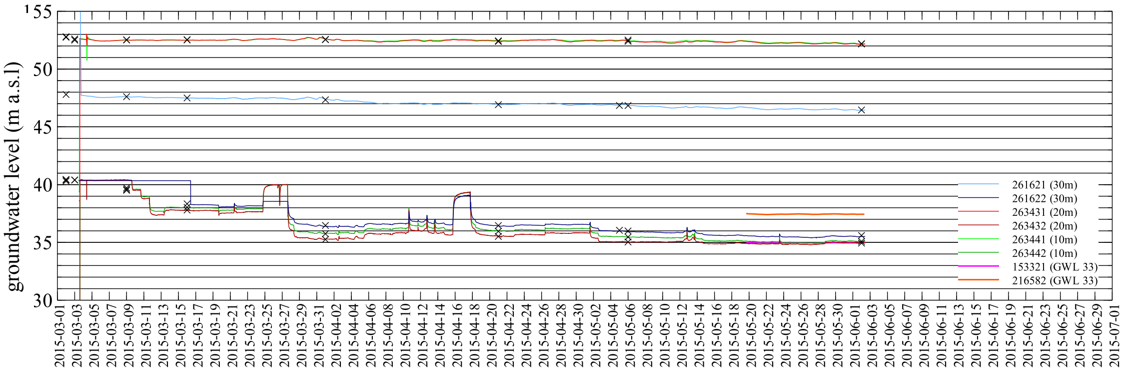


Figure 5: *Time series for period of testing at observation wells in 10 m, 20 m and 30 m distance of the vacuum wells on the northern site with screens within the upper and the lower range of Bösau dump. (Crosses assign measurements by hand)*

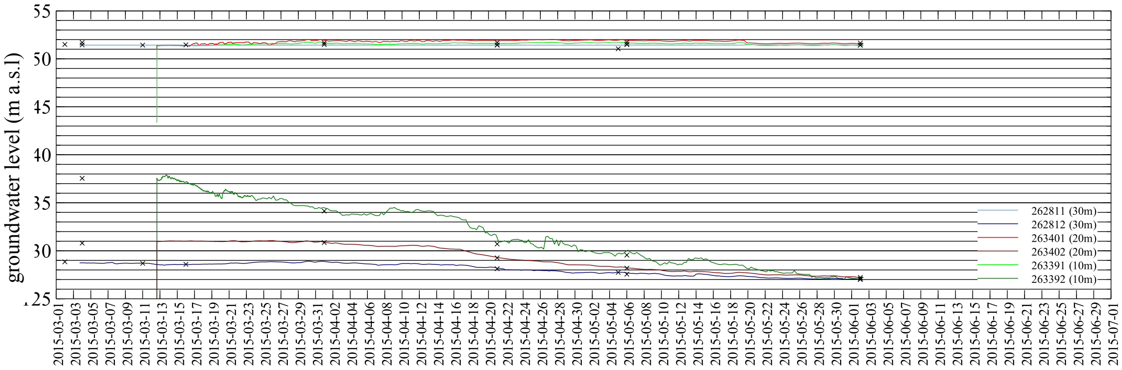


Figure 6: *Time series for the period of testing at observation wells in 10 m, 20 m and 30 m distance of the vacuum wells on the southern site with screens within the upper and the lower range of Bösau dump. (Crosses assign measurements by hand)*

A continuous and frequent hydrological monitoring of groundwater levels is executed at Bösau dump as well as at the adjacent dump and bedrock areas. 40 observation wells are measured every two months and 16 monitoring wells are equipped with data loggers.

Geophysics

With prevenient investigations and historical inquiry the boundary of the complex dump Bösau was described. To confirm this boundary and to locate possibly larger inhomogeneity within the Bösau dump, geophysical methods (geo-electric measurements, seismic reflection) were used. According to the structure of the vacuum dewatering system furthermore it should be investigated whether the geo-electric measurements are a suitable method of determining the dewatering success. These first measurements were carried out in the period from February to July 2015. A zero measurement took place in February/ March. Measurements have been repeated in May/June and in July 2015 (Hohlfeld et al. 2014).

The values of specific resistance are lower than expected. Only in boundary areas or in greater depths zones with values > 50 Ωm could be detected. Such very low values occur otherwise on saline groundwater.

Due to the complex genesis a clear allocation of specific resistances to certain materials is limited. However, highly saturated areas were identified, areas of influence of the flushing dump defined and distinguished from undisturbed areas. In all profiles a surface layer of low thickness with increased resistance could be detected. This might point to lower water contents caused by dehydration. With a thickness of about 15 – 20 m in all east-west profiles exists an area with high conductivities with clearly defined top and down boundary. The lower limit here is located approximately at the height of

131 m a.s.l. Further west the high conductive area becomes increasingly smaller and more heterogeneous.

The north-south extending profiles fit very well to the ones from west to east. Fig. 7 shows a 3D-panel of the geo-electric measurements.

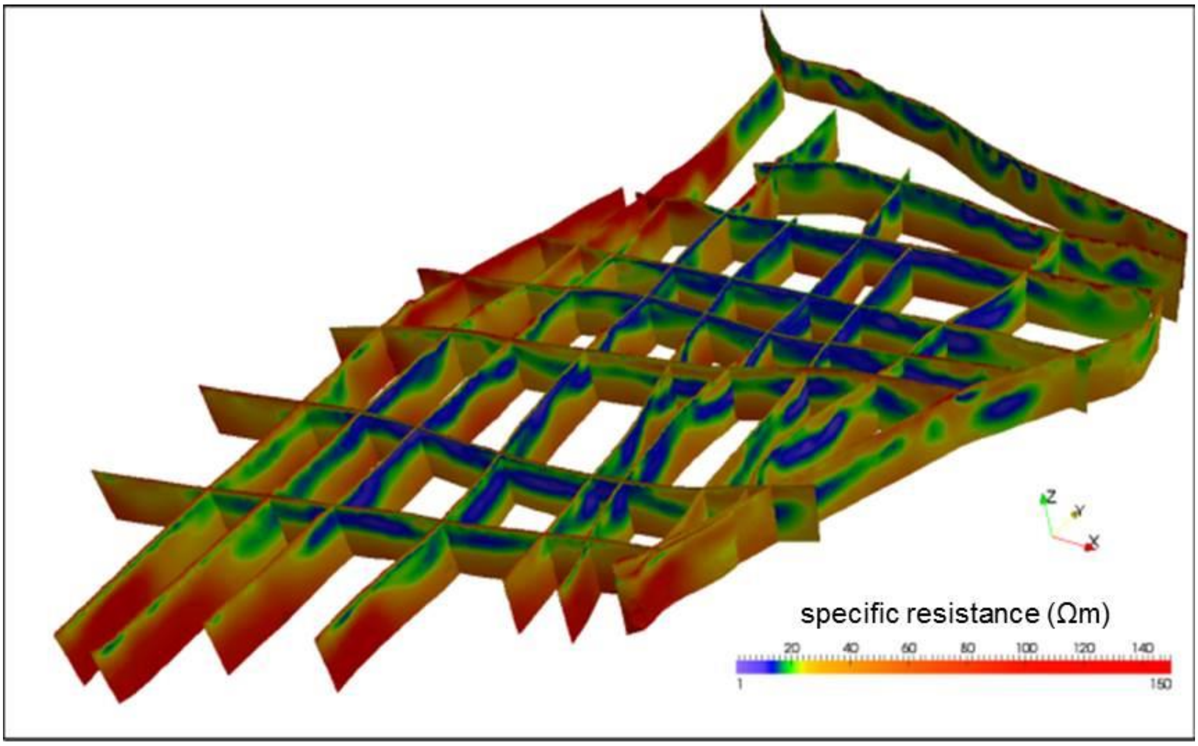


Figure 7: *Specific resistance 3D-panel of the geo-electric measurements.*

The additionally performed seismic reflection measurements confirmed the results of the geoelectric measurements substantially. The low informative value of seismic measurements might be caused by the heterogeneous speed ratios, which were probably caused by the widely varying water saturations at the Bösau dump.

The monitoring during the dewatering with the vacuum wells on the test sites was carried out on three profiles. Due to the limited extent of the impact area of vacuum dewatering only a slight change on resistance values was expected. More significant results should occur on measurements during dewatering on larger areas. Looking at the single profiles a change between the several measurements can hardly be recognized.

3. Conclusions

The aim of further investigations is the extraction of authoritative properties of the deposit materials from the complex investigations (three divisions of deposit forms, consistency differences and soil physical parameters) and to figure out correlations between different sensing methods. The objective is a more detailed knowledge of the complex dump in terms of soil mechanics and soil physics.

Despite the better resolution of Bösau dump after performing a secondary more detailed exploration the demarcation of less problematic areas remains difficult due to the pronounced inhomogeneity of the total body of the dump which will lead to geotechnical defiance during the prospective mining.

The technical feasibility and the basic need to operate vacuum dewatering for the improvement of soil physical properties at Bösau dump is confirmed by the present results.

With expectable average flow rates from 2 to 5 L/min and according to current knowledge a recoverable volume of about $0.65 \cdot 10^6$ m³ the operation of about 100 vacuum wells takes a time of 2.4 - to 6 years. Since the end of February 2016 five well clusters are operating in the south area of Bösau dump.

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Dewatering challenges in an large scale production hard rock open pit in northern Sweden

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Abstract

During the last years BOLIDEN increased production of Aitik mine up to 36 million tons of ore per year. The fast development of the pit in area and depth also leads to an increase of the hydraulic head and by that to stronger water inflows. Wet mining conditions influence the production efficiency negatively, especially during mining of the pit floor they can reduced the production efficiency dramatically.

To gain dryer mining conditions BOLIDEN implements a large scale dewatering system in Aitik. This includes the implementation of in-pit wells and cutting of recharge sources. To gain effective results from these measures, decisions of where and how to apply them need to be based on further research of the local hydrogeology.

The approach for this research described in this paper is the deep analysis of available information at BOLIDEN and results of an extensive sampling trip. Strategy of the sampling trip was to sample water inflows and surface waters in the vicinity of the pit, which might function as potential water sources.

Based on onsite measured parameters, the samples were grouped according to their behavior.

Water flow path hypotheses of how potential sources and inflows could be related were developed. Full analysis with a wide range of elements have been carried out for all samples. The results of these analyses were used to validate the flow path hypotheses. Especially higher Al-, Cu- and REE- contents, which were generated in weathered zones or tailings, were used as tracers to evaluate possible relations between surface waters and inflows.

By interpreting all information certain flow path suppositions were discarded and others became more likely. This new knowledge was used to avoid investments on probably ineffective measures. The new understanding of where certain inflowing waters are generated lead to further decisions for dewatering measures.

Key words: Dewatering, Hardrock open pit, local hydrogeology, flow path interpretation

Introduction to the topic

During the last years BOLIDEN increased the production of its Aitik mine up to 36 million tons of ore per year and further increases are planned. The fast development of the pit in area and depth also leads to an increase of the hydraulic head and by that to a higher amount of water that enters the pit.

Wet mining conditions influence the production efficiency negatively. Especially during mining of the pit floor the water inflows reduced the production efficiency dramatically.

To reduce or even fully avoid these effects BOLIDEN plans to implement a large scale dewatering system in Aitik. This includes an optimization of the current shotgun pattern according to which the horizontal drains are drilled, the implementation of in-pit wells and cutting of recharge sources.

To gain effective results from these measures, decisions of where and how to apply them need to be based on further research of the local hydrogeology.

Short Introduction to the Aitik mine

Aitik is located 60 km north of the Arctic circle, close to the city of Gällivare in Sweden. Aitik is the city´s largest private employer with about 650 employees. With a length of 3 km, a width of 1 km and a depth of 450 m Aitik is one of the biggest hard rock open pits in Europe. Furthermore Aitik is also one of the most efficient copper open pits in the world. In 2015 Aitik produced 36.361.000 t of ore, 67.000 t of copper, 61.452 kg of silver and 2.042 kg of Gold. Furthermore there is the mining of about 32.000.000 t of waste rock at the current production rate.

According to the current mine plan, Aitik will reach a final depth of 645 m in 2039, during that time the surface area will increase by roughly 30 %.

The bedrocks in Aitik are primarily gneiss and shale. Chalcopyrite and pyrite are the main valuable minerals. A 10 – 20 m thick layer of alluvium, typically moraine and peat, covers the hard rock of the deposit. Feature of the hard rock body is a strong fracturing, that can be seen on the majority of the exposed rocks in the pit slopes. Most of the joints seem to be open and show a very low infilling. It is believed that almost every ground water flow in the pit area occurs under fracture flow conditions. As the rock is very well jointed, it is easy to drain the rock mass itself, but the rock itself shows a low permeability about 5×10^{-7} to 10^{-8} m/s. In 2014 Aitik had a water output of roughly 4.400.000 m^3. Figure 1 gives a good impression on how water inflows spread through the slopes. On the left side of the image the slope seems to be quite dry, while the very well jointed shear- and orebody zone in the middle and the right side of the image is obviously wet due to the strong inflows.

The leading climate in Aitik is a humid subarctic continental climate with cool summers and no dry season. Based on weather records between 1996 and 2014, the mean annual precipitation in the area of Gallivare is about 668 mm and with average temperatures clearly below 0°C between November and March and 13 °C between June and August.

Figure 1 Wet and dry zones in Aitik north pit, Photo by Lars de wall

Sampling inflows – Basis of a new understanding

Our approach for the further research on the local hydrogeology is the deep analysis of available information at BOLIDEN and the analysis results of an extensive sampling trip. Strategy of the sampling trip was to sample water inflows in the mine and surface waters in the vicinity of the pit, which might function as potential water sources. Figure 2 gives an overview of the collected samples in and around the Aitik open pit.

In total 43 samples were collected, the samples were grouped according to their type into potential water sources and water inflows. Samples of potential water sources were collected from "artificial" (12 samples) and natural surface waters (3 samples). Water inflow samples were collected from the pit sumps (3 samples), conveying tunnels (6 samples), horizontal drains (12 samples) and uncontrolled inflows (8 samples).

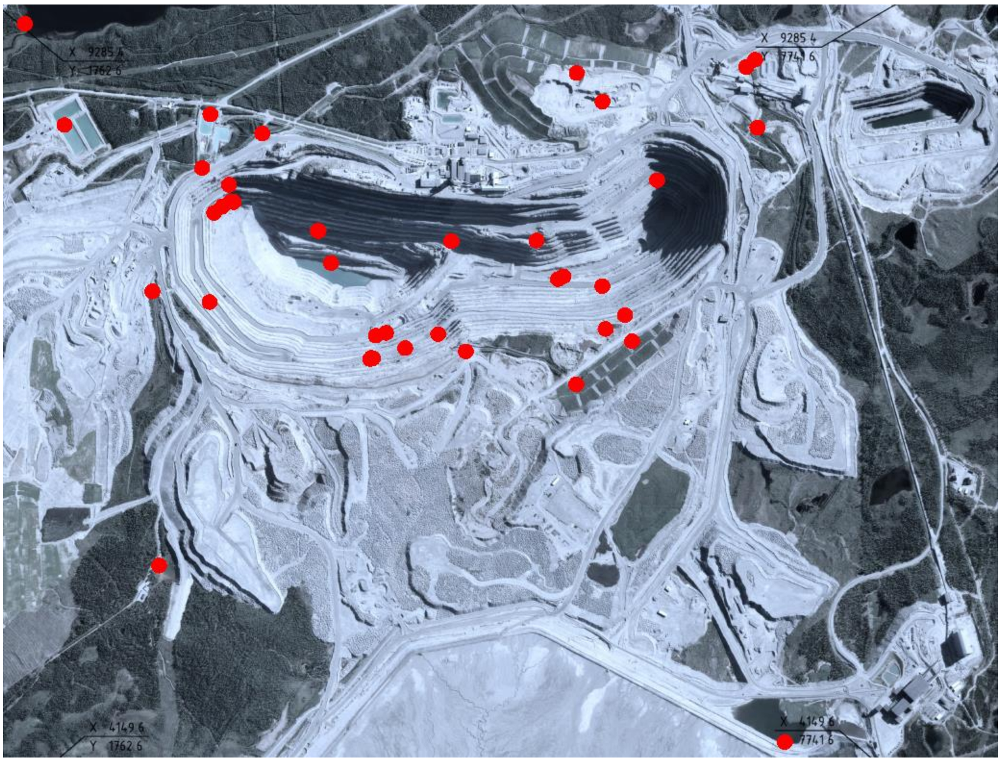

Figure 2 Overview of collected samples in and around Aitik

Analysis and Interpretation – Way to a new Understanding

Based on the onsite measured parameters, pH-Value, electric conductivity, redox potential, alkalinity and acidity, the samples have been grouped according to their behavior.

Water flow path hypotheses of how potential sources and inflows could likely be related have been developed. Basis for these hypotheses were the grouping and locations of the samples.

Figure 3 shows an example for such a hypothesis. The green dots represent inflows to the pit that were believed to be likely related to the nearby surface waters, represented by the red dots.

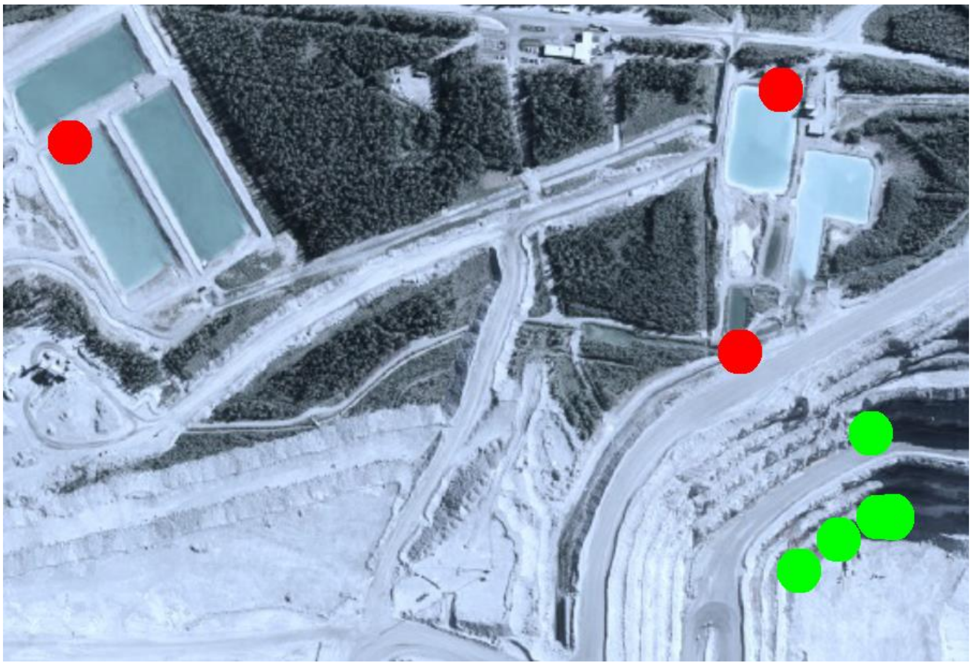

Figure 3 Example for sample relation hypothesis

Full analysis with a wide range of elements, a TC/TN-analysis and an analysis of the stable isotopes (^{2}H/ ^{18}O) have been carried out for all samples. The results of these analyses were used to validate the developed flow path hypotheses. Especially higher Al-, Cu- and REE- contents, which have been generated in weathered zones or tailings, were used as tracers to evaluate possible relations between surface waters and inflows.

Figure 4 shows the Al-, Cu- and REE- contents of the samples shown in figure 3, which were believed to be related. On the one hand the left group (red box), which represent the surface waters and by that the suspected inflow source, show noticeable Al-, Cu- and REE- contents. On the other hand the inflow samples (green box) do not show noteworthy contents of these elements. In order to this the suspected relation of both groups is very unlikely or the surface waters only have a very marginal influence on the inflows.

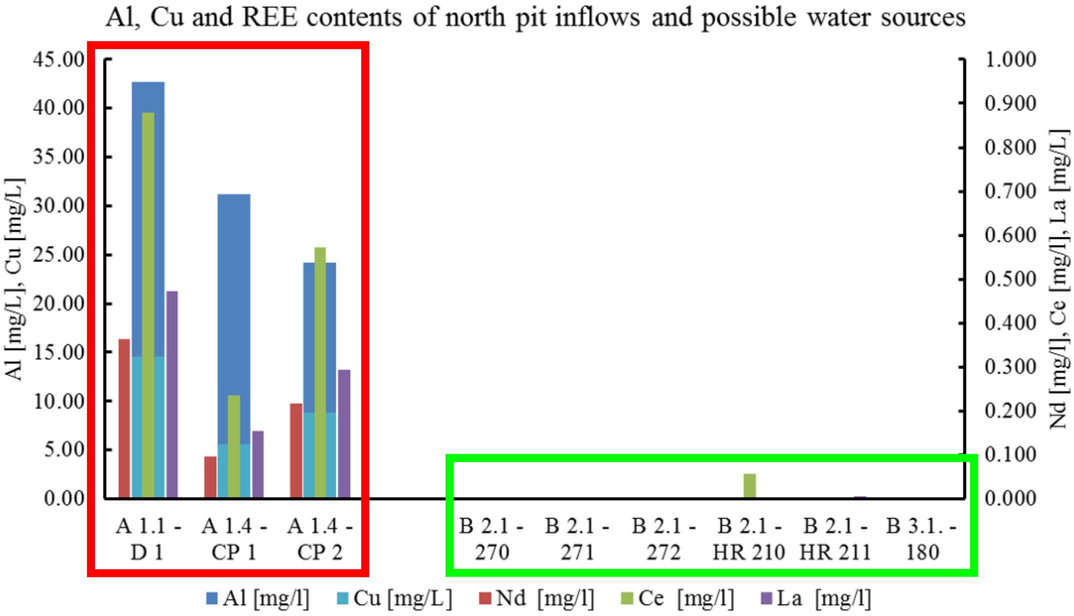

Figure 4 Example for sample relation hypothesis

Conclusions – A new understanding as basis for decision making

By interpreting the new collected data and the available information certain flow path suppositions or water relations could be discarded and other became more likely. These new knowledge was used to avoid investments on probably ineffective measures. The new understanding of where certain inflowing waters are generated lead to further decisions for dewatering measures.

Further research goal is to increase the understanding of the local hydrogeology and actual flow paths to provide information for the decision making with the higher aim of reducing the overall water inflows and increase the production efficiency and safety by gaining dryer mining conditions.

The significance of ground water flow modelling study for simulation of open cast mine dewatering and assessing the environmental impact of drainage

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Abstract

Simulations of open pit dewatering and the environmental impact assessment are performed using a ground water flow modelling. However, numerical models have certain limitations resulting from the existing uncertainties as to the assumed hydrogeological parameters and boundary conditions. They include the shortcomings in the identification of hydrogeological conditions, cyclic changes of precipitation as well as evapotranspiration and evaporation, the impact of local climate changes resulting from land management in the of mining and power generation activity areas as well as changes in schedules of mining and reclamation including post-mining flooding. Even though groundwater models have numerous limitations related to uncertainty of the parameters, they still provide the most comprehensive information concerning the aquifer system as of the time when they are developed.

Key words: open pit, lignite, dewatering, modelling,

Introduction

In mining industry, water-related problems are among the most important aspects which can decide whether a new mine will be feasible or reasonable. For the assessment of costs of mining operations both the rate of mine water inflow and the environmental impact of mine drainage is important. Insofar as in the past one would mainly focus on the aspects of the hazards connected with mine water inflow, at present most of the attention is focused on environmental impact assessment. To estimate the mine water inflow to open pit one typically applies the methods of hydrogeological analogy or hydrogeological balance.

At an early stage of deposit exploration, hydrogeological calculations are usually performed using analytical methods, the most popular of which is the large well method described in numerous textbooks. Further investigations are dominated by numerical methods. They are used throughout the whole mine life-cycle. Numerical methods enable to forecast the process of active mine dewatering as well as the process of flooding the post-mining excavations with greater accuracy, than any other methods. They can assess the impact of dewatering on groundwater, surface water, soil, flora, farmlands and forests, water chemistry, water intakes, land subsidence and others. Particularly, the process of flooding post-mining reservoirs with complex geometry and diversified hydrogeological conditions must rely on numerical models (Schwartz, Crow 1985).

Application of modelling methods throughout an open pit life-cycle

Numerical modelling is used during deposit exploration period and mining activity as well as after its completion. Its purpose is to deliver reliable forecasts of ground water inflow to the mine drainage system and the environmental impact of mine drainage with reference to different scenarios of the deposit opening up, its extraction as well as reclamation of post-mining excavations. In many cases, models are also performed in order to confirm or reject the scope environmental impact of an active mine. They usually pertain to the impact of dewatering on water courses, natural and artificial water reservoirs, ground water conditions, ground water resources, water intakes, soil, flora, farmland and forests, water chemistry or subsidence. The range of impact of mine dewatering is typically assumed to extend to a point where the ground water table was lowered by 1 meter, disregarding the permanent lowering of average multiannual water table.

By 1990’s, problems of reclamation of post-mining excavations had not been extensively addressed in research-related publications, since there were no many such a reservoirs (Uberman 1996). Not until the recent dozen or so years these problems have been more extensively addressed all over the world, for the reasons to estimate costs of works related to flooding the future post-mining excavations as well as assessment of their environmental impact. The most crucial elements in these studies were: the rate of flooding, restoration of ground water table, the impact of reservoir on ground water and changes in the water quality in reservoir and aquifer.

Specificity of application of modelling methods for purposes of surface mining

The procedure for developing a ground water flow model in mining conditions generally complies with the overall modelling methodology. However, it must account for the specificity of operation and drainage of mines. The ground water flow model developed for open pit mine should be a full three-dimensional (3D), with the hydraulic head specified for each model layer. It is particularly important in the areas adjacent to the open pit, especially near the slopes of the pit. For the assessment of the range of the cone of depression, one can apply a quasi-3D model which only represents the vertical flow in semi permeable layers (Szczepiński 2013).

In order to develop reliable forecasts, it is necessary to recognize hydrological conditions of the deposit as well as to identify all environmental, mining and technological factors which can affect the mine water inflow. The most important factors influencing mine water inflow and environmental impact of drainage of surface mines are: hydrogeological parameters of deposit and the neighborhood aquifers, aquifers recharge from precipitation, aquifers recharge from surface water, dewatering technology and management of post-mining excavations. All these data are required to developed a reliable conceptual model. Conceptual model requires not only detailed identification of hydrogeological conditions, but also right representation of the mine drainage system. It should be developed taking into account information on the location of deposit opening out, the mining face advancement, location and advancement of internal dump as well as the parameters of final excavation.

Simulation of mine drainage and its influence on the water environment is associated with a huge amount of data, more than for models created for other reasons. The water courses, lakes and reservoirs on the model area should be simulated taking into consideration the drying as well as the re-watering in the case of groundwater rebound. Recharge and evaporation boundary conditions should ensure appropriate representation of effective infiltration changes during water table fluctuation, whenever such changes take place.

As the mine drainage is the process variable in time and space, the models used in mining hydrogeology are solved in transient simulation. However, at the first stage - for natural hydrodynamic conditions prior to the deposit dewatering – the model should be solved in a steady-state conditions. Calibration performed under steady-state conditions enables preliminary determination of recharge and the horizontal and vertical hydraulic conductivity of aquifers. Model verification should be proceed in transient conditions taking into account preliminary well pumping before the drainage system is put into service. This enable to improve parameters determined in steady-state conditions and estimate the specific yield and specific storage coefficients of the aquifer. At the stage of predictive simulations, one is required to change certain input parameters and boundary conditions of the model used for calibration and verification of the model (horizontal and vertical hydraulic conductivity as well as specific yield and storage capacity). Outside the mining area, it is necessary to update boundary conditions related to decommissioning or construction of new water intakes, ditches or reservoirs, industrial and municipal waste dumps as well as to simulate relocation of rivers and other water courses. The new parameters should represent the advance of the deposit extraction, the overburden dump area and the post-mining excavations. Besides modification of boundaries conditions representing the dewatering system, updating the spatial conditions of the model layers and filtration parameters are required.

Documenting the results of modelling study in mining hydrogeology is more extensive compared to models used for groundwater resources assessment. However, it must account for all boundary conditions and parameters of aquifers subject to changes in time. While applying a model, one should envisage both natural conditions, the dewatering period, the post-mining excavations management as well as conditions after completion of reclamation period. The results thus obtained, including the hydraulic head in each modelled layer, the range of the cones of depression for all layers, the groundwater balance, the rate of mine water inflow as well as the hydrogeological conditions after reclamation completion, should be presented in both descriptive and graphical form for all the periods assumed.

Limitations of modelling methods

Numeric models have certain limitations and uncertainties related to the assumed hydrogeological parameters and boundary conditions. They include shortcomings in the identification of hydrogeological conditions, changes in groundwater recharge and modifications of mining schedules. Proper identification of hydraulic parameters, the nature of faults and fissure as well as karstic formation phenomena, is decisive for reliability of modelling studies. For example natural hydraulic barriers, such as faults filled with semi-permeable material or rock formations with low hydraulic conductivity compared to adjacent rock layers, can decrease the mine water inflow as well as to diminish the negative environmental impact of dewatering. Under natural conditions, i.e. those existing before the drainage commencement, the most efficient method to identify hydrogeological structures and parameters of rock layers is a trial pumping. While the deposit is being dewatered, the model should be subject to verification based on new information related to the actual response of the aquifer to the mine water drainage. It may lead to the necessity of adjusting hydraulic parameters of aquifers and semi-permeable layers in the model.

Despite the fundamental importance of recharge in the water balance, it is an element with the highest uncertainty, since its volume primarily depends on the accuracy assumed when calculating other elements of the balance equation (Healy 2010) Changes in the recharge may be consequences of many factors which were not accurately estimated or identified. These may include: unidentified leakage of surface waters into aquifers, water losses from the water supply and sewage disposal system, technological waters recharging the rock mass during drilling, changes of recharge caused by land management.

Assuming the amount of recharge based on average multiannual precipitations does not account for the cyclic deviations and trends resulting from climate variability. For instance, small precipitation may lead to increase of ground water table below a level referred to as the evapotranspiration extinction depth, which causes an increase in effective infiltration. On the other hand, the change of water deficit, i.e. the difference between potential evaporation form reservoir and the precipitation, affects the rate at which post-mining reservoirs are filled with water. It particularly applies to long-term forecasts which sometimes have more than 100 years.

Mining and power generation activity, including formation of large open pits and overburden dumping areas as well as the existence of powerful heat and steam emitters at nearby power plants, may lead to changes of hydraulic parameters of layers as well as local climate variations, influencing recharge form precipitation.

Post-audit analyses imply that ground water flow models can fail to forecast the future due to the wrong input parameters or different boundary conditions which are not compatible to the actual conditions. Due to changes in schedules of mining activities or reclamation of post-mining excavations, the input data used in the model should be verified and updated with reference to the most recent recommendations and assumptions. Continual improvement of the conceptual mod3el by collection of new field data wil imrove the numerical model (Anderson, Woessner 1992).

Conclusions

Even though ground water flow models used in mining hydrogeology have numerous limitations related to uncertainty of the parameters, they still provide the most comprehensive information concerning the aquifer system and the dewatering system as of the time when they are developed. However, they will always require verification based on new information emerging in relation to an actual response of the aquifer system to the drainage being conducted. They should also be subject to periodical verification with reference to recent information about the actual climate conditions, the response of the aquifers system to the dewatering as well as up-to-date schedules of deposit extraction and mine closure. The numerical modelling used in scientific studies as well as in applied hydrogeology is a combination of practical and scientific knowledge. Standardisation of modelling methods does not exclude the need for a subjective approach applied in solving every single problem during the entire modelling process.

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Linking waste rock dump construction and design with seepage geochemistry: an integrated approach using quantitative tools

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Abstract

The characterisation and assessment of waste rock has been the subject of considerable research and many guidance documents have been published internationally. While these documents provide detailed information on the technical aspects of geochemical characterization of waste rock, there is not great detail into how to integrate these studies into engineering planning decisions around waste management options. These planning decisions require quantitative assessment to balance environmental management (risk) and operational constraints (cost). For example what is the risk/cost tradeoff for using different placement methods e.g. end tipping vs paddock dumping. Because current industry practice and the majority of guidance documentation focuses on only geochemical classification, there is a disconnect between the outputs of the studies and the operational requirements for a direct assessment of placement method such that risk and cost can be quantitatively assessed.

Defining the contributing factors to the risk/cost tradeoff posed by disposal of waste based on a specific waste management approach requires a broader technical assessment approach and directs these assessments towards a semi-qualitative and quantitative methodology. Quantitative methodologies show an increase in the confidence of these assessments by providing logical, measureable assessments.

To address the need for a qualitative risk/cost tradeoff assessment approach OKC has developed an assessment process based around a quantitative risk tool. This tool captures multifaceted inputs, and employs an analytical model to provide quantitative analysis and outputs. This method of assessment allows risk to be assessed on the basis of waste placement technique, and whole waste facility engineering design, and not just on material properties such as geochemical characteristics in isolation. It also allows assessment of the benefit of progressive management measures as compared to deferring to final closure solutions such as covers.

Key words: Toe seepage, gas flux, sulfide oxidation rate

Introduction

The characterisation and assessment of waste rock forms the initial stage of waste management strategy planning. Prior to decision making, waste management strategies should evaluate both costs of waste management and risks associated with the exposure, stockpiling and placement of waste materials, such as spontaneous combustion, toxic gas production, and acid and metalliferous drainage (AMD). These risks are complex, are all interrelated, and are associated with air and water entry into the waste material where subsequent oxidation reactions occur (Lottermoser, 2010).

It has become common practice in the industry as part of waste characterisation to classify material in a deterministic manner on the basis of primarily geochemical risk factors and to define material types, for example, as potential acid forming (PAF). Material that is determined to pose significant risks of AMD such as PAF is then prescribed a specific management method such as "encapsulation" as part of a placement strategy to reduce potential AMD risks. However this method of assessment is prescriptive and polarised as materials are categorised into a few catch all categories such as PAF, which in turn results in polarised decisions such as all PAF must be managed in a set manner.

In the field AMD risks are known to be complex and interrelated and are strongly related to the structure of the waste and how this influences oxygen ingress and water flow into the waste pile, where subsequent oxidation reactions can occur (Javadi et al, 2012, Lottermoser, 2010). The influence of airflow, water infiltration and flow, and the site specific diurnal or seasonal variations in these are likely to be key risk drivers.

General factors that are known to control AMD risks are detailed in Pearce et al (2015) and include:

- Geometry of waste dump including footprint, height, slope area
- Sulfide and carbon content of material;
- Physical properties of material (grain size and distribution, saturation, weathering rate);
- Geochemical properties of material (intrinsic oxidation rates, carbonate dissolution rates, kinetically controlled metal/non metal release rate)
- Timing of waste placement and any closure mitigation engineering solution (such as a cover)
- Structure of waste rock due to placement (pathways for air and water movement); and
- Climate (temperature and rainfall).

Geochemistry forms only one of these risk factors, however it is interesting to note that typical industry approach to AMD assessments is for the study to be based for the most part on laboratory testing related to geochemical properties only. While these geochemistry based assessments are robust, they are essentially just methods to classify and categorize materials based on the results of tests carried out in laboratory conditions. The use of laboratory kinetic leach column data for example, although considered to be the gold standard to estimate field estimates of sulfide oxidation rates and seepage quality, requires careful consideration when extrapolating to field conditions. This is because scaling factors will considerably impact the validity of the results (Pearce et al 2015).

A simple summary of these observations is to state that although the characterisation of materials is important, the method and timing of placement, and the site environment in which they are placed are perhaps more important variables, and are often disregarded.

In order to evaluate risk based on multifaceted variables requires application of semi quantitative analysis such as the operation of an analytical model. OKC has developed an assessment process based around a risk matrix that captures these multifaceted inputs and employs an analytical model to provide semi quantitative analysis and outputs. This method of assessment allows risk to be assessed on the basis of placement technique and not just on material geochemical properties in isolation. A full description of this method is outside the scope of this paper and is described in detail in Pearce et al (2015). In summary the assessment process based around a quantitative risk assessment tool that utilises a series of complex algorithms to "model" how waste materials will react to placement in a given scenario. Outputs from this model are then collated into a risk matrix that captures these multifaceted inputs. This method of assessment allows risk to be assessed on the basis of placement technique, and incorporation of closure mitigation solutions and not just on material properties in isolation.

The analytical model developed evaluates convective gas transport, intrinsic oxidation rate (pyrite and carbon) spontaneous combustion, seepage, carbonate dissolution rate and acidity generation. The analytical model is a one dimensional, quasi-steady state model

Method

Waste rock dump construction and link to AMD seepage risks

Construction of waste dumps is mainly based on one of the following methods; end-tipping, paddock dumping, push-dumping, or encapsulation. The specific method used on a given site to construct a landform is generally based on availability of equipment, cost and the scale of construction and so construction methods are far from uniform across all sites. Aspects of WRD construction that relate to AMD risk (that are commonly overlooked) are the internal structure created as a consequence of the prevalence of end tipping material, and the resulting hydro-geological characteristics which control air (oxygen) and water flux throughout the waste material (Wilson 2011). Given that oxygen and water flux are major controls in the production and release of AMD to the receiving environment, construction is clearly a very significant variable to factor into AMD risk.

Work by Wilson (2011) and Pearce (2014) shows that for end tipped waste oxygen ingress will primarily occur at the bottom of the pile with gas flux being into the toe and basal rubble zone of the waste pile moving upwards through the free draining course material layers by the process of thermal advection. Vapour flux also occurs along with gas flux and is an important aspect of the overall redistribution of water within the waste, and moisture loss from waste masses, the process is termed advective drying and is described by Pearce (2014). This conceptual internal structure of WRDs constructed by the common practice of end dumping is an ideal scenario for the production of AMD given the ample supply of atmospheric oxygen and water.

Figure 1 shows an example of waste being placed by paddock dumping, and end-tipping. Co-disposal of material is clearly visible from the rock types at this site, and material segregation through end-tipping is visible between the base and the top of the tip head. A cross section through an end tipped waste rock dump is shown in Figure 1 that depicts schematically the internal structure that results from the end tipping process as a result of particle segregation. The segregation of material as shown in Figure 1 has been confirmed by WRD excavations in the work of Wilson (2011), and drilling of multiple waste rock dumps Pearce et al (2014).

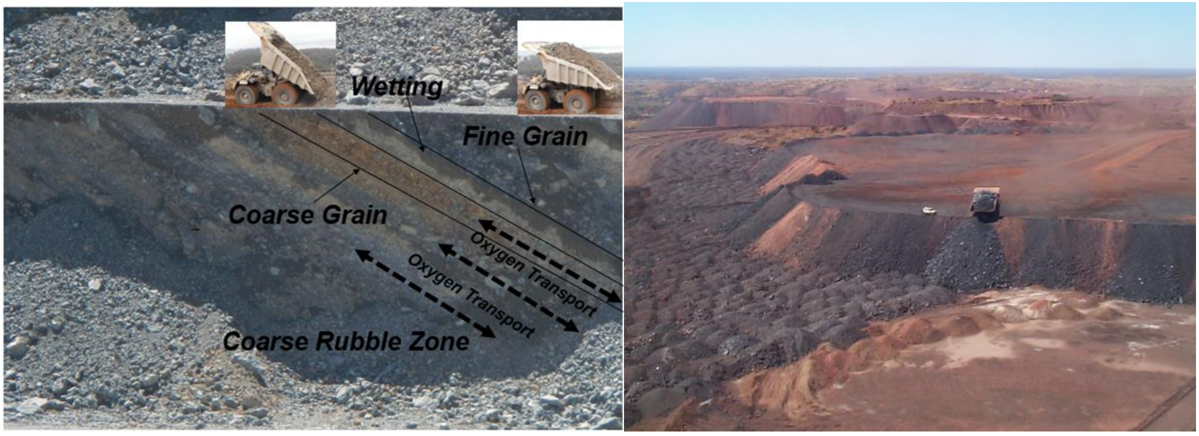

Figure 1 *Internal dump structure after Pearce et al (2016)*

The structure of the WRD will then dictate variables that directly control risks with respect to AMD due to the nature of material segregation. These features will have a direct influence on:

- Gas flux (oxygen ingress);
- Water flux (net percolation rates and vapour phase transport);
- Erosion and stability;

Conceptual model for seepage quality assessment from waste rock storage facilities

With respect to making quantitative predictions about future seepage quality that may discharge from a waste rock dump the key processes that will drive quality over time relate to the relative flux rates of gas, water and vapour through the waste as well as the properties of the waste itself. If the waste contains reactive material such as sulfides or organic carbon then the relative oxidation rate of these materials over time will be a key control on potential seepage loading. In conjunction with the oxidation rate, the relative rate of seepage through the waste over time will dictate seepage load and quality. These processes are interlinked to a high degree as shown by scenarios in Table 1. The scenarios shown are similar and involve the same material type in all cases, however one other key variable is changed in each scenario. Even though the material is the same in each scenario the seepage quality and load are significantly different in each scenario, thus the impact of changing variables other than material type is clearly significant.

It is clear from this scenario based conceptual level of analysis, that focusing on the waste classification in isolation is not a sufficient means to determine AMD risk and seepage quality (and to determine appropriate management strategies).

Table 1 *Waste rock dump construction controls on seepage quality*

Scenario	Waste material type	Construction method	Climate	Gas flux	Seepage flux	Seepage quality and load predictions
Solubility control	Pyritic black shale S>1%	End tipping	Semi arid	Very high	Very low, L:S ratios <0.1 per year	Very high loads and high AMD concentrations for decades
Oxygen limited	Pyritic black shale S>1%	Paddock dumping	Semi arid	Low	Very low L:S ratio <0.1 per year	High concentrations and loads for short period of time, low total loads
Well flushed	Pyritic black shale S>1%	Paddock dumping	tropical	Low	High	Low concentrations and loads

Figure 2 shows schematically the interrelated physical processes related to water and gas flux that are required to be assessed quantitatively to determine seepage quality. As well as the variables shown the climate of the site will be an over-arching variable that will influence these physical processes.

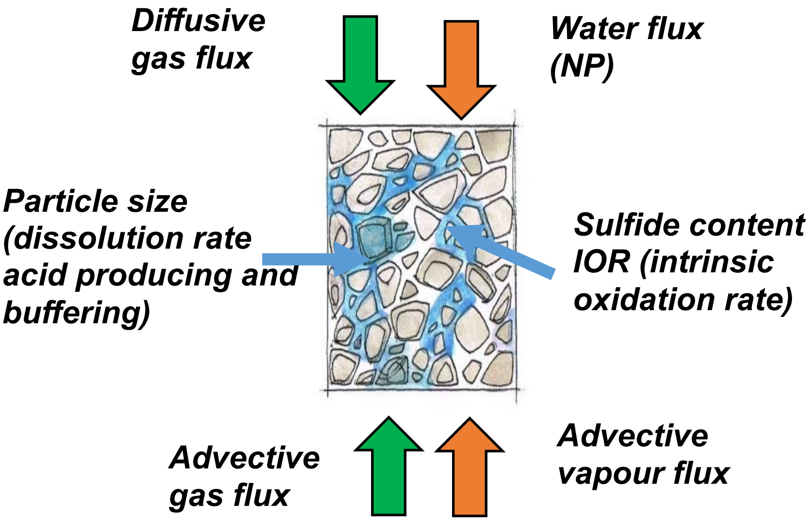

Figure 2 *Conceptual model showing controls on seepage quality*

The fluxes shown in Figure 2 are subject to significant temporal variability due to the nature of unsaturated zone hydrology. Material is generally placed in an unsaturated state and will over time move to an equilibrium state that is semi or fully saturated state. During this process the flux of water and gas through the pore spaces will occur at rates that vary on a relative basis over time. It is this relative nature of the flux rates that is the key concept that requires to be understood to explain the significant differences in seepage quality outcomes that can result from placement of the same material in a different manner (as shown in table 1).

It is beyond the scope of this paper to provide a detailed technical overview of all the contributing factors shown in Figure 1 and how they can be considered as part of the quantitative assessment method. Gas flux is considered in some detail herein however as an example of how these fluxes can be quantified and because this forms probably the most significant risk driving variable.

Gas flux

Convective transport of oxygen into waste rock is the dominant mechanism supplying oxygen to oxidation sites; and air convection driven by temperature gradients and partial pressure differentials are much more effective at transporting oxygen than diffusion processes in WRDs (Brown et al., 2014). To determine the effects of waste rock structure as a result of varying construction method has on gas flux potential in a qualitative manner, a waste rock management factor approach is described in Pearce (2015). A sliding scale was developed as part of this conceptual work to compare a well-constructed WRD, where oxygen is limited and the intrinsic oxidation rate (IOR) is decreased by another order of magnitude, and a poorly constructed WRD, where the IOR remains unchanged. A waste rock management factor (WRMF) was proposed ranging from 0.1 to 1.0.

- The WRMF is 0.1 for a well-constructed OSA that minimises tip height; uses paddock and push-dumping methods and has minimal fines segregation, preventing the formation of a basal rubble layer; and compacts lifts in 1 m to 2 m intervals.
- The WRMF is 1.0 for a poorly constructed waste rock dump that has a well-developed basal rubble zone and a strong segregation of coarse- and fine-textured materials.

A WRMF of 0.1 could also represent a WRD where diffusion is the dominant transport mechanism for oxygen into the WRD; a WRMF of 1.0 could represent a WRD where convection is the dominant. This simple sliding scale allows qualitative assessment of various waste placement techniques with respect to influence on gas flux and thus indicates an upper limit for oxidation rates (proxy for AMD risk).

Quantifying gas flux rates based on construction method

To take the assessment of gas flux further Pearce et al (2016) used extensive site monitoring data and detailed drill core analysis from a large scale waste rock dump drilling program to link temperature data and oxygen concentrations with gas fluxes, within actively monitored waste dumps. OKC have published the results of the large scale drilling and instrumentation project in Pearce & Barteaux (2014; 2015) that provide significant amounts of field data from internal waste rock dump investigations and monitoring programs. These projects included the completion of sonic drilling programs as part of the investigation of 12 WRDs in Australia. The mine sites are made up of multiple WRDs which have been constructed by various techniques including end dumping, and dumps incorporating encapsulation techniques.

Gas flux rates were calculated based on drill core data and data from instrumentation installed through dump profiles. Data from a 60 m high dump constructed with 8 m end tipped lifts and 2 m paddock dumped horizons indicated the weighted average air permeability through the waste was around $8.0\text{x}10^{-9}$ m^2. This is in line with other studies for example MEND (1997) where a mean value of 2.9 x 10-9 m2 (averaged over 24 measurements) was derived from waste rock dump air permeability investigation. The calculated gas flux based on these values was between ~$4.0\text{x}10^{-4}$ $m^3/m^2/s$ and ~-$1.0\text{x}10^{-4}$ $m^3/m^2/s$. After considering effects of material texture, saturation state and temperature on air permeability, it was estimated that the gas flux would be greatest at 15.5 m depth for both upward and downward flow, possibly achieving an upward gas flow rate between $1.0\text{x}10^{-4}$ $m^3/m^2/s$ and $1.0\text{x}10^{-3}$ $m^3/m^2/s$. Due to the spatial heterogeneity of the waste material properties flux rates will likely vary by order of magnitude in a temporal and spatial sense through the waste profile as gas flux rate is sensitive to material texture and temperature differential, but bulk averages are considered a suitable means of averaging out this variability.

The gas flux rate of $1.0\text{x}10^{-4}$ $m^3/m^2/s$ determined to be an appropriate weighted average for flux through the waste profile corresponds to an oxygen supply rate of $3E^{-5}$ $kg/m^3/s$. The importance of the flux rate is that this will act as the main limit to sulfide oxidation rates within the waste mass given that adequate moisture is present for reactions to occur (Pearce et al 2015). By comparing the expected oxygen demand (based on pyrite oxidation rates, from kinetic testing) to the modelled oxygen supply through the WRD (based on the gas flux rate) it is possible to determine if pyrite oxidation rates (POR) will be limited by oxygen supply. Testing on the fresh sulfidic materials within the dumps (prior to placement) indicated an average POR of 2.5 E^{-6} kg/m^3/s. The sulfidic material is present in a 20m thick zone therefore the potential supply of oxygen based on the calculated gas flux rate is about half of the demand load from oxidation at the rate determined by laboratory tests. The implication of this finding is that field oxidation rates relative to laboratory rates may only be limited by a factor of two by oxygen supply within a large proportion of the waste mass.

Geochemical analysis of drill core from the WRDs investigated supports the high gas flux rates indicated from monitoring, and the finding that oxidation rates may not be significantly (i.e. greater than an order of magnitude) limited by oxygen supply. Significant oxidation of sulfides has been recorded based on analysis of sulfide/sulfate ratios through the whole profile of the dumps. Core from WRDs up to and in excess of 30 yrs was assessed and approximately 1,500 samples were analysed from 49 boreholes. For the older samples (>30 years) the average and median oxidation rates 80% and 72% respectively. At higher grades of >1% sulfur the oxidation rate was lower around 60% average.

When oxidation rates in dumps constructed by different techniques are compared, the material in dumps constructed with 10m lifts with inter-bedded 2m compacted paddock dump layers was found to have oxidised significantly more slowly over time than that in 30 m end tipped lifts. This data supports the field monitoring data which indicates oxygen ingress rates should be lower in dumps using lower lift heads.

Predicting gas flux and oxidation rate based on waste rock dump construction

Field data was used as part of analytical modelling as a validation/calibration exercise to determine if numerical modelling could be used to determine optimal waste placement techniques. Thermal and airflow modelling were completed to estimate the volume of air flowing through waste material due to density dependent convective airflow cycles. The impacts of total air flow rates through the WRD were assessed along with pyrite oxidation models to determine overall temperature increases as a result of convective airflow rates. Convective airflow modelling takes into consideration three key influencing processes within the WRD waste material: water seepage; thermal conductive heat transport; and airflow. Numerical modeling was completed in GeoStudio (Geo-Slope International, 2012a) software suite, SEEP/W, TEMP/W; and AIR/W. In addition, seepage rates were calculated using VADOSE/W. Two model scenarios are considered here as part of this paper:

Model 1: “Segregation” Scenario: simulates gravitational segregation of the waste material into texture layers due to end tipping from a high tip height of 30m (i.e. coarser waste material has a propensity to roll to the base of a slope while finer material stays near the top of the slope); and,

Model 2: “Compaction” Scenario: simulates an OSA built from the bottom up with alternating layers of 10 m of PAF/NAF topped with 2 m of NAF. The top 0.2 m of the PAF material at NAF/PAF interface is compacted due to haul truck traffic while placing the NAF layer (Figure 3).

The results of the convective airflow models show that airflow is predominantly in the coarser textured waste material as a result of the higher air permeability of this material. However, it was also noted that airflow did occur through the finer and intermediate sized waste material, despite the reduced air permeability of these materials; most likely due to lower in situ moisture conditions. The models also show that the configuration of the waste materials greatly affected airflow rates.

In the case of the segregation scenario development of a convective cycle was observed in the model in the coarser textured layer, which transported air through the coarser textured layer into the WRD. This convective cycle was identified by comparing equivalent airflow rates into and out of the WRD. The weighted average airflow rate was found to be 1.9×10^{-4} m^3/m^{2}s.

In the case of the compaction model in first year of the model simulation, airflow rates were relatively constant, and reached a peak of 3.0×10^{-6} m^3/m^{2}s during this time. The weighted average airflow rate was found to be 1.55×10^{-6} m^3/m^{2}s. This lower flux rates are due to the presence of compacted layers between each layer of deposited material limiting airflow from breaching into the overlying layer and continuing the convective cycle. In effect, the convective airflow is “shut down” by these compacted layers.

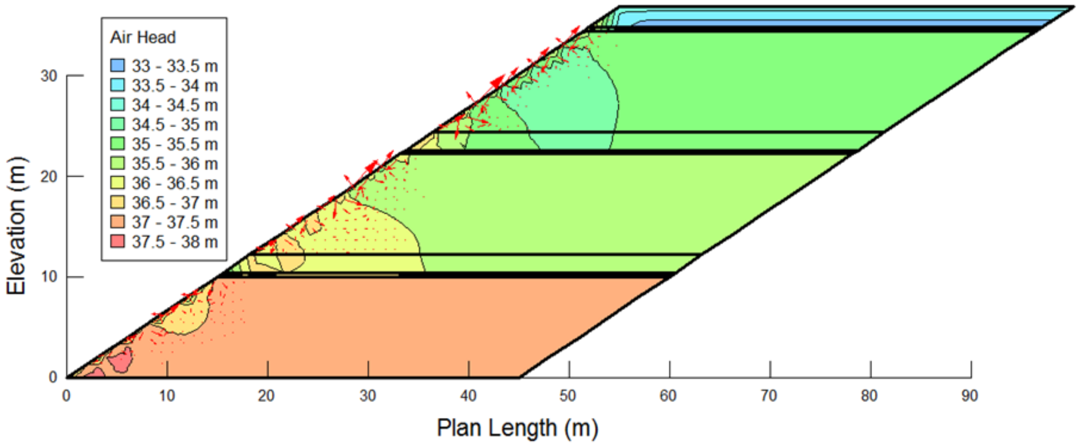

Figure 3 *Model 2 modelling results showing restricted air flux vectors*

The air flow rates calculated by numerical modelling are in very good agreement with site data and indicate that where coarse basal zones are present air flux rates through waste mass of around 1 x10^{-4} m^3/m^2s can be expected. This agreement between site data and model data supports the use of gas flux modelling to make predications of oxidation rate potential in waste rock dumps. The modelling of the compaction scenario indicates that the use of compacted finer textured layers and short lift heights significantly reduces the potential for air flux and therefore is a limiting factor for oxidation rates and thus AMD production.

Modelled AMD production rates based on waste rock dump construction

Based on the field data and modelling data generated and interpreted, a clear quantitative link between waste rock dump construction method and AMD production can be established. Given a field validated modelling approach has been developed, then this supports a quantitative method for assessing how waste placement and construction method can be optimized to reduce AMD risk for future waste rock dump construction.

Figure 4 shows the results of additional proprietary modelling completed by OKC based on the field validated approach where by AMD production was quantitatively assessed against tipping height for a proposed waste rock facility.

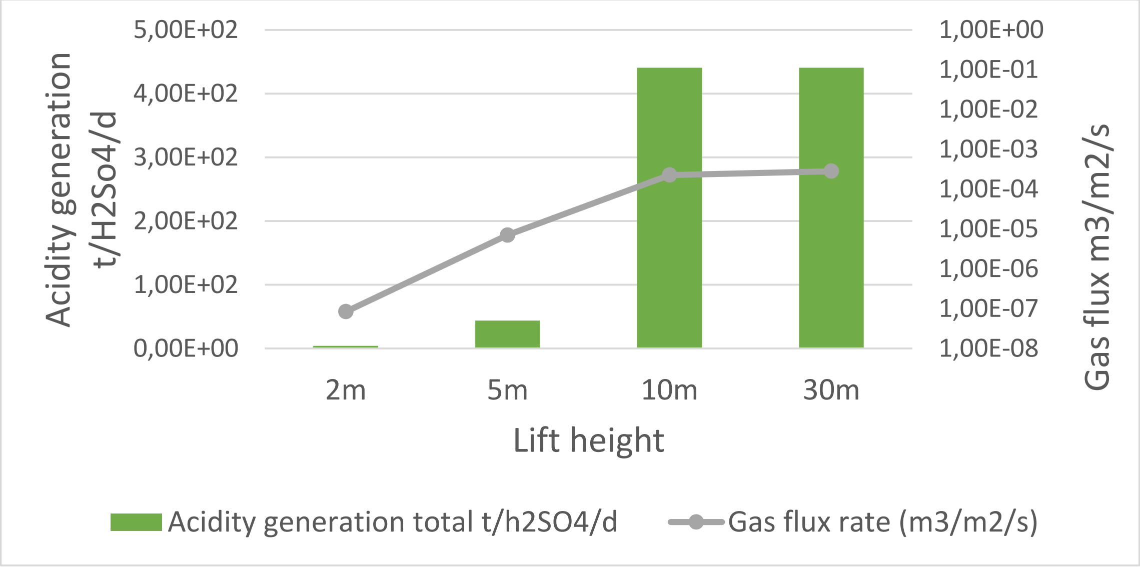

Figure 4 *Analytical model outputs for acidity generation as a function of lift height*

The results of this assessment show the clear benefits of using a quantitative approach to assessing waste rock dump construction method as part of mine planning and mine closure risk assessment. The clear benefits of using low tip heads (paddock dumping) as an alternative to large height end tipping is obvious. Although it is an accepted fact that paddock dumping is lower risk than end tipping, the fact that the relative difference can be quantified means that the risk/cost tradeoff can be completed at the mine planning stage and mine closure risk and cost estimation can be improved significantly.

It is interesting to note that gas flux is not directly related to AMD production, this is because at some point gas flux rates are higher than required to support oxidation demand from reactions and therefore more gas flux does not increase AMD production. This is seen in the move from 10m to 30m tip heights where gas flux increases but AMD production does not.

Conclusions

The significant finding of the study is not that the method of waste placement has a significant control on AMD risk, this is known and accepted in the industry but rather that this risk can be assessed on a quantitative basis. The fact that the relative difference can be quantified is important as this means that the risk/cost tradeoff assessment of how waste rock dumps are constructed can be completed at the mine planning stage, and mine closure risk and cost estimation can be improved significantly.

The secondary implications of this finding is that the management of reactive waste during construction as a result of placement technique is likely a key risk driver for future AMD release, due to challenges with controlling gas flux in periods where waste dumps are “open”. This conclusion is perhaps contrary to widely held views that AMD risks can be largely managed at closure. It is clear that an assessment of waste rock dump construction requires consideration when final closure solutions such as covers are being selected and relied on as the main closure mitigation solution for AMD management.

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Modelling approach to predict peak inflows at the Argyle block cave mine, Western Australia

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Abstract

Argyle Diamond Mine is situated in the East Kimberley region of Western Australia. Block-cave mining is ongoing below the mined-out South Bowl pit. Average annual rainfall is about 800 mm. A constant flow of groundwater between 60-100 L/s enters the cave zone laterally from various permeable layers in the surrounding country rock. In addition, ephemeral runoff from the overlying pit rapidly infiltrates into the surface of the cave. In 2014, two major rainfall events occurred: 175 mm falling in 48hrs on 15th-16th January; and 213 mm falling in 72hrs on 6th-8th February. The January 2014 rainfall event caused a short term peak mine inflow of 500 L/s, whilst the February 2014 event caused a peak inflow of 1200 L/s.

A rainfall-runoff-frequency model was created to assess runoff volumes reaching the base of the pit. This was coupled with a numerical flow model developed to assess the passage of water from the pit floor to the mine extraction level. The model incorporated rock mass hydro-geomechanical changes based upon the predicted future Life of Mine cave zone propagation. The coupled model was calibrated to the two major 2014 runoff events. The model was then used to simulate a series of potential future rainfall-runoff events and future underground inflows. The analysis was used to develop a Trigger Action and Reponse Plan (TARP) for the future flood management.

Calibration demonstrated that peak inflows to the mine workings were found to be highly sensitive to the propagation of the caved zone to the pit surface over mine life and prior water content of the cave zone. Current pump capacity and operational alarms were found to be insufficient to deal with extreme inflow events. The model results were used to develop new criteria for activation of seasonal pumps within the mine.

Key words: Mine water, Block cave mining, Groundwater model, Flood management, Water balance

Introduction

Argyle Diamonds Limited (Argyle) is wholly owned by Rio Tinto Ltd and operates the Argyle diamond mine in the East Kimberley region of Western Australia. The region has tropical-monsoon climate, receiving approximately 90% of its rainfall during high intensity, highly variably cyclonic events in the wet season from November to April. Mining began in 1985 as an open pit operation but has recently transitioned to underground block cave mining. The block cave operation lies beneath the South Bowl open pit and started production in 2013.

The block cave operation intercepts groundwater within saturated zones surrounding the ore body, and also receives vertical inflows from infiltrating surface water captured by the overlying open pit. As underground mining has progressed, so the block cave operation has caused much greater hydraulic connection between the base of the open pit and the underground workings. Further enhancement of the cave zone permeability is likely to occur as future mining progresses. This presents a significant hazard for mine operations during the wet season when large volumes of surface water may be generated within the surface area of the pit.

A dynamic water infiltration model was required to assess inflows from the pit floor to the underground. The model needed to provide a range of possible outcomes and associated risks which could be used to address long-term issues related to underground pumping capacity and strategy.

Methods

A multi-phased approach was adopted to contribute to the development of a new TARP for future flood water management. In Phase 1, a surface water balance model developed in the GoldSim modelling platform was used to predict volumes of water reaching the base of the South Bowl pit. In Phase 2, a groundwater model of the cave zone was developed in order to predict future inflows to the underground mine, based on outputs from the surface water balance model. Finally in Phase 3 an operational mine water balance model was developed to assess the installed underground pumping capacity and available storage in response to inflows predicted by the groundwater model.

Phase 1: Development of a water balance model for the South Bowl pit

The principle objective of this phase was to estimate the volume of water reaching the pit which may infiltrate to the cave zone. Historically, prior to the commencement of the block cave operation, any water reaching the base of the pit has ponded to form a seasonal pit lake. However, in the last 2 years the material at the base of the South Bowl has become fractured and fragmented (Figure 2.1) as the cave zone has extended upward to the pit floor. The subsequent increase in permeability of the material has meant that a lake no longer forms and most water rapidly infiltrates.

The GoldSim modelling platform was used to create the rainfall-runoff water balance model for the South Bowl pit catchment. GoldSim is a generic dynamic simulator for deterministic and probabilistic modelling of functional relations between several elements or variables. A conceptual model of the pit water balance was developed to identify the main water balance elements as shown below in Figure 1.

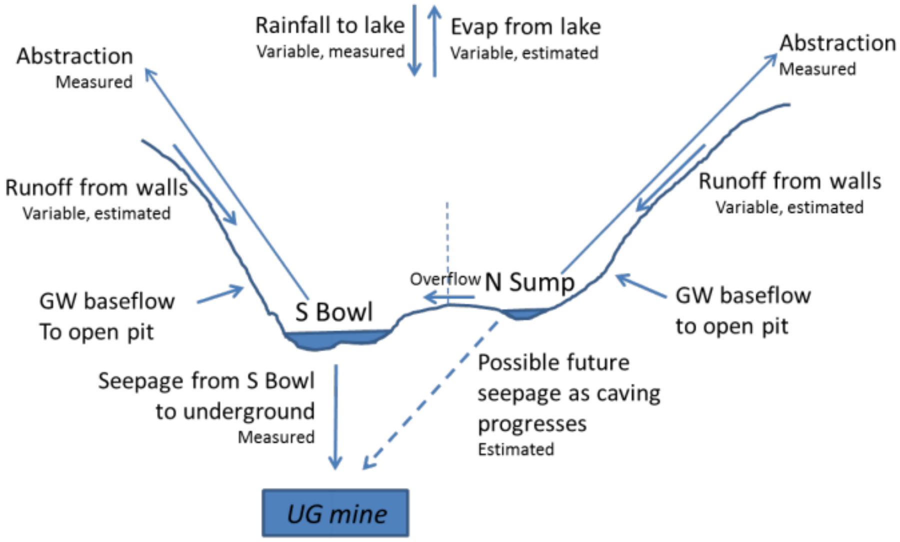

Figure 1 *Schematic of rainfall-runoff water balance components.*

The majority of water balance elements were known with a reasonable degree of certainty. A total of four years of daily rainfall and pan evaporation records were available from a nearby mine rain gauge and a Bureau of Meteorology site at Argyle aerodrome. The catchment area of both the North and South bowl and a stage volume relationship for both two pit lakes were calculated using spatial analysis software. The baseflow to the North Bowl and South Bowl was estimated from end of mine life pit dewatering rates and the daily record of pumping rates from the pit sumps post-closure.

Estimation of a runoff coefficient involved greater uncertainty. Previous studies have reported widely variable runoff coefficients, ranging from 11% to 40% of rainfall. These values were used as a starting point for calibration. Light rainfall events are either absorbed by the surface materials to reduce the soil moisture deficit, or held near surface by capillary forces and subsequently evaporated. For the purposes of the water balance, the threshold value for runoff to occur was set to 3 mm/d of precipitation. In addition, a dispersion factor was added to account for significant delayed pit lake abstraction rates observed, for example, four days after a significant flooding event in 2011. Conceptually this simulates shallow interflow through near surface fractures within the over-break zone.

During an early flooding event in 2011, prior to extensive development of cave zone, seepage from the South Bowl was calculated to be 2 – 2.2 l/s per metre of water depth at the base of the pit. Permeability was adjusted during time-variant calibration to account for the continued development of the cave zone. Since early 2013 a pit lake has no longer formed, therefore permeability was increased sufficiently to account for this in the water balance model. From this point all water reporting to the South Bowl is assumed to infiltrate to the cave zone.

The model was primarily calibrated using pit water levels measured in the South bowl. Calibrated historical model results are shown in Figure 2. Calibration was mainly achieved through varying the most uncertain parameters, namely the runoff coefficient and the pit floor hydraulic conductivity. This resulted in a final calibrated runoff coefficient of 25 %, and a runoff threshold of 3 mm. Time-varying hydraulic conductivity values were applied to simulate pit floor seepage, and were increased three times over the calibration period such that no pit lake formed beyond early 2013.

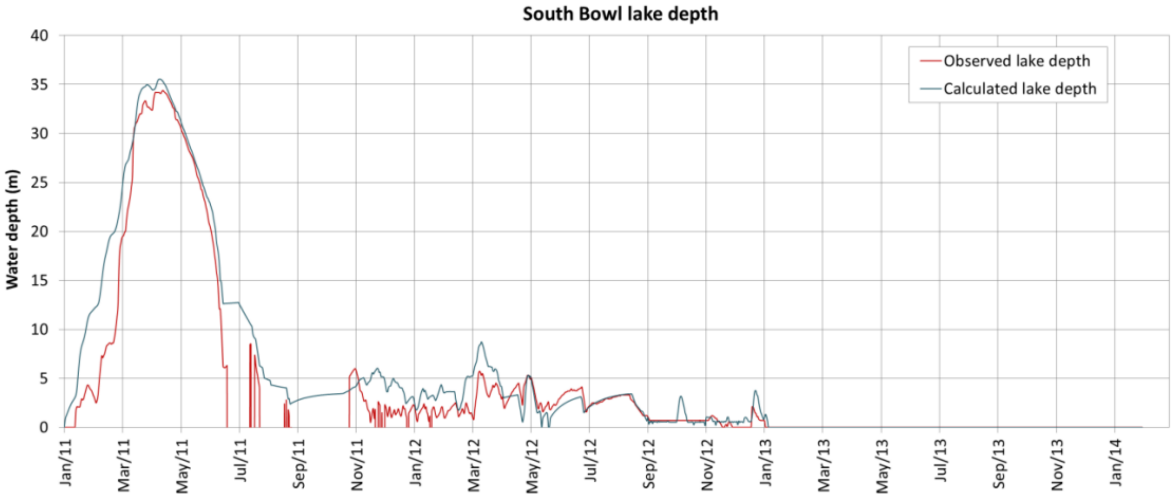

Figure 2 *Predicted versus observed pit lake depth*

Once calibrated, a series of predictive models (scenarios) were setup and run to provide time-varying inputs for input to the cave zone groundwater models. These comprised 4 scenarios:

Scenario 1, or Basecase, cycles an 'average' year of rainfall to create an average condition dataset. The year 2007/2008 was chosen as the yearly total rainfall of 770 mm was very close to the long term average of 784 mm/y. In addition, there were two short term rainfall events exceeding a total of 80 mm, and several isolated rainfall events would allow for inflow and recession curves to be generated for several periods. Average monthly evaporation rates and pit abstraction rates were also used.

A sensitivity analysis was run on the Basecase model to understand how changes to different parameters could affect model predictions. This work focused on the parameters known with the least certainty: runoff coefficient and runoff threshold. Rainfall was also adjusted, as whilst it was measured on site it is possible that the magnitude varied across the pit catchment.

It was found that the runoff threshold was the least sensitive parameter, and resulted in only a small change to the pit lake levels. Changing the rainfall depth and runoff coefficient by 20% resulted in a larger change to the calibrated peak lake level of +/- 5.2 m (or ~14.5%) and +/- 4.5 m (or ~12.5%) respectively, compared to the Basecase calibration. In early 2012 when the lake level is lower, the absolute levels are all within 1 m of base case, and from mid-2012 to January 2013 there are no significant differences seen. The results for these parameters are similar as they are inter-related in a similar fashion to catchment size and runoff percentage. As long as catchment size and rainfall are measured correctly, the errors associated with an inaccurate runoff percentage estimate are minimised.

Scenarios 2 and 3 involved respectively decreasing and increasing the 2007/2008 rainfall series by 20%, whilst maintaining basecase parameters. These series were then run from February 2014 onwards, when the historical rainfall series ends. Resultant peak flows reporting to the base of the South bowl were 766 l/s and 1167 l/s in Scenarios 2 and 3 respectively.

Scenario 4 involved simulating different rainfall events for different return periods as calculated by the Australian Bureau of Meteorology. IFDs (Intensity Frequency Duration) totals were available for 1 year, 2 year, 5 year, 10 year, 20 year, 50 year and 100 year return periods. The IFD data were created using the 2013 datasets as documented in Green et al. (2012). As the water balance model ran on daily timesteps, total rainfall depths for 24, 48, 72 and 96 hours were used.

Phase 2: Development of the cave zone seepage model

In order to improve the prediction of potential future inflows, a groundwater model of the cave zone was developed to assess the infiltration of recharge from the surface (the base of South Bowl) to the underground workings. The groundwater model is centred on two orthogonal sections, which coincide with those used in the geotechnical studies undertaken in FLAC 3D (Geonet 2013) to determine the geomechanical state of the rock mass throughout the mine development. The geotechnical modelling results facilitated the adjustment of the rock mass hydraulic parameters over time to generate a dynamic predictive time series of potential seepage from the surface to the workings.

The two key sections are shown in Figure 3a. The structural geology and the underground workings are shown in Figure 3b. The groundwater model incorporates:

- Detailed lithological representation of the subsurface.
- Inclusion of the underground workings.
- Significant geological structures, including the major faults that were incorporated within the geotechnical modelling.
- Hydraulic properties, which were initially determined from previous studies.
- Displacement contours, detailing changes in rock displacement throughout the development of the mine, as calculated in the 2013 geotechnical model.
- Calibration to rainfall and groundwater inflow data from early 2011 to mid-February 2014.

The groundwater model was developed using the SEEP/W finite element code, and consists of two orthogonal sections of known widths. As such the resultant inflows to the mine were scaled proportionately to the total area of the South Bowl. The groundwater model was initially calibrated to ensure that baseflow of approximately 100 L/s reported to the workings. The pit water balance model generated rates of water flow to the base of the South bowl for the historical period between 2011 and 2014, and was used the recharge input to the groundwater model. The model start date was set as January 2011.

A second calibration stage was then undertaken, focusing on the historical period between July 2013 and January 2014. This stage focused on matching modelled and observed inflows as the cave zone developed additional permeability and and an enhanced hydraulic connection with the base of South bowl. Deformation contours generated in the FLAC model were used to guide the distribution of enhanced permeability in the cave zone. Results from the first two calibration stages are presented in Figure 4. Also plotted are the actual recorded mine inflows, the GoldSim water balance recharge series and the simulated recharge to South Bowl in the groundwater model.

In general inflows show a reasonably close match to observed inflows, particularly in 2013 and 2014.

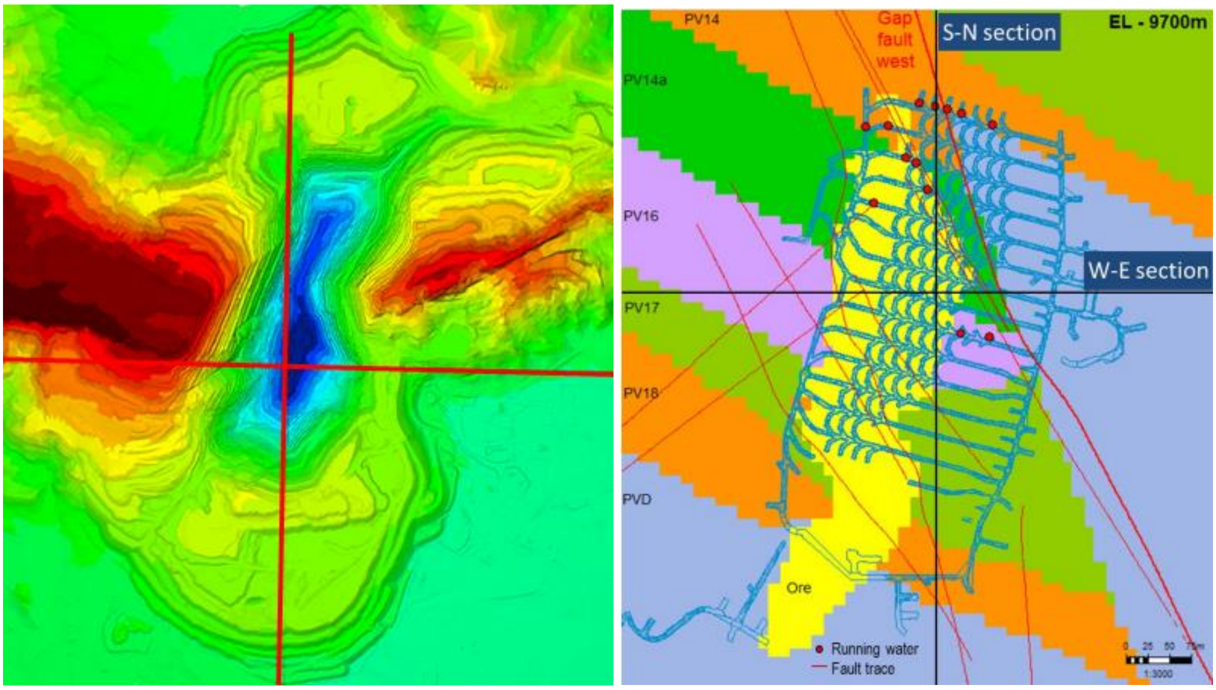

***Figure 3**. a) Location of the two sections in relation to the open pit, b) Location of the two sections in relation to the underground workings.*

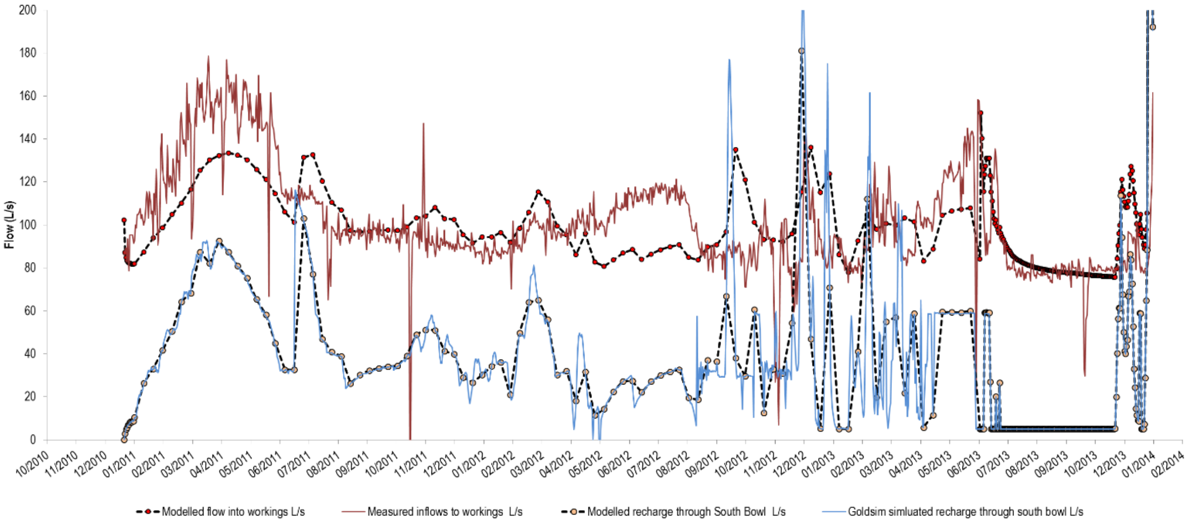

***Figure 4** Historical calibration to mine inflows*

The third and final stage of calibration focused on January and February 2014, where significant inflows of up to 1245 L/s were recorded entering the workings in response to two significant storm events. Calibration focused on fine tuning hydraulic parameters using a more recent displacement contour distribution representing geotechnical conditions in late 2013. The mine inflows modelled for both of the storm events in early 2014 are plotted in Figure 5. The first inflow peak in response to the January storm is overestimated by approximately 100 L/s whilst the second peak in response to the February storm event is underestimated by approximately 300 L/s. The discrepancies, particularly for the first peak, can be attributed to how the recharge is distributed throughout the day in the model rather than during a 2-3 hour period where Hortonian runoff would be expected to accumulate rapidly in the base of the pit. Since only daily rainfall and mine inflow data are available, it is neither possible nor defensible to create a representative hourly resolution recharge input file which could generate the appropriate inflow peaks to the mine. Peak inflows are predicted at the correct times, and recovery between peak flows is handled well as demonstrated by the trough between the two peaks in Figure 5.

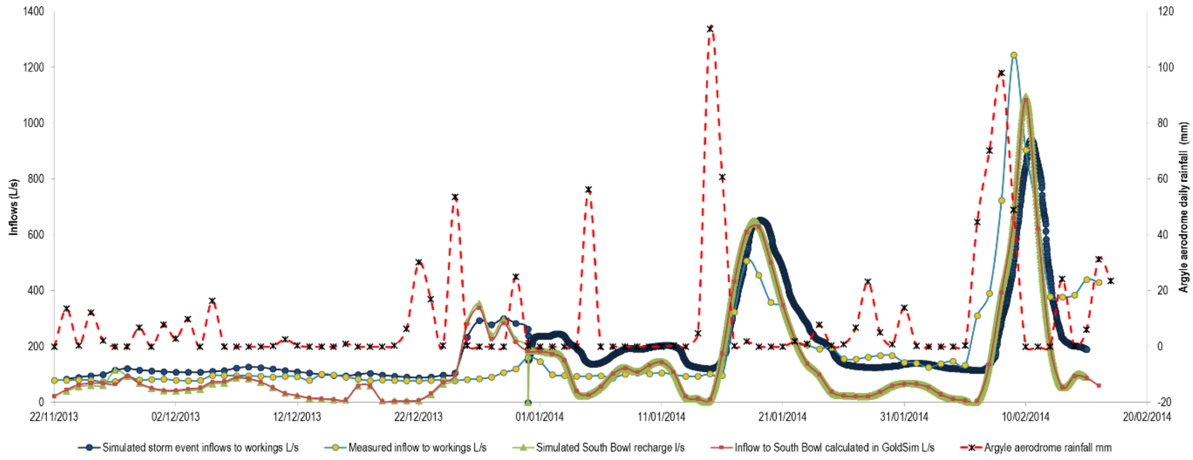

Figure 5 *Calibration to the January and February 2014 storm events*

Based upon the calibrated model, a series of predictive scenarios were run as described below.

Scenario 1: Baseline predictive model based upon the representative South Bowl recharge time series generated in the Scenario 1 GoldSim water balance model up to the end of 2020:

- 2014-2017: Final calibration displacement contours, representing geotechnical conditions at the end of 2013.
- 2017-2020: Predicted displacement contours for 2016 used. Both a pre-subsidence and post-subsidence pit floor were modelled with this displacement contour set. Magnitude of the subsidence of the pit floor was set at 100m, which corresponds to that predicted in the geotechnical studies.

Peak inflow rates to the mine were found in general to increase in response to greater rock deformation. The effect of any increase in storage was small during significant storm events. Inflows rates slightly increased with subsidence of the pit floor, which also led to a decrease in response time of inflows to precipitation by 1 to 2 hours.

Scenarios 2 and 3: Sensitivity analyses: +/- 20% rainfall. Recharge time series were produced by the GoldSim water balance model with modified rainfall. These runs served as a verification that simulated inflows varied accordingly with an increase or decrease in rainfall.

Scenario 4: Simulation of 24, 48, 72 and 96 hour storm events (time series also produced by GoldSim water balance model). The simulation of infiltration through the cave zone in response to representative return period storms provides the necessary data to develop a tool which can be used to estimate the likely inflows to the mine under various future storm conditions. The scenario was run with both the deformation contours used in the final calibrated model and those representing fully mobilised conditions after 2016. Subsidence of the pit floor was also considered. The maximum modelled peak inflows from all scenarios are summarised in Figure 6. Invariably 72 hour storms produce the highest peak inflows to the mine. 48 hour storms produce greater peak inflows to the mine if ground conditions are fully mobilised, although prior to 2016 the 96 hour storms tend to produce higher peak inflows as the ground is less permeable, which tends to promote concentration of inflows from longer duration storm events.

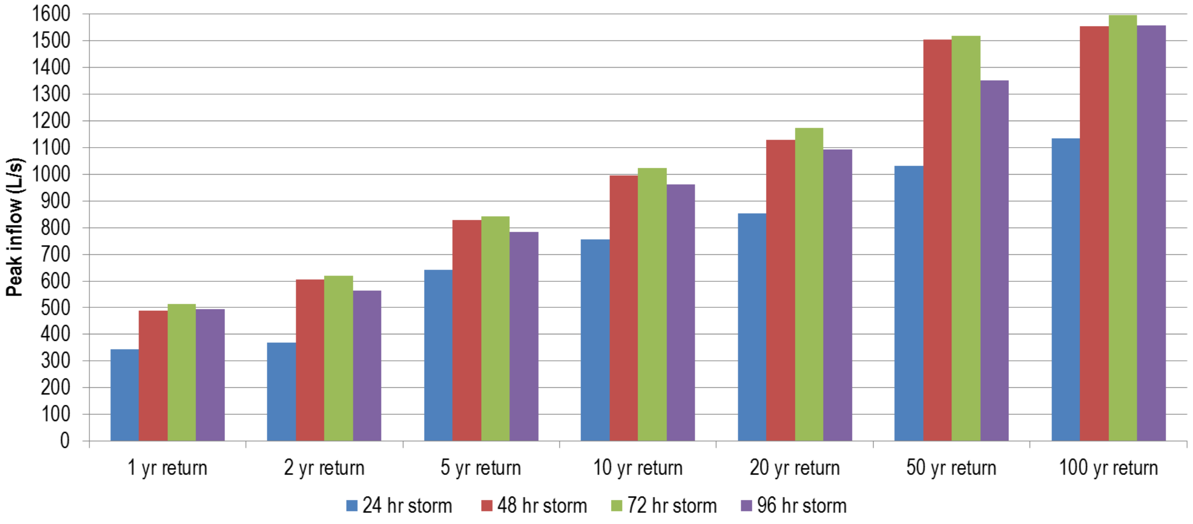

Figure 6 *Summary plot of maximum predicted inflows by storm event*

Scenario 5: This scenario was designed to evaluate the impact on mine inflows of pre-wetting of the rock mass by antecedent rainfall events. Sensitivity runs consisted of (i) a 2 year, 24 hour storm event preceded by a 1 year, 24 hour storm, and (ii) a 10 year, 24 hour storm event preceded by a 5 year, 24 hour storm. The recovery time between the storm events was progressively reduced to simulate the recharge from the second storm event occurring through partially saturated ground, and how this may impact the predicted peak inflows to the mine. Pre-wetting by antecedent rainfall was found to significantly increase simulated peak inflows to the mine if both storms events occurred within a period of 4 to 6 days.

Phase 3: Development of an operational mine water balance

In order to account for underground water storage and both duty and seasonal pump pumping capacity, a water balance model of the mine was constructed using the inflow results from the groundwater model. The water balance model was designed as an operational tool to assess the effectiveness of alternative dewatering system configurations in response to various storm events with the aim of contributing to the development of a new mine TARP. The model incorporates:

- The duty dewatering pumping rate (DDP)
- The seasonal dewatering pumping rate (SDP)
- The threshold water volume for activation of the SDP

The input to the water balance was provided by the groundwater model hydrographs assuming maximum cave zone development represented by the fully mobilised 2016 displacement contours and subsidence of the pit floor. Scaling factors to account for the preferential flow paths can be modified to compare alternative pumping rates and underground water storage configurations

Results from simulations using the current SDP trigger volume showed that inflows could be managed for 24 hour, 48 hour, 72 hour and 96 hour storms with 5 to 10 year return period with current underground storage capacity. However, with the exception of 24 hour storms, events with a return period greater than 20 years would generate inflows that would overwhelm current installed dewatering systems and underground storage.

The water balance was re-run using a lower SDP trigger volume. It was found that this enabled the mine to cope with inflows from all storm events with the exception of 50 to 100 year events of a duration greater than 24hrs. It was therefore recommended that the trigger should be set to this lower threshold, and reduced further in the wet season if necessary to better cope with high inflows.

An additional alarm for high intensity rainfall was also recommended, triggered once rainfall intensity reaches 30mm/hr. This is a conservative approach, as the groundwater model and operational mine water balance showed that rainfall exceeding this value would have the potential to generate inflows to the mine exceeding the capacity of the DDPs.

Conclusions

A multi-phased modelling approach was used to generate input for an operational mine water balance model. A surface water balance model was developed to estimate total volumes of flow reporting to the base of the South Bowl pit, and an infiltration model was developed to model seepage of groundwater through the cave zone to the mine workings. Output from these two models was then used as input to the operational mine water balance model to undertake an assessment of the current underground dewatering capacity, providing critical input to the development of the new TARP. The model can be used to estimate potential inflows to the mine in response to a range of representative storm events, and provides Argyle Diamonds Limited with the means to refine their dewatering strategy to better respond to future rainfall events.

Acknowledgements

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Mine Water Balances – A New Proposed Approach

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Abstract

The industry has developed a dogmatic acceptance of one method for managing this uncertainty and risk -- using probabilistic water balance models. The currently accepted modeling standard in the mining industry leaves the client vulnerable to a different kind of risk – over engineering. This leads to high and unnecessary project costs. This paper encourages a different approach, succinctly stated in *Harvard Business Review*, "instead of trying to anticipate low-probability, high-impact events, we should reduce our vulnerability to them." This can be effectively done with a hybrid deterministic water balance.

This paper is not advocating for the abandonment of probabilistic water balance models, but is rather a cautionary warning towards the pitfalls of probabilistic water balances. It is a call to action for mine water experts to reframe their frame of thought process while designing and documenting water balances. It is insufficient to look at a model simply in terms probability and degree of certainty. The modeler must take a step further and understand the model's dynamics, including when and where the project is most vulnerable to extreme events, and why the vulnerability exists. A thorough documentation of vulnerabilities and recommendations for managing each identified vulnerability, as well as other unforeseen vulnerabilities should be provided to the client as part of a deliverable.

Key words: Mine water, modeling, water balance

Introduction

Effective and accurate management of water resources in a mine water balance model is crucial to the design, development, and operation of a mine. Moreover, the management of uncertainty in a water balance model is an essential element in the water balance design. The industry has developed a dogmatic acceptance of one method for managing this uncertainty and risk -- using probabilistic water balance models. In fact, the cyanide code now requires some probabilistic modeling for water balances. However, probability-based water balances carry a high risk of mismanagement and misapplication. The misuse of probabilistic models is widespread, and the ramifications vary from overly conservative water management design to catastrophic mine water related failures. This paper presents common pitfalls for probabilistic water balance models and presents a case study of a more holistic, hybrid water balance model that was prepared for a Pre-Feasibility Study (PFS) of a gold mine in Brazil.

The currently accepted modeling standard in the mining industry leaves the client vulnerable to a different kind of risk – over engineering. This leads to high and unnecessary project costs. This paper encourages a different approach, succinctly stated in *Harvard Business Review*, "instead of trying to anticipate low-probability, high-impact events, we should reduce our vulnerability to them." This can be effectively done with a hybrid deterministic water balance.

Misuse of Compounding Events

It is important to note that the Monte Carlo analysis can be both a powerful and a very dangerous tool in water balance modeling. Monte Carlo analysis is powerful because it can evaluate the net impact of combined probabilities. This can create robust models that accurately quantify risk. However, Monte Carlo analysis also has the potential to "run away with itself" and combine several low probability events together in a scenario with a very low probability of occurrence that is not within the range of probable events in the field. Figure 1 shows how this can occur.

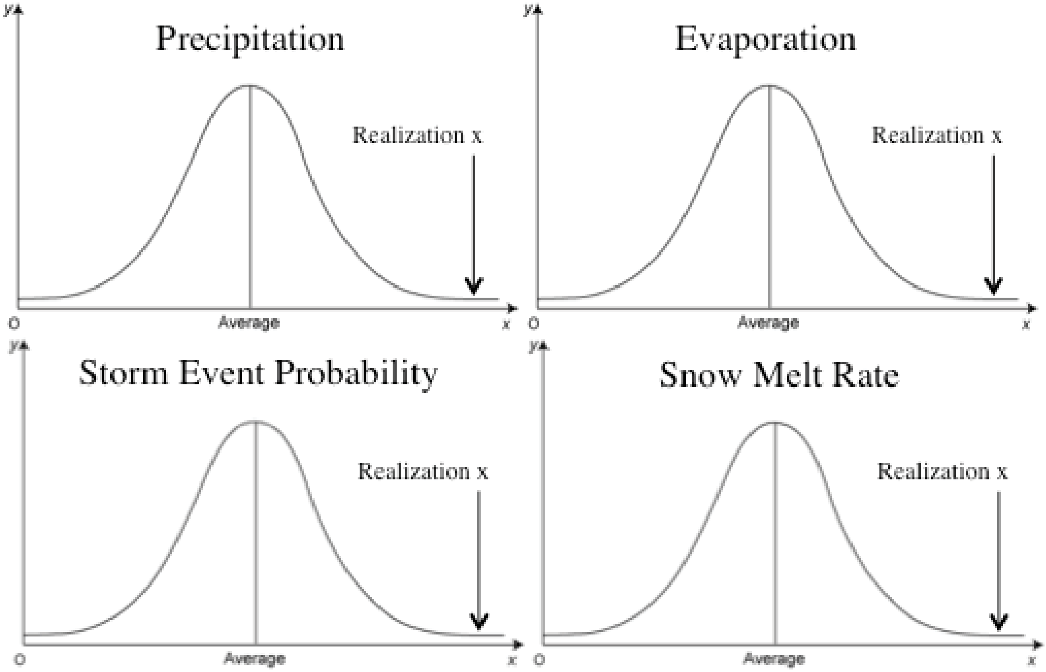

***Figure 1** Example of Monte Carlo Overprediction*

By selecting a realization (the word used for Monte Carlo iteration) with several low probability, high flow events (ex. Realization x, shown on the right of the distribution curves shown in Figure 1), one can select a scenario that has an insignificant probability of existing. If the engineers are trying to take a conservative approach, selecting Realization x seems reasonable – it is the realization that provides the largest ponds, and the least likelihood of a discharge of Mine Impacted Water (MIW) to the environment. However, this logic must be double-checked. Sizing a pond to satisfy 95th percentile conditions for six parameters results in a design that is sized for an event that has a 0.000000016% chance of occurring. One must confirm that Realization x is possible within the range of conditions in the field.

For a recent mining project (confidential) located in a mountainous and snowy region, a probabilistic water balance was performed. The realization selected as the design criteria was the 95% percentile flow in the model. This realization included:

- No consideration of sublimation (up to 30% of annual precipitation);
- 70% runoff from a Waste Rock Dump (WRD) during operations (likely impossible, but at the least, requiring an exceptionally short intense storm event;
- Exceptionally heavy rainfall and snowfall; and
- Exceptionally rapid snowmelt.

The probability of all of these events occurring simultaneously was insignificant – far lower than the 1 in 100 threshold in the design criteria. The end result as an Acid Rock Drainage treatment plant designed to treat 150% of the total annual precipitation on the basin. This clear case of over-engineering severely damaged project economics.

"10,000 Iterations" Fallacy

Probabilistic models also lull the user into a false sense of confidence in the results. For example, a GRE staff member participated as an expert witness in a court case regarding estimates of required mine closure costs (Breckenridge, 2008). During the proceedings, GRE witnessed a mine closure expert, defending his probabilistic model of anticipated mine closure costs, he stated in his testimony, "We ran 10,000 realizations and as a result, have a high confidence level in the results." Indeed, a model with 10,000 iterations does sound like a robust model. However, if the initial assumptions are not correct, additional realizations do not improve the accuracy or confidence of the result. In the aforementioned example, the model used input distributions that were neither realistic nor accurate. Therefore 10,000 realizations based on flawed distributions creates 10,000 incorrect results, rather than one robust and correct result.

Furthermore, the user in a stochastic model programs in distributions for key factors, such as rainfall, storm intensity, etc (see Figure 1). Because the result of an individual realization is generated at random, the modeler does not have control over the placement of extreme stress events, such as a 100-year storm, within each realization. In 10,000 realizations, the 100-year storm event is present in 100 of the realizations, but the timing of that event is at random As a result, it is possible that a model with 10,000 realizations will never evaluate the effect of a 100-year storm during the worst possible conditions. This may be catastrophic if the storm occurs at a vulnerable point in a mine's timeline, such as when the mine water containment system lags behind mine footprint expansion.

GRE endeavoured to avoid these pitfalls by creating a hybrid water balance that incorporated uncertainty, yet retained transparency, user control, and helped clients improve project economics.

Holistic, Hybrid Water Balance Model, and Alternative Approach to Probabilistic Modeling

The Aurizona mine, owned by Luna Gold, is located in Maranhão State, Brazil, as displayed in Figure 2. The project sits on a peninsula that extends into the Atlantic Ocean, and tidally-influenced water exists less than 5km to the east and west of the mine. The Aurizona mine is an open-pit mine with conventional wet tailings disposal in a location that receives, on average, 2,760 mm of precipitation annually, with nearly all precipitation occurring in a pronounced 6-month long wet season. The Aurizona mine produced from 2006 to 2015 and is currently in a retooling period to allow for a mine expansion and changes in the process circuit.

Figure 2 *Aurizona Mine location in Maranhão State, Brazil*

Background Information and Conceptual Model

The objective of the Site Wide Water Balance (SWWB) is to provide an integrated approach to managing the project water resources and determine if the mine has excess water (that must be discharged to the environment) or a water deficit. This is done by balancing the water sources, water storage, and water losses site-wide to create a comprehensive picture of Project water use and supply. The model must consider climate, runoff conditions, and any other factors that affect the availability of water. The end result is a comprehensive picture of water flows around the site for each month of the year and each year of mining operations. The final objective is to resolve the water supply and/or the water discharge conditions so that the operation can adequately operate and so that environmental regulations can be met. The water balance also supplies a plan on how and when the Tailings Storage Facilities (TSF) must be raised.

The Vené TSF (See Figure 3) is currently used as the primary water storage facility for plant operations, and a pool is accumulated during the rainy season to ensure dry season operations. This requirement brings a series of disadvantages including increased TSF seepage; slow tailings consolidation rates, the need for accelerated raises in order to ensure safe operations, and decreased operational flexibility. In the future, the mine will use the Boa Esperança pit as a water storage reservoir. Under this proposed scenario, reclaim water from the TSF would be pumped back to the plant as quickly as possible, while fresh water makeup would be pumped from the Boa Esperança Reservoir (Reservoir). Excess water would be discharged tested for quality, and discharged into a nearby river from the Reservoir.

The model was designed in two conceptual blocks: a water balance for the TSF and a water balance for the Reservoir. Water inflows and outflows into the TSF include: runoff from precipitation (+), tailings slurry water inflows (+), evaporation (-), tailings entrainment (-), plant return water (-), TSF seepage to groundwater (-), and Reservoir excess water (-). Water flows into the Reservoir from most sources of mine influenced water (MIW) on the site. Water inflows and outflows into the Reservoir include: TSF excess water (+), runoff from the WRD (+), runoff from plant (+), runoff from interior catchments (+), direct precipitation the Reservoir surface (+), Piaba pit dewatering (+), groundwater seepage into the Reservoir (+), evaporation (-), return water to plant (-), and discharge to environment (-). Figure 3 displays the project's facilities.

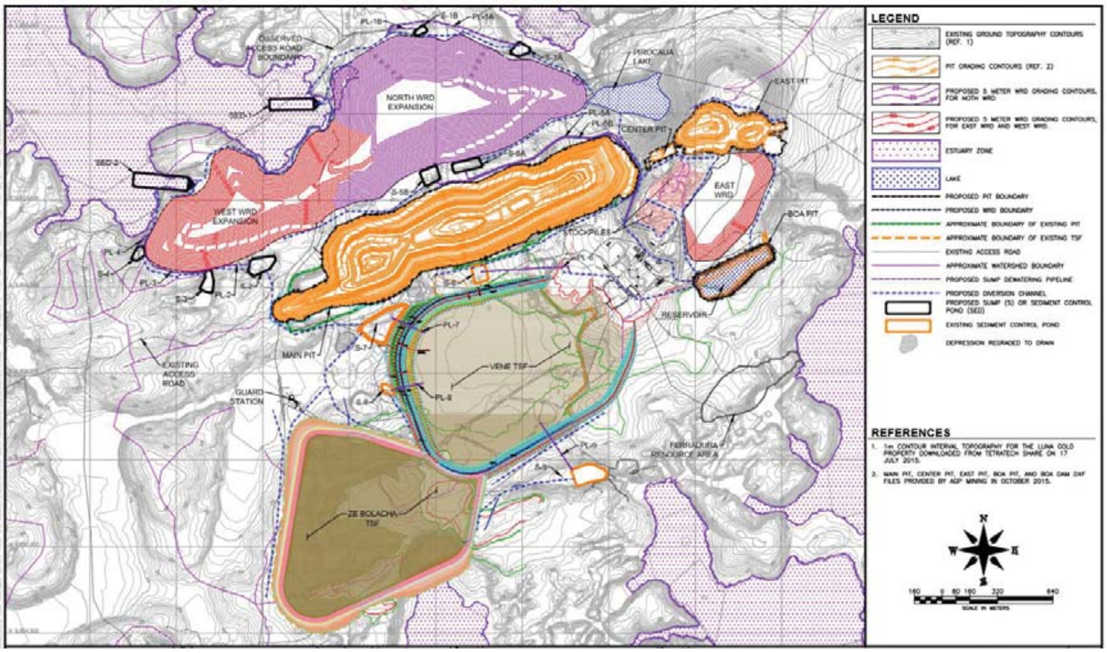

***Figure 3** Aurizona Mine General Facilities Arrangement*

Water Balance Model Parameters

The primary information the client gleaned from the SWWB included:

1. Scheduling TSF dam raises;
2. Determining excess water discharged to environment;
3. Determining freshwater makeup water requirements;
4. Determining the site wide flow of water and pumping requirements; and
5. Determining the number and location of discharge points back to the natural drainages for environmental permit compliance.

Holistic, Hybrid Water Balance Model

Water balance results and associated risk should be defined not only in terms of probability, but also in terms of vulnerability.

Instead of Monte-Carlo style probabilistic analysis as the method to resolve model sensitivity to extreme wet or dry conditions, GRE applied a deterministic approach to climate variation and model response. GRE evaluated the probabilistic climate data as one would do for a probabilistic approach, and selected specific conditions:

- Typical year conditions (50th percentile);
- Extreme wet year (85th percentile);
- Extreme dry year (15th percentile); and
- 100-year storm event.

These conditions were programmed into the spreadsheet using date toggles permitting the application of extreme wet or dry conditions, or an extreme storm, at monthly time steps within the project development. This allowed for the placement of extreme events at vulnerable times in the mine life.

Extreme wet and extreme dry conditions were applied to the entire mine life to simulate the project under extreme stress at both ends of the spectrum to identify project pinch points. Prolonged, multi-year droughts raise concern as to whether sufficient makeup water is available to supply the plant demand without drawing below the minimum TSF Pond volume of 150,000 m^3 (a required minimum to control dust). Conversely, extreme wet conditions put the greatest stress on the storage capacity of the Project and pose the threat of exceeding the maximum permitted discharge of 2,000 m^3/hour (555 L/s) from the Reservoir.

Analysis of Makeup Water Results

Plant demand is preferentially met through water from the TSF; however, additional water is required from the Reservoir in some months to offset shortages from the TSF Pond and to prevent the TSF Pond volume from dropping below 150,000 m^3. During typical precipitation conditions, the water balance is designed to draw 100% of the plant makeup water from the TSF Pond in January through May. During the driest months of September through November, the plant demand is met with 50% from the TSF and 50% from the Reservoir. In the remaining months, June through September and December 75% reports from the TSF and 25% reports from the Reservoir. In general, if the TSF lacks sufficient available water to meet the designed discharge schedule, the remaining plant demand is satisfied with water from the Reservoir.

However, extreme dry conditions require an adjustment in ratio of TSF water to Reservoir water that is pumped to the plant. The water balance is designed to draw 100% of the plant makeup water from the TSF Pond in January through May. In the remaining months, June through December, the plant demand is met with 50% from the TSF and 50% from the Reservoir. In general, if the TSF lacks sufficient available water to meet the designed discharge schedule, the remaining plant demand is satisfied with water from the Reservoir. Figure 4 displays side-by-side comparison of the plant water source during typical conditions (top) versus extreme dry conditions (bottom).

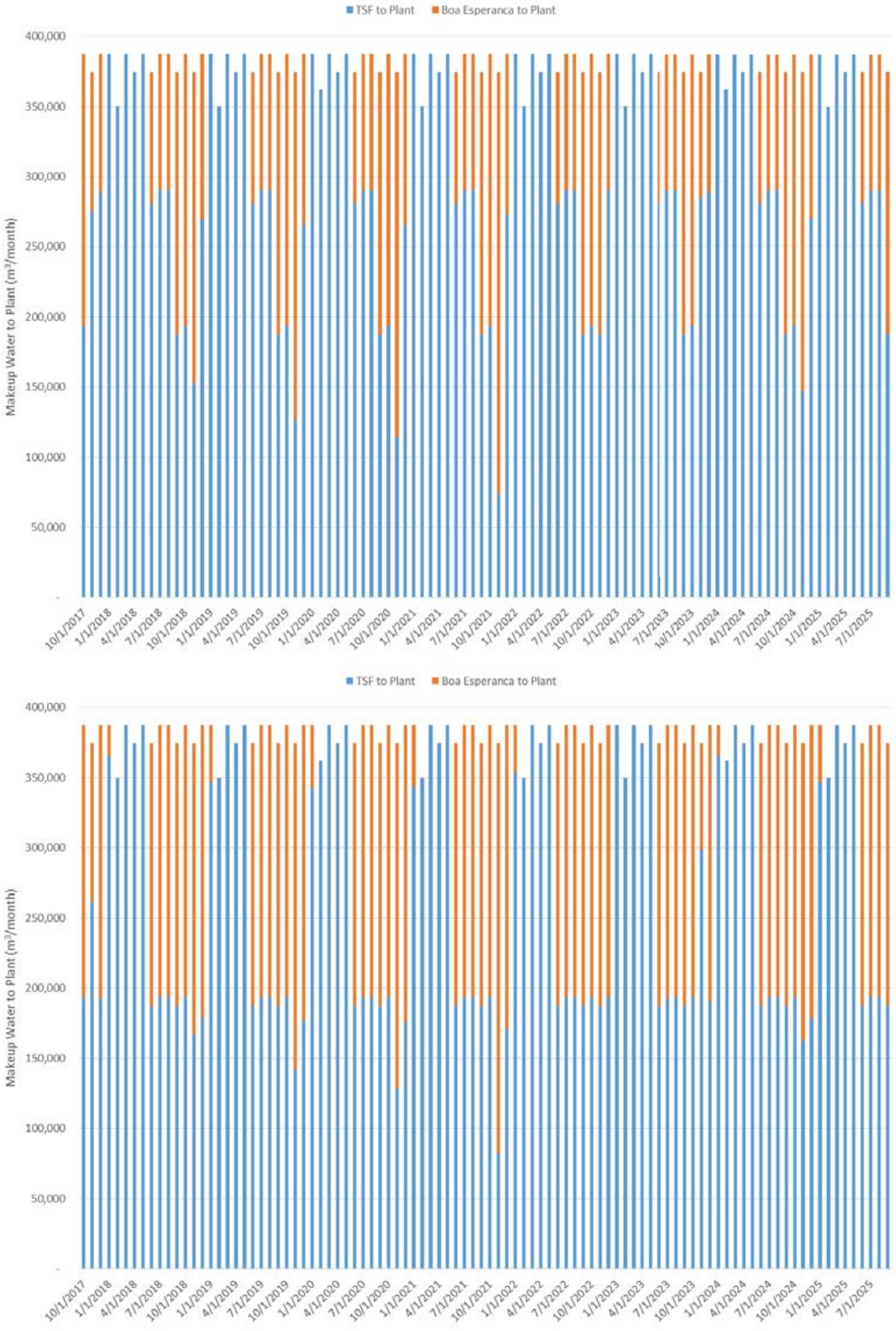

Figure 4 *Plant Water Source*

The water balance demonstrates that sufficient water is available within the system to supply the processing plant, even during an extreme multi-year drought. However, the system requires active monitoring of vulnerabilities and the appropriate response to mitigate the vulnerability in order to be successful. For example, if the Environmental Manager on site observes that the Project area is currently in a drought but fails to appropriately adjust the TSF/Reservoir pumping ratio to the plant, the plant may run out of water. If this example were to occur, the mine would have to endure the costly expense of pumping makeup water from an external source like a nearby river to be able to continue processing at full capacity, or they would have to drastically scale back processing until precipitation sufficiently replenishes the TSF and Reservoir. Both options result in a loss of revenue.

Conclusion

This paper is not advocating for the abandonment of probabilistic water balance models, but is rather a cautionary warning towards the pitfalls of probabilistic water balances. It is a call to action for mine water experts to reframe their frame of thought process while designing and documenting water balances. It is insufficient to look at a model simply in terms probability and degree of certainty. High-quality commercially-available packages create a dangerous “black box” methodology where mine water engineers fail to confirm and evaluate the results of the model against common-sense and hydrologic standards. This risk is compounded by the lack of transparency present in these models. Frequently, neither the engineers nor their clients are able to comprehensively analyze and track the reason why a particular result has been calculated.

The modeler must take a step further and understand the model’s dynamics, including when and where the project is most vulnerable to extreme events, and why the vulnerability exists. A thorough documentation of vulnerabilities and recommendations for managing each identified vulnerability, as well as other unforeseen vulnerabilities should be provided to the client as part of a deliverable. It is of tremendous value to tell a client, for example: “Your containment of MIW is most vulnerable during the construction of the third phase HLF expansion. Under these circumstances, if you are to receive a 100-year storm, you may overtop a pond.” This answer is far more specific and more useful than: “you have a 95% probability of overtopping a pond.” This is exactly the kind of thinking advocated by the *Harvard Business Review*. In the example of the HLF expansion risk, the mine can include a design for temporary diversion berms, re-schedule the construction during a drier time of year, or evacuate available pond capacity in anticipation of the period of greatest risk. These methods are far less expensive than simply building the biggest pond produced by the probabilistic model. The hybrid approach allows the mine to reduce the vulnerability to low probability events, a requirement of all mine water design, but do to it more intelligently.

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Strategies to Avoid AMD in Active Lignite Mining

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Extended Abstract

One task during the groundwater re-rise in the future dumps of MIBRAG lignite open pits is the influence on surrounding water bodies as a result of the pyrite weathering in the overburden. This sulphide weathering is caused by the excavation and mass movement of sediments by ventilation and leads to a geochemical change with a release of iron, sulphate and acidity into the tipping water (figure 1, left) and is embedded in a variety of hydro-geochemical buffer reactions, such as the important carbonate buffering [1].

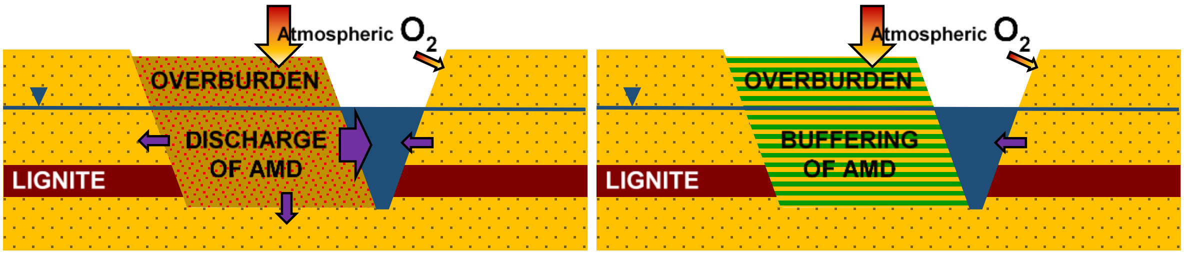

***Figure 1**: uncontrolled discharge from AMD (left) or structured buffering (right) in lignite opencast [4]*

Modern surface mining is carried out in a manner, which prevents or minimizes future AMD problems as much as possible. For this purpose, an approach was developed, where geological, geochemical and technological aspects are examined [2], [4]. By superposing geochemistry and geology, problem areas were marked and countermeasures introduced by changing the mining technology. Thus in future, there will be a significant reduction of AMD from the dump bodies (figure 1, right) [2], [3], [4].

Weathering tests were performed to characterize the AMD potentials geochemically by measuring the parameters “Hydrolytic Acidity” and in eluates pH-level, conductivity, and the discharge of iron, trace metals and sulphate. Figure 2 (left) shows the sediment and time dependence of the weathering. The cohesive and sandy Quaternary/Aquifer #1, releases nearly no iron, sulphate and acidity. The Aquifer #2 (lower part) and Aquifer #3 are the main AMD-polluters with a high release of iron, sulphate trace metals and acidity. The other tertiary materials show a smaller release of AMD-pollutions. The weathering tests show the relevant oxygen exposure time during normal operation (up to 3-4 month) and in boundary areas (up to years).

Blending the planned mining technology by mixing the buffering marl (solid carbonate contents) with the main AMD-polluters of Aquifer #2 (lower part) and #3 in various ratios, buffering tests were implemented for normal operation times. Figure 2 (right) shows that for shorter weathering time (~50 days) a mass addition of 10 to 20% of glacial till is necessary to prevent the release of iron, trace metals and acidity and to reduce the sulphate release; for longer time periods a mass addition of 40% glacial till.

In the current central German opencast lignite mines, enough buffer material is available to tilt dump sides with good geochemical conditions.

With structured tilting, an optimal use of the buffering potential is possible. The future mine water runoff from the dump bodies will only have low concentrations of iron and heavy metals.

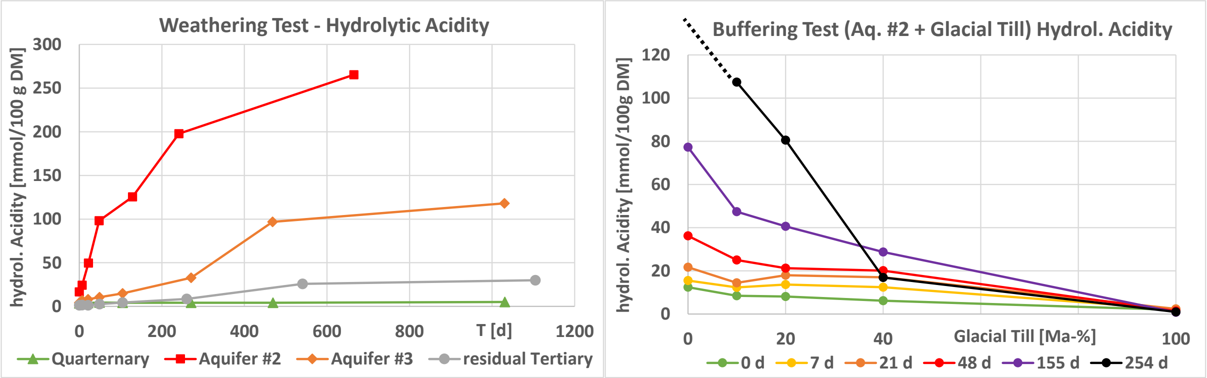

***Figure 2**: Hydrolytic Acidity in Weathering Tests of different Investigation Units (left) and Buffering Tests Aquifer #2 + Glacial Till (right) [3], [4]*

During the research activities, a new dump structure was created. Rather than in unstructured blocks or conical strips, the overburden will be dumped now in fine layers to enlarge contact area between buffering and acidifying sediments. Based on the investigation, the exposure times of the problematic sediments to atmospheric oxygen should be as short as possible and glacial till or geochemically neutral sediments should promptly cover them.

In sum of all measures, it is possible to save the cost-intensive admixing of buffer materials such as lime or dolomite.

Key words: acid mine drainage, advanced mining technology, buffering, dump structure, geochemistry, glacial till, groundwater, mine water, pyrite weathering, trace metals

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CHAPTER 7

Mine Closure, Remediation and After-Care

Mine Closure Wiki – Databank for Mine Closure

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Abstract

Mine closure is an essential part in the development of eco-efficient, sustainable mining. When mines close they leave behind open spaces (ground workings) and piles of mineral waste materials which may deteriorate the environment in the long-term, if not closed properly. Extensive knowledge on suitable closure technologies and related research methods as well as on site-specific factors affecting selection of proper closure technologies are required for successful closure. To reach the best results, planning of mine closure should be started as early as possible - ideally during the feasibility study phase, before any mining operations begin.

To provide guidance on mine closure and to reduce negative environmental, societal and economic impacts of closure, Geological Survey of Finland (GTK) and Technical Research Centre of Finland (VTT) developed Mine Closure Wiki – a wiki-based technology resource on mine closure. The objective of the Wiki is to promote the selection of technical methods for the closure and to facilitate smoother closure planning and permitting.

The Mine Closure Wiki includes the best practices and legislation pertinent to closure, systematic evaluations of the key closure methods and technologies, and benchmarked case studies on the performance of closure technologies. The Wiki is an open internet resource intended as an every-day tool for mining operators, authorities, consultants and researchers for planning, permitting, executing, and monitoring of mine closure. The Mine Closure Wiki was published in October 2015.

Key words: Mine closure, technology resource, mine closure process, water treatment, water management, waste management, monitoring

Introduction

Mining of metals and other commodities provides a basis for the needs of today’s modern society. As the mineral resources are nonrenewable and the mining always changes the environment in its vicinity, mining need to be carried out in a sustainable way. Unlike for most other industrial activities, the timing of mine closure is typically known already when the mining activities are commenced and the planning for the mine closure can also be started. As such, mine closure is an essential part of an eco-efficient, sustainable mining project. After mine closure, open spaces (ground workings) and piles of mineral waste materials are left behind, and they may deteriorate surrounding environment in the long-term, if a mine site is not closed properly. Possible post-mining environmental impacts of mine excavations and waste facilities include, for example, changes in water quality and effects on aquatic biota as a result of low quality mine drainage. To close a mine successfully, extensive knowledge on suitable closure technologies and on site-specific factors affecting selection of proper closure technologies is needed. To reach the best results, planning of mine closure should be started as early as possible - ideally during the feasibility study phase, before any mining operations begin.

In Finland, mining history dates back to the 16th century (Puustinen 2003). Since then, there has been more than 1000 mines exploiting metal ores (Cu, Ni, Zn, Co, Cr, Fe, V; ~ 400 mines), industrial minerals (apatite, talc, quartz, feldspar, wollastonite; ~ 300 mines) and limestones (~ 300 quarries). The period of modern mining has been considered to have started in 1911, when the first flotation plant in the whole

Europe was established at the Orijärvi mine site in Southern Finland. The large-scale mining began in Finland somewhat later, in the beginning of the 1930s with the launch of exploitation of the Outokumpu multimetal ore deposit in Eastern Finland (Puustinen 2003). Today, the number of mines operating in Finland sums up to 30 of which eight exploit metal ore deposits and twenty two industrial minerals or limestones (GTK 2016). In addition, there is a continuous interest on the unexploited deposits in Finland which can be seen in the vast number of areas claimed for mineral exploration by the Finnish and international companies throughout the country (GTK 2016). Several of the currently exploited deposits are to be exhausted within the near future and many of the new mines are expected to be relatively short-lived with the comparatively restricted mineral resources and modern efficient mining methods. Consequently, it is foreseen that during the next decade there will be a number of mines requiring closure. The environmental legislation pertinent to mining in Finland has largely changed during the last decade and mine closure aspects have gained more importance. As a result, the current and future mining operators, permitting authorities, and consulting companies urgently need consistent information on mine closure to close mines successfully without extra burden to the environment.

This paper describes a databank of mine closure, the Mine Closure Wiki, which was developed to provide guidance on mine closure planning, execution, and monitoring to help to avoid negative impacts of mine closure on environment and society. Institutions world-wide have previously provided guidance on mine closure (e.g. Heikkinen et al. 2008, ICMM 2008, DMP 2015). The now presented Mine Closure Wiki is intended to be the first easily updatable technology resource in the Wiki environment with the ambitious aim to cover all aspects of mine closure.

Development and content of the Mine Closure Wiki

The Mine Closure Wiki was developed during Tekes funded Green Mining project “Closedure”, which was made in cooperation with the Geological Survey of Finland (GTK) and Technical Research Centre of Finland (VTT). It is an open internet resource freely available for all interested parties at the GTK Wiki platform: http://mineclosure.gtk.fi. It provides data on mine closure process, research methods pertinent to closure, closure technologies and their performance, and mine closure monitoring procedures. The development of the Mine Closure Wiki is based on the earlier Mine Closure Handbook (Heikkinen et al. 2008) that required updating.

The structure of the Mine Closure Wiki is presented in Figure 1. The key themes of mine closure in the Wiki are mine closure process, waste facilities and waste management, water management and treatment, and post-closure monitoring. Mine closure process covers aspects such as concepts for mine closure, general objectives of mine closure, stakeholder engagement, closure planning, legal requirements for mine closure and management of soil contamination. Water management, water treatment, wastes and waste facilities and monitoring sections all contain subsections for closure objectives, closure technologies, case studies evaluating the performance of closure technologies, and research and development carried out on the key issues during the Closedure project. In the monitoring section, check-lists are provided for chemical and physical stability of parameters that should be observed to ensure performance of selected closure technologies and to meet the objectives of closure. A description of the Closedure project and its content is also presented in the Wiki.

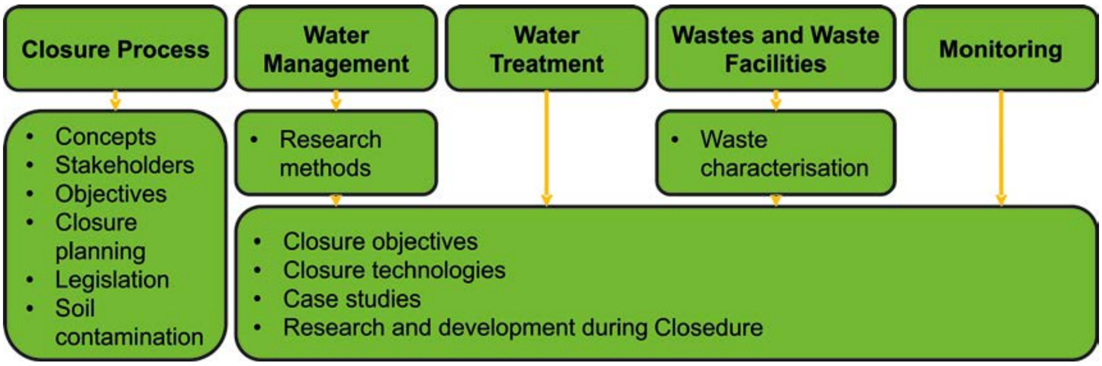

Figure 1 *Structure of the Mine Closure Wiki.*

Data for the Mine Closure Wiki was collected using three different templates to ensure consistency of the information included in the Wiki. These were templates for methods descriptions, technology evaluations, and descriptions of existing cases. The template for technology evaluations is presented as an example in Table 1.

Table 1 *Template for the technology evaluations.*

Title	Content
Introduction	
Description of the technology	Overall description of the technology, development stage, links to cases
Appropriate applications	Suitability, advantages and disadvantages of the technology
Performance	Capacity, maintenance needs, environmental cost aspects; proven and documented applications, successes and failures
Design requirements	Site specific data needs; Requirements for the materials and appliances; Management of potential discharges; Monitoring/control needs
References	

Wiki articles were written by approximately 30 researchers from different fields of mine closure from GTK and VTT. All the articles published at the Wiki went through an internal review by the project leaders and a language check if needed. Currently, the Wiki comprises ca. 200 articles on the key closure issues. In the following chapters, brief summaries of the contents and main approaches of each key theme are presented.

Mine Closure Process

While most of the content in the Mine Closure Wiki concentrates on the technical methods that can be employed when closing various processes and facilities at the end of mining, the Closure Process section looks into managing mine closure throughout the life of the mining project. This is a major task because the process has to be started early in the project and sustained throughout the operations even though the eventual goal may be in the distant future. Mine closure also involves most of the departments in the mining organization and many of the subcontractors that all need to work in sync and be aware of the goals of closure.

External and internal stakeholders are in a key role in mine closure. External stakeholders need to be informed of mine closure and they can contribute their views, local knowledge, concerns, and expectations regarding mine closure and post closure life in the region. This not only helps in minimizing risks but also sustaining the benefits of the mining project after closure. Considerable literature is available on stakeholder identification and engagement and these are referred to in the Wiki. The role of environmental impact assessment (EIA) is emphasized here, because the timing and objectives of closure planning and EIA are similar. The result of the stakeholder consultations should be a balanced, realistic, and achievable closure outcome that makes the planned post closure uses of the site possible.

Defining optimized closure objectives is a key element in mine closure planning (fig 2). The objectives guide all mine closure planning and also help in defining the exact scope of the closure for e.g. financial considerations. The objectives are designed to minimize the risks related to closure while at the same time maximizing the opportunities related to post closure life and communities in the region.

The Closure Management Plan (CMP) is the main vehicle to achieve the closure objectives and manage the process. It is a continuously updated set of documents that contains all the individual action plans and accumulates the results of the already completed actions. Continuous reduction of uncertainties and continuous closure of facilities is central to modern closure management. In addition, the mine must be ‘operated for closure’ so as not to compromise the closure objectives but rather contribute to them in all designs and daily operations. This requires that all internal stakeholders are constantly aware of the essentials of the CMP and take the closure objectives into account in their decision making.

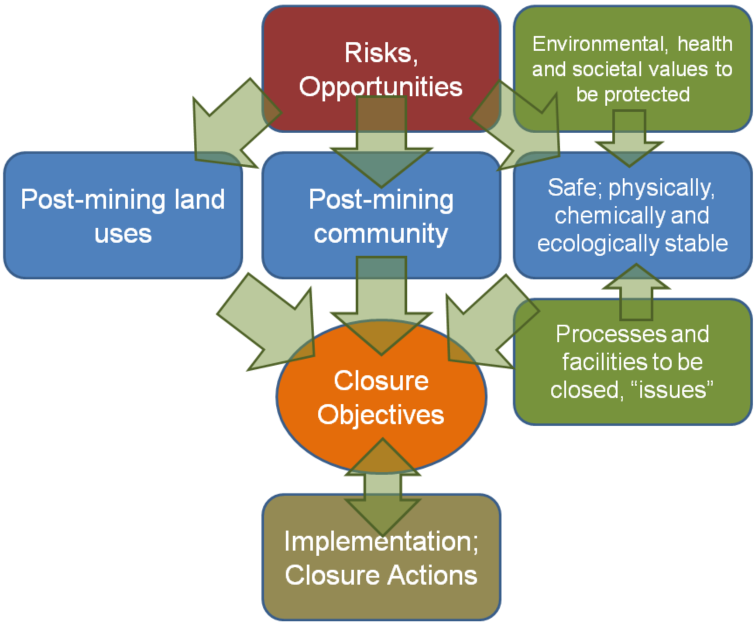

Figure 2 *Factors to consider when defining mine closure objectives to simultaneously minimize risks and maximize sustainable benefits.*

In the Mine Closure Wiki, all the above aspects of mine closure process together with legal requirements for closure and management of soil contamination are discussed.

Water Management

Mining affects water quality at a mine site, but also alters hydrological and topographical characteristics of the site, which has further influence on the surface water and ground water quantities and runoff, soil moisture, and evapotranspiration. The degraded water quality and altered runoff conditions may pose a significant risk to water resources and aquatic environments. Therefore, all waters entering, exiting and circulating at a closed mine site need to be managed to reach an acceptable water management status. To reduce costly water treatment and possible problems caused by, for example, heavy rains or other high discharge events at a closed mine site, it is also important to keep the unaffected surface runoff and groundwater separated from the possibly polluted waters and divert them past the mining operations. Overall, an environmentally sound post-closure water management plan is needed to prevent any adverse effects on the environment.

Water management designs should consider the mine closure already during the active mining phase. Using a pro-active approach throughout the operation phase and planning the water management to meet also the post closure standards, such as gravity driven runoff, erosion resistant water management structures, water treatment, and regulatory compliance, provides an ecologically, economically and socially durable solution (DWAF 2008). The water management structures should be designed resilient to physical and chemical erosion to ensure long life span and low maintenance costs. (Younger et al. *2*002, Wolkersdorfer 2008). The planning of the post-closure mine water management requires participation of a multi-disciplinary team of professionals and authorities. In post-closure water management research, the hydrogeochemical behaviour and hydrodynamic development are the most essential aspects along with a thorough hydrological and hydrogeological understanding. (DWAF 2008)

The water management technologies evaluated in the Mine Closure Wiki include, for example, diversion ditches and channels, dams, mine flooding, and protection pumping. In addition, the Wiki describes various methods essential in water management, such as flow rate measurements, hydrogeological characterization methods, isotopic studies, and post-closure modelling methods including, for example, water balance modelling and flow modelling.

Water treatment

Due to the diversity of ore deposits, every mine site and its waters are unique and, therefore, also the water treatment objectives are site-specific for each mine site. There is an extensive group of variables which affect on the quantity and quality of mine water even within a single mine and a sound understanding of the hydrogeology and hydrodynamics of each mine is crucial also for water treatment. Furthermore, also local environmental, climatic and socio-economic conditions and requirements affect the decisions on the post-closure treatment of mine site waters. Thus, there is not a single solution for water treatment in mining. (Taylor et al. 2007, Wolkersdorfer 2008).

Treatment techniques used at a mine depends on the water chemistry, the severity of the contamination, contaminants, flow rate, water volume, and the objectives of the treatment (e.g. water quality standards, use of water after treatment). The general objectives of post-closure water treatment typically include:

- Restoration of water quality to a level that does not present any long-term risks to the environment or human health,
- Long-term functioning of the technique and stability of the treatment products/residues,
- Integration with other water management measures (including management of tailings areas),
- Sufficient capacity for peak floods and adaptation to seasonal fluctuations,
- Accordance with the regulative requirements (legislation, environmental and other permits).

Mine water treatment technologies are usually divided into active and passive methods. Active treatment technologies require the input of energy and chemicals, whereas passive treatment methods are based on natural chemical and biological reactions without or little nutrient and energy addition. Since the passive treatment technologies cannot usually be adjusted according to the changes in water quality and flow rates, they are used to treat mine waters with low acidity and low flow rates. The advantage of active treatment technologies is that it can be engineered to accommodate essentially any acidity and flow rates of mine waters. Furthermore, the active technologies can be adjusted instantaneously in response to the changes in water quality and flow rates. However, all this adjusting usually requires frequent maintenance and regular labour inputs. In contrast, passive technologies are self-sustaining processes, they require only infrequent maintenance and function well without or little human interference when established. Thus passive treatment technologies are commonly used at closed mine sites. (Younger et al. 2002, Taylor et al. 2005, Wolkersdorfer 2008). The suitability of passive and active water treatment systems is based on influent water characteristics, mainly acidity, pH ranges and flow rate (tab 2). Mine Closure Wiki presents both active and passive water treatment technologies suitable for mine water treatment.

***Table 2** Acidity and pH ranges and flow rates for passive and active treatment methods (modified from Taylor et al. 2005)*

Treatment technique	Average acidity range (mg $CaCO_3$/l)	Average acidity load (kg $CaCO_3$/day)	Average flow rate (l/s)	Average pH range	Max attainable pH
Active	1.0–10,000	1.0–50,000	No limit	No limit	14
Passive	1.0–800	1.0–150	<50	>2	7.5–8

Wastes and waste facilities

Management of mining wastes, especially tailings and waste rocks is one of the major challenges during mining activities and mine closure. In the worst case, mismanagement of wastes leads to detrimental impacts on the surrounding water bodies and soils due to the generation and transport of low quality mine drainage. The ultimate objectives in sustainable mining are to decrease the amount of waste that requires final disposal, to increase material efficiency and to decrease their environmental impacts (fig. 3). Mining wastes can often be used, for example, in earth construction at the mine site or elsewhere, in landscaping or as a backfill of mine voids. Some mining wastes may even be utilized as a raw material, for instance, for cement or bricks. As the environmental impacts and also the raw material potential of wastes largely depend on the geology and mineralogy of the mined deposit, mineralogical and chemical characterization of wastes is essential. However, in many cases geotechnical or environmental characteristics of wastes prevent their further use and long-term disposal is required.

Comprehensive waste characterization is needed to design adequate waste management systems for wastes for long-term disposal. Characterization typically includes evaluation of both the geotechnical and environmental behaviour of wastes. Based on the characterization, selection of sufficient basal and dam structures for facilities is carried out. During the production phase, waste management includes various waste disposal techniques such as blending and layering, raising of dams, use as a backfill in mining voids and treatment of water effluents of the wastes. In mine closure, negative environmental impacts from mine wastes are typically prevented by different cover structures, landscaping the waste facilities and, in many cases, by treating the effluents. It is important to note that the planning of closure of facilities should already be considered during the design phase of the waste facilities, because decisions made during the design or operation will ultimately impact the options available in closure. In Figure 3, a flow sheet for overall management of mining wastes is presented.

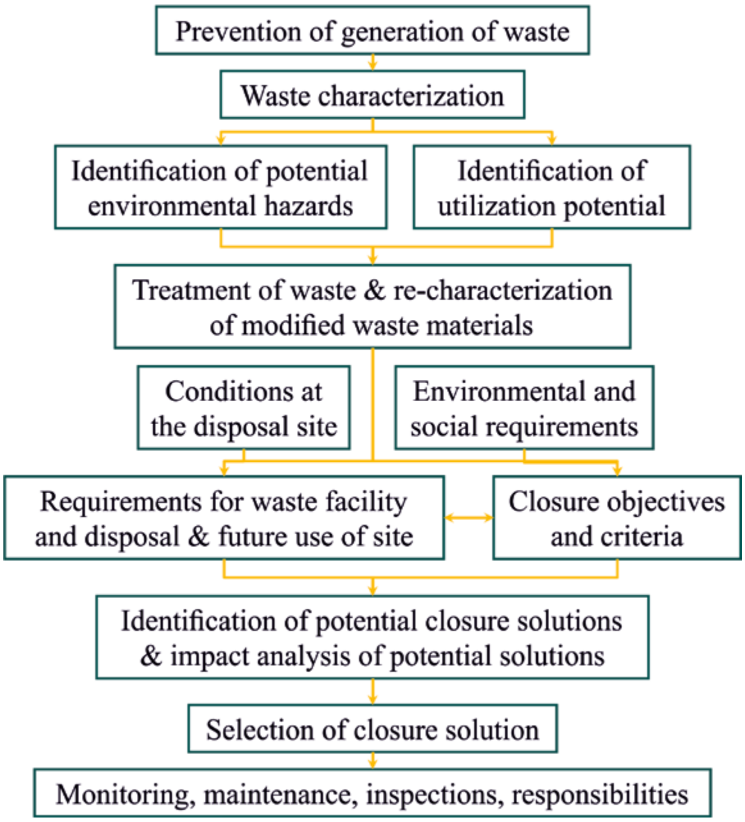

Figure 3 *Management of mining wastes throughout the life-cycle of mining operations.*

Mine Closure Wiki provides thorough evaluation of different methods applied in the mine waste characterization including methods measuring overall chemical and mineralogical contents of wastes to identify potential harmful substances and their occurrence in wastes, potential of wastes to produce acid mine drainage, and leachability of contaminating agents from wastes. In addition, methods used in determining physical and geotechnical properties of wastes are included.

The closure technologies for wastes and waste facilities have been divided into two groups in the Mine Closure Wiki: to those applied already before or during operations, and those used in the actual closure phase. The evaluated technologies include, for example, various basal structures for waste facilities, technologies to reduce acid production potential of wastes (e.g. desulphurization, layering), cover structures (dry cover, water cover), backfill technologies, and passivation methods.

Monitoring

Monitoring is needed after mine closure to ensure that all the chosen closure technologies perform as intended and in accordance with the closure objectives and criteria. Through monitoring it should be possible to demonstrate that the mine site is safe and poses no environmental or health risks. Furthermore, monitoring should be used as a proactive tool to identify potential defects in the rehabilitation process or structural failure, and to facilitate a rapid response in a case of failure. Structures remaining at the site after closure and requiring monitoring include, for example, underground workings, open pit, waste rock and overburden piles, tailings facilities, and the remediated industrial area.

In many cases, extensive monitoring is needed to reach the above mentioned goals, and monitoring may include various methods to ensure physical, chemical, biological and socio-economic stability of a closed mine site. Chosen methods and parameters are site-specific and depend on the structures and activities remaining at the site, and the nature, type and size of the mining. Duration of the monitoring also depends on the nature and size of the operations and may continue for decades after mine closure. In Finland, and in many other countries, a post-closure monitoring plan accompanying a mine closure plan is submitted to the environmental authorities for approval before actual mine closure activities can begin. Typical questions for drafting post-closure monitoring include:

- what is to be monitored (which impacts and variables)
- how is monitoring implemented (sampling, analytical techniques, installation of monitoring network)
- what is the frequency and duration of monitoring (schedules and timing of sampling intervals)
- who is responsible for monitoring (who will undertake monitoring and ensure compliance)
- how is the record keeping arranged (Heikkinen et al. 2008).

Table 3 presents examples of features to be monitored and typical inspections in post-closure monitoring. The Mine Closure Wiki provides guidance on suitable monitoring methods and sampling techniques, including methods used in geotechnical and water quality monitoring.

Table 3 *Examples of targets and typical inspections carried out in post-closure monitoring (modified after Heikkinen et al. 2008)*

Typical features to be monitored	Typical inspections in post-closure monitoring
• condition of structures preventing inappropriate access • physical and chemical stability of waste facilities and embankments – and performance of potential cover structures • rate and quality of mine workings flooding • performance of water treatment systems • success of revegetation programs	• visual inspections of embankments and waste facilities • quality and volume of drainage from waste facilities • quality of downstream aquifers and water bodies • revegetation rates, biodiversity and density

Who can benefit from the Mine Closure Wiki?

The Mine Closure Wiki is intended as an every-day tool for mining operators, authorities, consultants and researchers for the planning, permitting, executing and monitoring of mine closure. The Wiki is freely available for everybody for reading and acquisition of information but commenting of the articles requires registration. Contributions on the Wiki are invited from mine closure experts throughout the world, especially on the latest, updated information on the available closure technologies and their performance and case studies presenting the applications of various technologies. For registrations and contributions, inquiries can be sent to: mineclosure@gtk.fi.

Management of the Mine Closure Wiki

The Mine Closure Wiki is managed and updated by the Industrial Environments and Recycling unit of the Geological Survey of Finland. Updates will be made as a part of the basic task of GTK and during current and upcoming research projects. Comments and proposals for the development of the content of the Wiki can be addressed to: mineclosure@gtk.fi.

Conclusions

Mine Closure Wiki (http://mineclosure.gtk.fi) was developed in the Finnish Closedure project by GTK and VTT to provide guidance and support for mine closure for mining operators, environmental authorities, consultants and researches working with mine closure issues. The primary objective of the project was to establish an open internet resource of mine closure that is freely available to all interested parties. The Mine Closure Wiki currently holds approximately 200 articles covering different aspects of mine closure, such as the mine closure process, water management and treatment, management of wastes, and monitoring of performance of closure solutions. Evaluations of methods and main closure technologies are provided from these main themes supplemented with case examples of the performance of key technologies. The Mine Closure Wiki is managed and updated by the GTK and contributions are invited from mine closure experts throughout the world.

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Surface water management and encapsulation of mine waste to reduce water pollution from Frongoch Mine, Mid Wales

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Abstract

Abandoned metal mines are the principal cause of failure to achieve Water Framework Directive (WFD) standards in Wales, with 1,300 mines impacting over 100km of rivers. Frongoch was one of Wales' most productive lead mines during the 18th and 19th centuries, consequently becoming one of our most polluting abandoned mines. NRW received financial support from the European Regional Development Fund (ERDF) via the Welsh Government (WG) to implement a remediation scheme and reduce impacts.

A stream was diverted in 2011 to prevent it flowing into mine workings that discharge via Frongoch Adit, reducing its metal load. A perimeter channel was created in 2013 to direct surface water away from spoil towards a new flood attenuation pond. Three hectares of mine waste were re-profiled and capped in 2015 to minimise water ingress and to convey clean runoff via drainage channels into a series of ponds, creating a new wetland habitat. Wide consultation at design stages ensured the remediation didn't adversely affect the mine's unique features or statutory designations. NRW engaged ecologists to enhance biodiversity and archaeologists to supervise construction.

Although further monitoring is required, this project demonstrates how water quality improvements can be achieved with low ongoing maintenance, whilst providing local biodiversity and landscape benefits. The scheme will not achieve compliance with WFD in all recipient watercourses, but virtually all water from the mine is now controlled via one surface water and two groundwater discharges, one of which has reduced in volume by 80%. These discharges have flow gauging weirs, providing opportunity for ongoing research and development for institutions, innovators and regulators. This paper discusses the scheme, its achievements and opportunities going forward.

Key words: Metal mine remediation, Water Framework Directive, lead, zinc, cadmium

Introduction & historical background

Frongoch Mine is situated in a rural setting near the village of Pont-rhyd-y-groes, ~245m above ordnance datum (AOD), 17km south east of Aberystwyth. It was one of Wales' most productive lead mines during the mining renaissance of the 18th and 19th centuries, producing 58K and 50K tons of lead and zinc ore respectively (Bick 1996). Prior to remediation, Frongoch was ranked as Wales' second most polluting mine (Mullinger 2004), annually discharging 23 and 1.5 tonnes of zinc and lead.

Mineral ownership at Frongoch belonged to the Earls of Lisburne and mineral rights changed to the west of the watershed, where the same lode was mined at Wemyss Mine (Fig.1). A lease of 1759 is recorded, though Frongoch remained a small mine until 1790, when new management invested. The mine operated initially as Bron-y-Goch and Llwynwnwch mines, but the most successful period was 1834 to 1874, when the two leases were consolidated (Bick 1996).

The capacity of upstream reservoirs was increased to improve seasonal availability and a steam engine introduced ~1842 to aid dewatering (Bick 1996). The Wemyss mine was acquired around this time and its adit was extended to connect with the Frongoch 24 fathom level. In all, thirteen levels were driven, generally at 22m intervals. Shafts terminated at varying levels, the deepest at ~282m (Jones 1922).

The French mining engineer Moissenet visited in 1860 to record the industrial processing and found that even though four vast reservoirs were used, water was scarce at surface and recycled for hydropower at the large 60hp waterwheel at Wemyss Pumping Station. Moissenet recorded the processing from north to south with stamp, crusher and winding houses, jigging tables, gravity separation using water and round buddles, the Lisburne buddle and Zenner rotating table (Bick 1996).

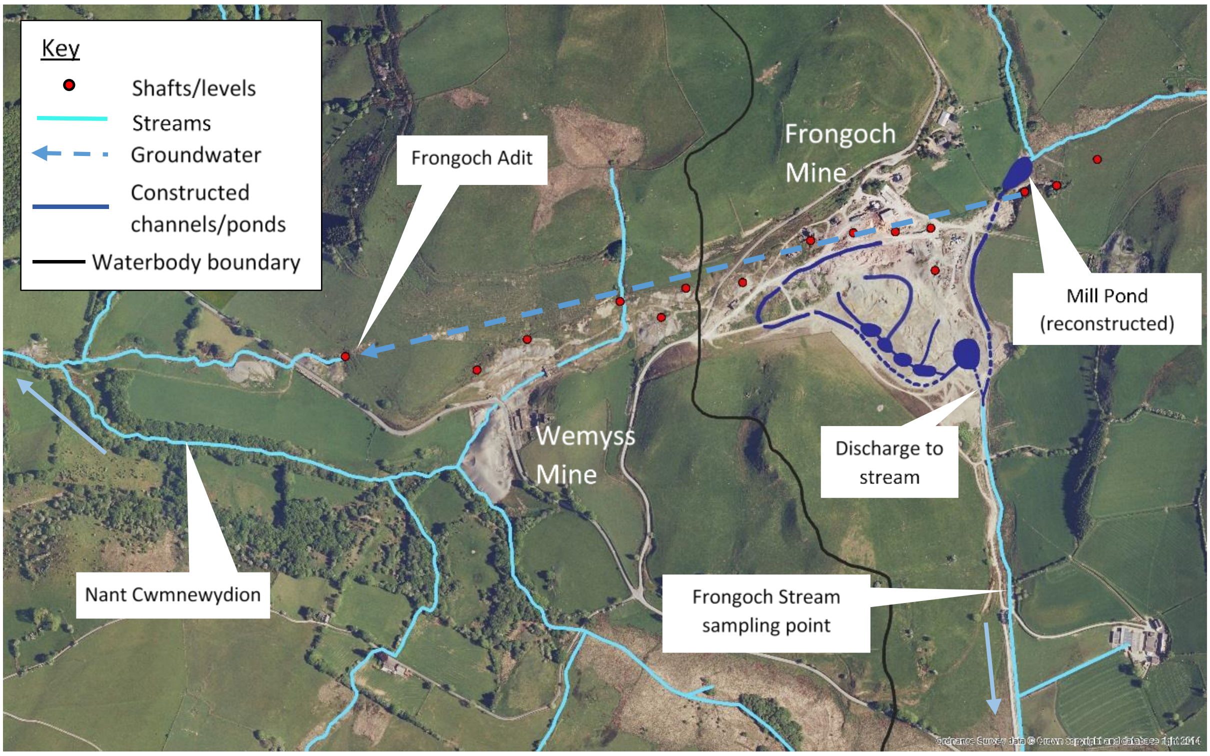

Figure 1 Aerial photo of Frongoch and Wemyss mines in 2009 showing surface and groundwater pathways, including channels and ponds constructed from 2011 to 2015.

Although the galvanising process was UK patented in 1837, reportedly only lead was mined from 1859 to 1876 with sphalerite production generally avoided due to low commodity prices. Much sphalerite was therefore perceived to have passed to the spoil heaps. Although the mine had flourished with proven reserves at depth, it became unprofitable due to coal import costs and hard ground at depth. A new owner extended Vaughan's Shaft to ~282m, but found the vein too hard to exploit, so from 1879 began stripping the walls of remaining mineralisation and removing *in situ* supporting pillars (Jones 1922).

The Belgian Société Anonyme Minière modernised the mining in 1898, adopting electricity generated from the Pont Ceunant hydro-electric scheme (Bick 1996). The onsite ~1.2ha reservoir used for operating the Wemyss wheel became redundant and was probably adopted as a tailings lagoon, either on introducing hydro-electricity or when mining ceased and the dressing mill was used for reworking the dumps in 1903. The venture collapsed in 1904 (Jones 1922).

Final large-scale working of mine spoil dumps occurred in the 1920s when sorted mine spoil was transported ~2.8km by aerial ropeway to the Gwaith-Goch dressing mill in the Ystwyth valley (Bick 1996). An option of extending the Grogwynion deep adit, also in the Ystwyth valley, by driving it a further ~1.3km north and draining Frongoch to a level of ~139m was not pursued (Jones 1922).

Geology, hydrology & geochemistry

Frongoch is situated on the Devils Bridge Formation in the Early Telychian Stage of the Silurian Period. It is a thick basin "slope apron" sequence of thinly interbedded mudstone and sandstone turbidite couplets, and is quoted as being over 900m thick. The Frongoch Borehole drilled onsite confirmed the sequence to be over 250m in thickness. The strata in the Central Wales Orefield has been widely faulted by two fault sets. One trends NNE-SSW along anticline and syncline structures that bear little mineralisation, whereas the second, like the Frongoch Fault, has cross cutting faults that strike broadly ENE-WSW and are near vertical and mineralised. The faults subject to high pressure fluids resulted in rounded breccia and gangue hosted ore-rich veins from less than 1m to 30m thick (British Geological Survey 1997).

The mine was worked for a length of ~1.5km and the vein reported as consistently 11m thick. The greatest yield was a 220m section by Vaughan's Shaft where the galena ore was 3.6m to 7.2m wide (Jones 1922). The vein contained two separate galena rich lodes and a sphalerite lode on the footwall. The metal lodes were perceived to taper with depth along strike, but were consistent in width; the south galena lode 1.8m wide and north galena lode 6.4m at 260m level in Vaughan's Shaft (Jones 1922).

Several thousand tonnes of mineral dumps were moved to the east of the site in 2003 and bear world class Pb-Zn-Cu supergene minerals formed over three stages. Consequently, this site was designated as the Mwyngloddfa Frongoch Site of Special Scientific Interest (SSSI). The earliest Tertiary supergene stage is represented by large pyromorphite and cerussite crystals and the rarer second stage formed during post glacial weathering is represented by the same microcrystalline species plus wolframite. The post mining stage yields bechererite, caledonite and susannite plus rare lead bearing species corkite and hinsdalite often found in oxidised zones of polymetallic sulphide deposits (Cotterell & Todhunter 2007).

Soils are generally thin and the upland terrain offsite lends itself to deep, shallow or modified peat horizons and glacial till on topographic lows with onlapping soliflucted head deposits with varying gravel content on the slopes (Palumbo-Roe *et al.* 2012). Superficial deposits onsite include coarse spoil, coarse sand graded mine spoil and, in the former reservoir, fine sandy silt-clay tailings.

Rainfall upstream on the Ystwyth is ~2000mm/yr. Drainage at Frongoch is governed in the west by the Nant (Stream) Cwmnewydion, which drains to the Afon (River) Magwr and Afon Ystwyth, and in the east by Frongoch Stream, which joins the Nant Cell and thence the Afon Ystwyth upstream at Pont-rhyd-y-groes. A number of large reservoirs were constructed to support mining, including Pond Rhosrydd and Pond Glandwgan to the north west, while Llyn Frongoch and Llyn Llwynwnwch supplied water to Mill Pond from the north east. The onsite ~1.2ha reservoir fed the Wemyss pumping house.

The hydrology and hydrogeology was substantially changed by ore extraction and development of open workings between Llwynwnwch and Edward's shafts at the north east of the site. Modification of drainage had enabled surface water from Mill Pond to cascade directly into open workings, flowing along the worked lode and discharging at the Frongoch Adit portal (~185m AOD) (Fig.1). Surface water runoff is from north to south across the mineral processing area towards the tailings lagoon and Frongoch Stream; during storm events this was considerable and eroded fines. A culvert discharges to Frongoch Stream (~231m AOD) and yields a seasonal discharge that originates from the dressing floor direction.

The Conceptual Site Model has developed particularly around the fine-rich tailings lagoon. Trial pits along this lagoon confirmed 0.6-1.15m of heterogeneous silty clays, frequently finely laminated and sandy (fine), becoming sand and peaty at the base laying upon ~1.2m or more peat and 1m of silty clay on slate gravel (Palumbo-Roe *et al.* 2009). Electrical resistivity tomography and ground penetrating radar indicated the upper silty clay (~1.2m) to be the lagoon base with a more conductive zone extending well below (Kuras *et al.* 2011). Later excavations corroborated a highly fractured bedrock with overlying clay rich till and isolated, generally beneath the lagoon, peat horizons (Palumbo-Roe *et al.* 2012). Outside the lagoon footprint, gravel to coarse sand mining waste and cobbles extended laterally.

Gravel in head deposits on surrounding hills conveyed drainage towards the site onto till deposits allowing some recharge of tailings. Perched groundwater was identified in a remnant launder, on the lagoon base, but also on till. The implied groundwater pollution of the fractured bedrock was subsequently confirmed as an attenuating plume (Bearcock *et al.* 2010).

Groundwater flows rise in the mine workings via an old stope (~190m AOD) to 24 fathom level near the watershed and thence drain via Frongoch Adit (Palumbo-Roe *et al.* 2012). The culvert into Frongoch Stream is also capable of draining the tailings and/or the glacial till, and lead concentrations increased in a tailings borehole in winter, implying seasonal flushing of lead precipitates (Bearcock *et al.* 2010).

ICP-AES analysis yielded relatively low concentrations in the shallow samples and those beneath the tailings lagoon base. Lead was between 1-40g/kg, but enriched up to 127g/kg at 1.4-1.65m in finely laminated clays, which were the most leachable in sequential extraction. Zinc ranged from 40-112g/kg throughout the unweathered tailings profile and cadmium from 0.05-0.4g/kg (Palumbo-Roe *et al.* 2009).

Chemometric data processing (CISED) did not reveal carbonate components, but revealed sulphates in near surface and sulphides or oxyhydrides at the lagoon base and beneath. Galena was present from 0.74m and enriched (~10%) at 1.4-1.65m and anglesite [$PbSO_4$] traces detected from 0.74-1.4m. Surface bianchite [$(Zn,Fe)SO_4 6H_2O$] efflorescence was observed during a dry summer with an appreciable amount of zinc recorded in deionised water extraction. This is indicative of deeper sulphide weathering, upward capillary transport and sulphate precipitation in the shallower unsaturated zone, which is more readily soluble during wet dry seasonal cycling (Palumbo-Roe *et al.* 2009).

Environmental impacts

Based on the 2015 classification, all of the watercourses downstream of Frongoch Mine are failing to achieve the environmental quality standards required by the WFD, mainly due to elevated concentrations of zinc. Frongoch Mine is the primary cause of the zinc failures in Frongoch Stream, Nant Cell, Nant Cwmnewydion and Afon Magwr. It is also one of the two major sources of zinc in Afon Ystwyth, the other being Cwmystwyth Mine (Stokes 2012).

Fish population surveys carried out by Environment Agency Wales (EAW) in 2009 confirmed Nant Cwmnewydion was virtually fishless until its confluence with Afon Magwr, approximately 3.5km downstream of Frongoch Adit. Fish were also absent in Frongoch Stream and in Nant Cell downstream of its confluence with Frongoch Stream (2km downstream of Frongoch Mine) when they were surveyed in 2013. The invertebrate fauna was impoverished downstream of inputs from Frongoch Mine in both Frongoch Stream and Nant Cwmnewydion in 2009, with the number of taxa increasing with distance from source (Keenan 2015).

Remedial options appraisal

In February 2011, EAW (funded by WG) diverted Frongoch Stream to stop it overflowing from Mill Pond into an open stope at the north east of the mine, as recommended by Atkins (2010). The stream was diverted back into its original watercourse via a 450mm culvert from Mill Pond, leading to a concrete cloth lined channel on the eastern perimeter of the site, which remains relatively clean upstream of runoff and groundwater inputs from the mine.

An assessment of options for reducing the metals load to Frongoch Stream from the tailings dumps at Frongoch Mine was undertaken (Atkins 2011). Four options were considered, ranging from re-profiling of mine spoil (do minimum) to re-profiling and capping mine spoil and providing vegetation and runoff treatment (most expensive). The overall aim was to reduce the volume of water entering the contaminated mine waste from direct infiltration of rainwater or from runoff entering the site from surrounding hillsides, thus reducing the opportunity for metals to be mobilised.

A grant of £690K from ERDF was matched by £460K from NRW for a project from January 2013 to June 2015. The total funding was less than the indicative cost for the most expensive option, so the design needed to be scaled to the available budget, with minimal ongoing maintenance costs.

Implementation of the preferred option

Atkins proposed construction in two phases to allow works that didn't require planning permission to be progressed under EAW's permitted development rights, while planning permission was obtained from Ceredigion County Council (CCC) for the remaining works. The phasing of the project also allowed experience obtained from Phase 1 to be incorporated into Phase 2.

Phase 1 was carried out by EAW between January and May 2013. A drainage channel was constructed along the northern and western perimeters of the site to intercept clean surface water and reduce the amount reaching mine waste. The channels were not lined as it was hoped the natural soils would be low permeability, however, the extent of the former tailings lagoon proved to be greater than expected, resulting in a portion of the perimeter channel passing through mine tailings. A pond lined with Geosynthetic Clay Liner (GCL) was built to receive flows from the perimeter channel and attenuate flows entering Frongoch Stream. The downstream flood risk was further reduced by the installation of a hydro-brake in the pond outfall, restricting the discharge to a maximum of 160l/s.

Following the completion of Phase 1, further geochemical assessment of the site was carried out in collaboration with Swansea University (Mustard 2013). Water quality data were collected during heavy rainfall events and a detailed characterisation of the different soil types across the site was completed with a portable X-ray fluorescence (pXRF) spectrometer. Soil samples were collected at key locations for laboratory 'wet analysis' and leachate testing. This study highlighted an area of particularly metal-rich material that roughly correlated with the area of the historical tailings lagoon and through which the Phase 1 channel flowed. The design of Phase 2 was modified to ensure priority was given to preventing surface water coming into contact with the most contaminated material.

Phase 2 was tendered and contractors were asked to quote for varying amounts of low permeability capping across the site to enable the works to be scaled to the available budget. A contract was awarded to include the full extent of proposed capping, with construction taking place between January and June 2015. Mine waste was excavated and deposited in the north of the site where it was re-profiled into a more regular landform to promote runoff. A series of cascading wetlands were created on the footprint of the former tailings lagoon in the south west of the site to encourage suspended solids to drop out of runoff and provide additional habitats for wildlife. These two areas were capped with a minimum of 300mm of locally sourced low permeability clay, with the wetlands and transfer channels also benefiting from the addition of a GCL below the clay. Drainage channels lined with GCL and low permeability clays were constructed to carry runoff into the wetlands. A section of pipe was placed in the Phase 1 perimeter channel to convey relatively clean water through the former tailings lagoon and under the new wetland area. The trench was backfilled with excavated fine tailings and capped. All capped areas were finished with 100mm of restoration soils, which included surplus capping material and naturally occurring site-won soils. This was seeded with a nurse crop of *Agrostis capillaris* (Common Bent) to establish fast vegetation cover, offering protection to the soils and stabilising slopes against erosion. Restoration soils in the drainage channels were afforded the additional protection of turf reinforcement matting.

In total over 23,000m^2 of the site was afforded a lower permeability cap during the Phase 2 works, and validation testing provided confidence that this was compacted sufficiently to attain the permeability requirement of 1×10^{-8}m/s. Topographical surveys confirmed an average clay thickness of 396mm, with over 450mm in some areas (up to 50% greater than required), which adds to the overall performance of the cap. The effect of the remediation on the landscape can be seen in Figures 2 and 3.

Constraints & mitigation

An environmental assessment was commissioned to assess likely impacts and set out measures to avoid or reduce negative impacts. The Environmental Report (Environment Agency 2012) was circulated to statutory consultees and other key environmental stakeholders for comments before finalising the designs for Phase 1. An updated version of this report (NRW 2013) was circulated for consultation before being sent to CCC with the planning application for Phase 2.

An initial scoping exercise identified potential environmental effects that could be screened out from further assessment due to their low impact. The remaining effects that were assessed included ecology, planning policy, recreation, public access, water resources, hydrology, soils, landscape and visual impact, cultural heritage and archaeology. An Environmental Action Plan was produced to outline the actions required to mitigate impacts of the works. Following mitigation, the majority of the permanent impacts were expected to be positive, including water resources, water quality and visual amenity. The only permanent negative impacts identified were cultural heritage and archaeology.

Frongoch Mine is within the Upland Ceredigion Landscape of Outstanding Historic Interest. Design development ensured that the unique historic features associated with the former mining operations were avoided, including the engine and crusher houses within the adjacent Scheduled Ancient Monument (SAM). The remediation changed the character of the mine, but the effect on landscape was predicted to be positive in the long-term as vegetation becomes established and naturalised. The most important ecological habitats on site are the lichen and bryophyte rich areas of Calaminarian grassland type. These areas were identified by surveys and their location was taken into account during the design of the earthworks. A number of stands of Japanese knotweed were present, which were avoided by the works where possible and managed by annual spraying. Habitats Regulations Assessment (HRA) screening concluded that there was no likely significant effect of the remediation on the Grogwynion Special Area of Conservation (SAC), approximately 6km downstream of Frongoch Mine.

Figure 2 *Photo of Frongoch Mine looking from north west to south east in October 2010.*

Figure 3 *Photo of Frongoch Mine looking from north west to south east in April 2016.*

A desk-study of the mine's industrial heritage, undertaken during the scoping exercise, divided the site into zones according to archaeological potential (Murphy 2012). This study informed the design of the remediation scheme, which avoided the SAM and a number of unscheduled building remains in the centre of the site. EAW excavated six archaeological trenches in August 2012, which were evaluated to identify buried remains across the site, create a deposit model clarifying the extent of overburden protecting these sites and identify areas in which structures were likely to be disturbed by the proposed works. Features of interest included the well-preserved remains of two buddle-pits, several wall-lines, tram rails, tramway banks, a reservoir bank and timber structures. The depth of these features varied from 0.2m to 1m below existing ground levels (Poucher 2012).

The archaeological evaluations demonstrated remarkable survival of structures depicted on historical maps, but also identified many features that were not on these maps, so an accurate plan of sensitive features couldn't be ascertained from these maps alone. A watching brief was therefore required during ground works in sensitive areas where the level of archaeological survival was unclear. The Phase 1 watching brief confirmed the presence of archaeological remains across the former mine site, but these were less frequent around the perimeter of the mine (Shobbrook 2013). Following Phase 1, open area excavations were pursued on a series of processing features that would be affected by the proposed Phase 2 works. The Phase 2 design was subsequently modified to avoid disturbing these features and to re-bury them. As a result of these design changes, few archaeological remains were recorded during the Phase 2 supervision (Murphy *et al.* 2015).

Monitoring & results

Results of fortnightly monitoring show an 80% reduction in flow from Frongoch Adit following the 2011 stream diversion (Table 1). Although metal concentrations in the residual flow increased, the zinc, lead and cadmium loads reduced by 44%, 63% and 58% respectively. The main benefit of this diversion was to increase dilution in the recipient Frongoch Stream, causing zinc, lead and cadmium concentrations to reduce by over 70%, while there was no observable change in metal concentrations in Nant Cwmnewydion downstream of Frongoch Adit.

Occasional metal concentration spikes were recorded in Frongoch Stream during construction and may be attributed to temporary disturbance of the former tailings lagoon. Since completion of the remediation scheme in July 2015, metal concentrations in runoff from the capped areas have been considerably lower than those observed prior to remediation, but other sources are still contributing to the metals load to Frongoch Stream. Most of these sources are now captured within the final discharge from the flood attenuation pond, including runoff from uncapped areas and a groundwater discharge discovered during the remediation. There is, however, a separate discharge to Frongoch Stream from an old drainage culvert, which hasn't reduced since the capping and has accounted for 47% of the observed zinc load in the stream post-remediation.

Local rainfall in the period from July 2015 to February 2016 was 50% higher than the long-term average; this will have influenced metal loads within this period. Therefore a longer period of post-scheme water quality and flow monitoring is required to fully evaluate the effectiveness of the remediation scheme. Additionally, stream sediment samples have been collected for analysis of metal concentrations, and monitoring of fish and invertebrate populations is planned for summer 2016.

Table 1 *Water quality and flow data from Frongoch Adit, the final discharge from the remediated site and from Frongoch Stream downstream of the final discharge (data from July 2004 to March 2016).*

Sampling location	Time period	Flow (l/s)	Total Zn (µg/l)	Total Pb (µg/l)	Total Cd (µg/l)	Zn load (kg/day)	Pb load (kg/day)	Cd load (kg/day)
Frongoch Adit	Pre-diversion	90	5,500	360	10	36	2.6	0.08
	Post-diversion	17	13,800	670	23	20	1.0	0.03
Final discharge	Pre-Phase 2	7	115,600	6,010	257	24	3.0	0.05
	Post-Phase 2	9	49,500	1,980	88	17	2.0	0.03
Frongoch Stream	Pre-diversion	17	13,300	1,220	27	18	1.4	0.03
	Post-diversion	65	3,600	270	8	22	2.0	0.05
	Post-remediation	89	2,900	200	6	28	2.1	0.05

Conclusions & future work

This project demonstrates how water quality improvements can be achieved with low ongoing maintenance, whilst accommodating statutory designations and providing local biodiversity and landscape benefits. Further monitoring is however required to fully evaluate the improvements with regard to WFD objectives. Residual groundwater discharges and areas of uncapped mine waste are still preventing achievement of water quality targets in the receiving watercourses, but a reduction in flow from Frongoch Adit and isolation of other groundwater sources should make future treatment more feasible and cost-effective. Virtually all water from Frongoch Mine is now controlled via one surface water and two groundwater discharges, all of which have flow gauging weirs that provide ongoing research and development opportunities for institutions, innovators and regulators.

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Environmental Remediation of Abandoned Mines in Portugal – Balance of 15 Years of Activity and New Perspectives

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Abstract

Portugal has an important legacy of degraded former mining sites with clear environmental and public health impacts and safety problems. Since 2001 they are being subjected to environmental remediation operations by EDM- Empresa de Desenvolvimento Mineiro, S.A. under a legal regime of concession assigned by the Portuguese State and approved by the Decree-Law Nº 198-A/2001.

From an inventory of 175 abandoned mining areas, 61 of which in radioactive minerals and 114 of polymetallic massive sulphides mines, EDM had until 2015 remediated most of the old mines with more significant negative environmental and public health impacts, having concluded the remediation works in 90 mining areas and there were ongoing remediation works in 10 mining areas. An important effort has been made to achieve these results and the definition of a clear strategy for the remediation of the old mining areas as well as comprehensive set of characterization studies, plans, and detailed projects were key factors. Additionally a pre and post remediation environmental monitoring and maintenance is ongoing in the old mining areas that include the operation and maintenance of several mine water treatment plants.

This paper briefly presents EDM adopted model and strategy for the environmental remediation mission, the most representative actions concluded in Portuguese old mining sites remediation with different and adapted solutions for mining wastes confinement and mine water management, including active and passive treatment systems, and a balance of these fifteen years of intense activity, lessons learned and perspectives for the future.

Key words: Environmental remediation, abandoned mines, Portugal

Introduction

Portugal, although being a small country in the EU, has a high geological, geotectonic and geodynamic diversity which generated particular conditions concerning its geological resources and a relevant mining legacy, especially as a result of the post-industrial revolution period where mining activity grew and assumed a strong expression in Portugal. In result of this situation, a significant number of old abandoned mines can be found spread over all over Portugal, due the exploitation of basic and precious metals mainly in Alentejo (Iberian Pyrite Belt) and Trás-os-Montes, of tungsten and tin (North and Center of the country) and also of radium and uranium in the Beiras Granitic Region (Figure 1). The exploitation of radium and uranium minerals took place from the second decade until the end of the 20th century. This activity had importance at international level.

The main environmental impacts in old mines are related to polymetallic massive sulphide is acid mine drainage resulting from old mining works and wastes that generate chemical contamination in water and soil, that may also be contaminated by air dust dispersal. In the case of radioactive mines the main environmental impacts include acid mine drainage as a direct result from exploitation methods with static leaching and/or in situ and from ore concentrates production, but especially the radiological risks for public health and environment as a result of the presence of mining wastes and tailings.

Given the environmental hazards associated with many of these old legacy mines, and considering the evolution of the relevant mining and environmental legislation, namely the Environmental Framework Law (DL 11/87), the National Plan of Environment Policy (1995), the Mining Framework Law (DL 90/90) and the European Directives, the Portuguese Government has committed itself for its environmental remediation, and in 2001, entrusted to EDM – *Empresa de Desenvolvimento Mineiro*, SA, a state-owned company, the responsibility for the recovery of all degraded old mining sites under an exclusive concession contract approved by the Decree-Law nº 198-A/2001. The scope of the concession is very clear and it includes only "abandoned mines" and, considered as old and deteriorated mines that constitute a potential public health or environmental risk, requiring the State intervention, where the Polluter Pays Principle could not be applied.

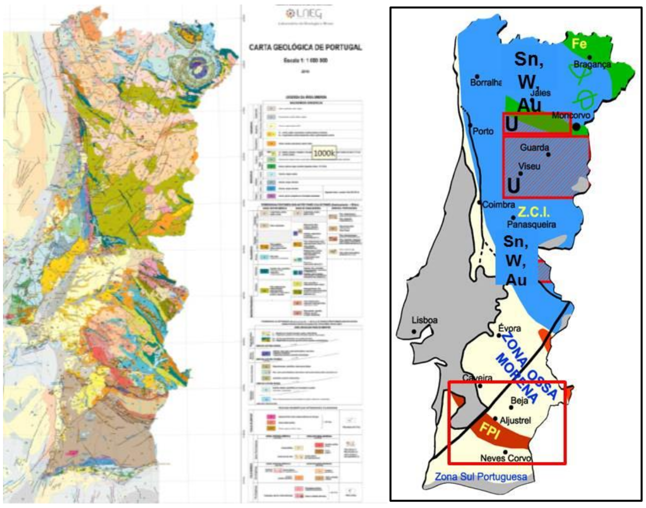

Figure 1 *Mainland Geologic Map of Portugal, 1:1000.000 (Ribeiro ML et al. 2010) and Metallogenic Portuguese Belts (EDM 2011).*

The objectives of the concession are to eliminate the risk factors for public health and safety resulting from old mining areas, rehabilitate the surrounding landscape and natural conditions of development in accordance with the previous or potential land uses in order to provide conditions for future use of reclaimed areas such as agricultural or forestry uses, tourist and cultural promotion, or another that promotes the community development, and to ensure the preservation of significant heritage of old mines, both economic and archaeological and the valorization of archaeological remains related to mining activity.

Intervention Strategy

EDM defined the strategy for the environmental remediation of the old mining areas (Figure 2), and started with the inventory and detailed characterization of abandoned and degraded old mining areas and the prioritization of environmental remediation interventions on the basis of technical and scientific analysis (Phase 1).

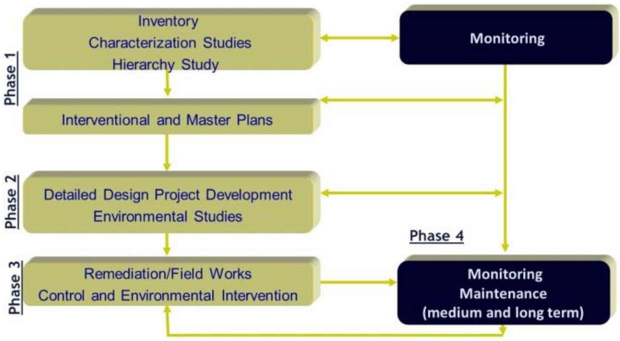

Figure 2 *EDM Strategy phasing for environmental remediation.*

Furthermore conditions were established for ensuring funding for the development of characterization studies, master plans, environmental studies and execution of projects that supported investment decisions and their priority (Phase 2). The phase 3 consisted in the realization of the remediation works and it is continuously on-going, and integrates for each area the adequate project management activities, the supervision of construction works including the health and safety, environmental and archaeological supervision. During all these phases and also after the environmental remediation works it is assured the monitoring of all relevant aspects such as soil, water, wastes, and air environments, as well as implemented a medium and long term maintenance plan.

In total EDM is responsible for the environmental rehabilitation of 175 abandoned mining areas identified in Portugal, 61 of which in radioactive minerals (more relevant are Urgeiriça, Cunha Baixa, Quinta do Bispo, Bica and Vale de Abrutiga) and 114 in polymetallic sulphides (more relevant are São Domingos, Aljustrel, Lousal, Caveira, Argozelo, Covas, Montesinho and Terramonte).

For all these mining areas EDM has performed a Base Characterization Study that included descriptive records, as location, concession date, excavation type, ore beneficiation steps, geomorfology, mining wastes, impacts and other relevant aspects.

In order to help define the priority of intervention in these mining areas EDM developed a Hierarchy Study for the Rehabilitation of Abandoned Mining Areas (Nero 2003), based in an Analytic Hierarchy Process that relied on three fundamental principles (decomposing, weighting and evaluation) of relevant aspects such as safety, environment, heritage, population and landscape.

Considering the specific risks and characteristics of radioactive ores, and also the remediation solutions, EDM classified the old mining areas in two groups: uranium and radium mining areas and polymetallic massive sulphide mining areas; for which had development Master Plans defining typified solutions in order to optimize the remediation works, subject however to further detailed design projects and adjusted solutions case by case in each mining area.

Methods / solutions

Common principles of actuation in the remediation of old mining areas consist in the elimination of risk factors associated with underground works and open pits, elimination or mitigation of the contamination source, typically through the adequate **confinement and sealing of mining wastes** *e.g.* waste rock, tailings, etc., ensuring also the physical stability of these waste deposits for the long term period, and in an adequate **mine water management** including the controlled water flooding of underground mines and open pits, the separation of clean waters from contaminated waters and ensuring the adequate treatment systems, either through passive or active treatment systems, and to guarantee a proper decommissioning and demolishing of degraded and unnecessary infrastructures and soil decontamination. In this paper we will briefly present some examples of solutions implemented with success in the environmental remediation of old abandoned mines sites by EDM in Portugal.

Confinement and sealing of mining wastes

For the confinement and sealing of radioactive mining wastes EDM designed a multilayer cover system (Figure 2) consisting of both geological and synthetic materials to be disposed over the surface of the tailings after previous geotechnical stabilization (Pereira *et al*. 2014; Pereira *et al*. 2004b; Janssens *et al*., 2006; EDM, 2008).

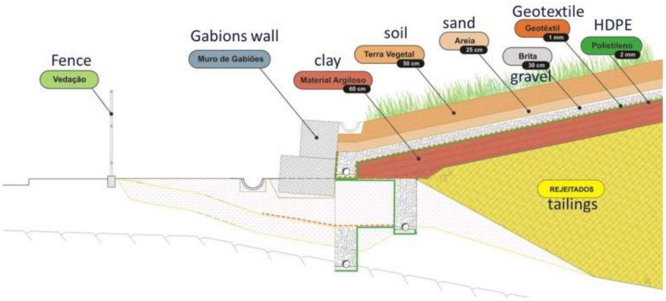

Figure 2 *Multilayer cover system for radioactive mining waste confinement.*

This solution is complemented with the construction of a peripheral concrete structure provided with surface and two deep drainage systems to separate surface run-off and contaminated seepage, and was firstly designed for Barragem Velha (Old Tailings Dam) at Urgeiriça Mining Area, where the radioactive tailings from the chemical treatment processment of the Radium and Uranium ore was disposed since 1951. This tailings dam was located over a former small valley containing a streamline with occasional water flow and occupied an area of 13 ha and with an estimated volume of 1.4 million m^3 of tailings very heterogeneous particularly in terms of radium (226Ra) concentration which varies from 3.4 to 52 kBq/kg (Pereira *et al*. 2004a,b). The depth is also very variable, ranging from a few meters to about 70 m. The taillings material was disposed directly over hercynian granites with variable degree of rock matrix alteration and fracturation. Apart from a small proportion of the uranium remaining from the uranium dynamic lixiviation extraction (around 10%), the sludge deposited in the tailings contains all the other radionuclides of the decay chain of this chemical element that can be mobilized by natural processes thus migrating into the environment (Barbosa *et al.* 2015). This solution of *insitu* confinement was selected due to the high amount of tailings here disposed for decades, and considering all aspects including the environmental impacts and costs of transportation, and therefore it was more advantageous compared to the creation a new disposal site with bottom and top cover sealing.

The effectiveness of the cover was estimated through numerical modeling by Pereira *et al*. (2004a) based on the RESRAD code, pointing to a negligible dose (less than 1 mSv/yr) to the nearby population after remediation in contrast with an average effective dose of 39 mSv/yr before the confinement based on the external radiation measurements.

The monitoring results after the conclusion of the remediation works proved the effectiveness of the solution, with very significant reduction in the superficial radiometry (Cintilometry, SPP2) from a maximum of 15.000 cps to 300 cps, and external radiation from a maximum of 7,5 mGy/h to 0,35 mGy/h (Figure 3), being the average effective dose less than 1 mSv/yr as predicted.

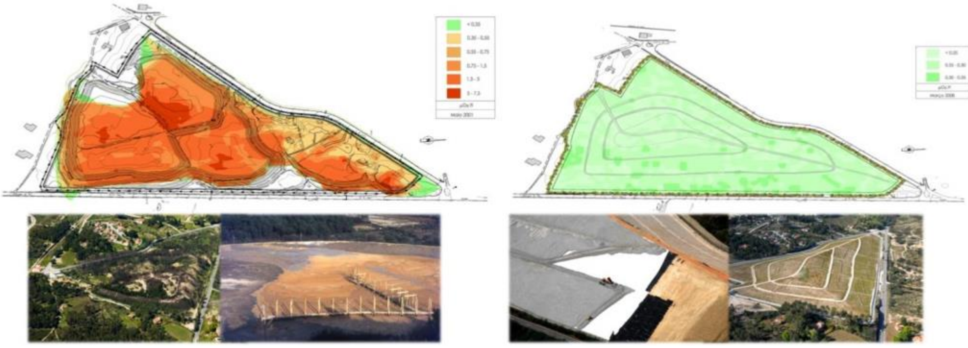

***Figure 3** External radiation results in Old Tailings Dam at Urgeiriça old mining area before and after the remediation works.*

EDM also implemented a set of radon probes at three different depths and layers namely in the tailings both below (2,4 m depth) and above the sealing cover (1,0 m depth) and also in the top-soil (0,2 m depth) for online monitoring of the radon gas concentration and emissions due to the proximity to Canas de Senhorim village. The results (Figure 4) proved that radon concentration measured at different levels of the cover of the Urgeiriça tailings is characterized by very different average values below, inside and above the multi-layer cover, showing that the sealing structure is performing as expected and effectively reducing surface radioactivity levels, although these concentrations also display very different temporal patterns and daily fluctuations (Barbosa SM *et al*. 2015).

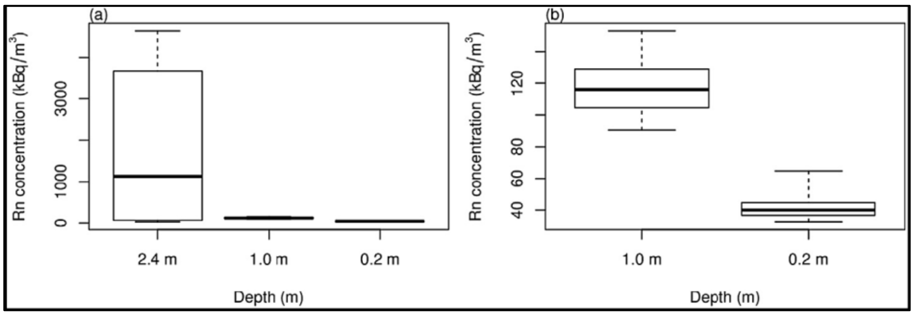

***Figure 4** Boxplots of the radon concentration values (left) measured at the 3 depths and (right) detailed view for the shallower measurements (Barbosa SM et al. 2015).*

In the case of polymetallic massive sulphide mining areas the waste confinement solutions had as main objectives to eliminate or avoid the acid mine drainage by reducing the water and air contact with the waste rock and tailings, as well as to reduce the air and water dispersion and contamination. Therefore the solutions consisted in the impermeabilization of these waste deposits with natural (clay) or artificial (HDPE Liners) layers and to ensure the adequate clean water drainage and diversion, like the old mining areas of Aljustrel which had a sealing with clay (Figure 5) and Lousal with a hybrid solution with HDPE liner and an asphalt cover to allow the future use of the area for parking of the railway station and mining museum (Figure 6). In particular, the selection of clay as solution for confinement should be used carefully as the type of clay and impermeabilization coefficient should be analyzed to ensure proper sealing, and only if this material is available near the mining area since the costs of transport of this material could easily turn this solution not feasible.

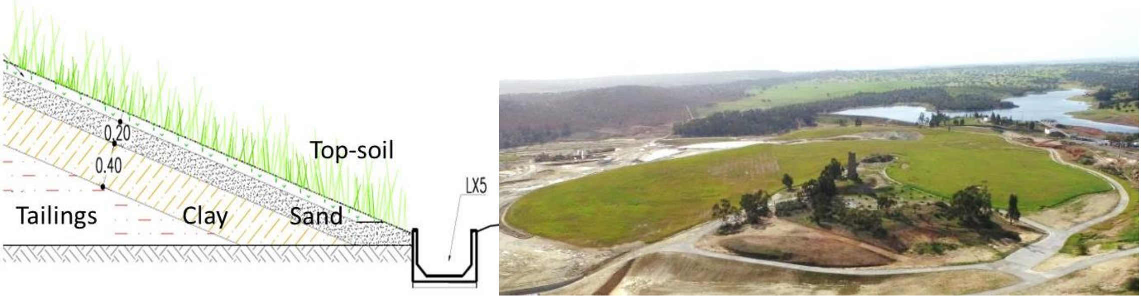

Figure 5 *Clay cover system in Aljustrel old mining area and photography after remediation works.*

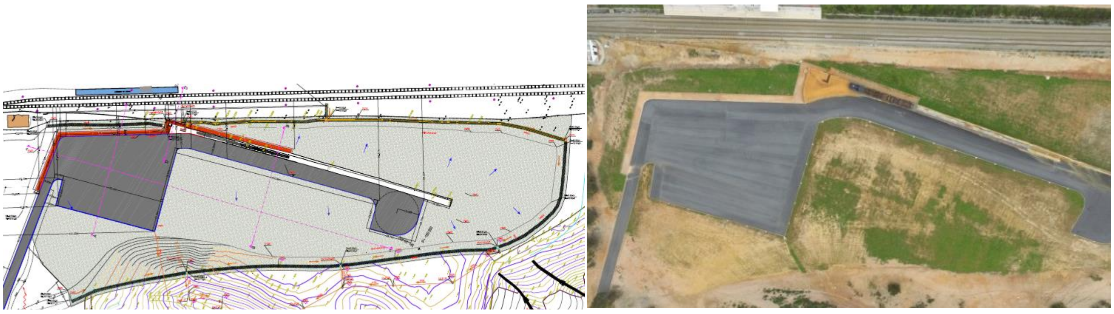

Figure 6 *HDPE and asphalt cover system in Lousal old mining area and photography after remediation works.*

These solutions are less complex than the multilayer cover system designed for the radioactive mining waste since the need to mitigate the radiological impacts, namely the gamma radiation attenuation and radon emissions is not present. However, they proved to be effective in the objective to avoid the entrance of rain water in the mining waste deposits and therefore contribute to drastically reduce the amount of acid mine water produced.

Mine water management

The mining wastes confinement has as one of the main objectives to prevent the contact of rainwater and runoff with the wastes to avoid the leachates generation. The confinement solutions should be complemented with clean water and leachate separate drainage systems, as presented in Figure 2. The clean water drainage systems have the objective to drain the rainwater and surface run-off within the mining area, and to divert the upstream hydrographic basin flows and streams to downstream the mining area avoiding the contact of the clean water with the mining wastes and the generation of high volumes of leachates and contaminated waters that will require treatment (Figure 7).

Figure 7 *Aljustrel cleanwater diversion channel and Vale d'Abrutiga surface run-off drainage system.*

The collection of leachates and other contaminated mine waters depends on the occurrence of these waters. In seepage waters or mine gallery drainage one solution is the construction of a wide barrier for collection and direct the flow towards treatment through open channel, eventually filled up with limestone (open limestone drains). However, to collect the percolated and subsurface contaminated waters it is necessary to construct subsurface drains that can also create a barrier for the propagation of the waters outside the boundaries of the mining waste area (peripheral subsurface drains). By adding limestone in these drains and ensuring the soil cap, the drain also functions as an *anoxic limestone drain* (ALS) (Figure 8).

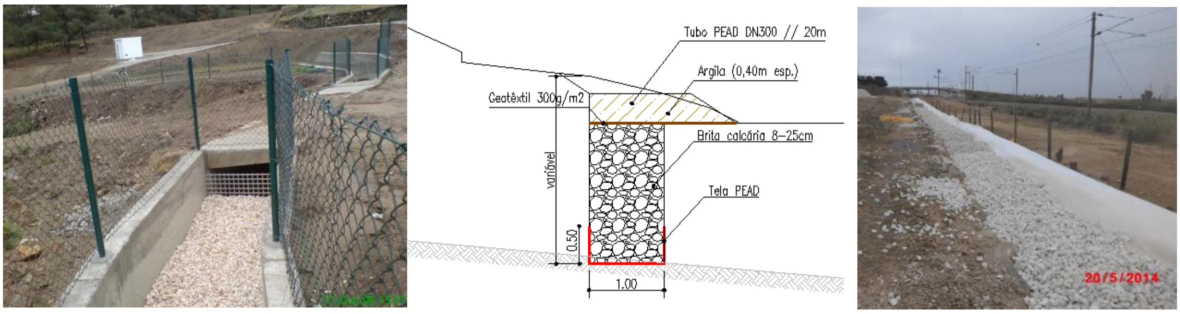

Figure 8 *Mine gallery open limestone drain (left) and anoxic limestone drain before soil cap(center and right).*

After collection, the contaminated waters are treated either recurring to active (ATS) or passive treatment systems (PTS). In 2015 EDM had treatment plants for uranium and radium contaminated water in Urgeiriça (ATS and PTS), Cunha Baixa (ATS and PTS), Quinta do Bispo, Castelejo, Bica (ATS and PTS), Vale da Abrutiga (ATS and PTS) and Prado Velho. In these cases the active treatment systems consist in adding lime milk or sodium hydroxide and barium chloride in a set of mixing tanks followed by sedimentation ponds/tanks (Figure 9).

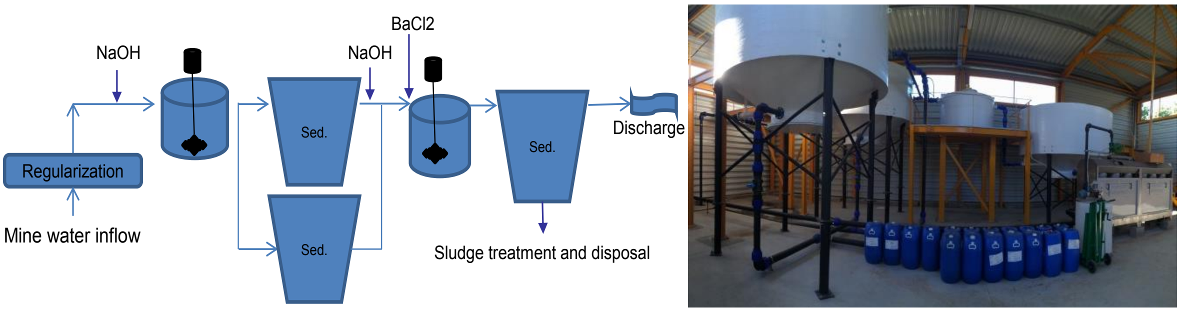

Figure 9 *Cunha Baixa active treatment process and photo.*

The discharge of treated mine water meets the regulatory standard limits for effluents discharge into watercourses, including the more restrictive limits the use for human consumption in the case of Ra-226. Manganese concentrations are still one gram per liter superior to the legal effluent discharge limit value of 2 mg/L, nevertheless this is not considered a relevant exceedance because of the mining framework of the area and background geochemical composition of groundwater's (Diamantino *et al.* 2016).

The passive treatment systems have some variations but in general include successive steps of aeration and or open limestone drains, sedimentation ponds, biological treatment (aerobic wetlands), and final filtration in limestone, barite and activated carbon, as shown in the example of Cunha Baixa passive treatment system (Figure 10).

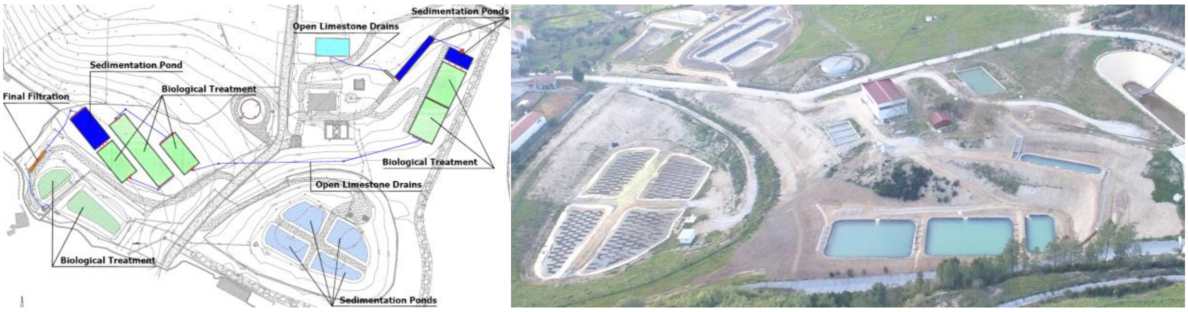

Figure 10 *Cunha Baixa passive treatment process and photo.*

In Polymetallic Massive Sulphide Old Mining Areas, affected by acid mine drainage (AMD), EDM currently has passive treatment systems in Lousal (Figure 11), Aljustrel, Jales, Terramonte and Argozelo, and backup active treatment systems in Lousal and Aljustrel. The passive treatment systems depend on the mining area and characteristics of the mine waters, however could include aeration channels, sedimentation ponds, alkaline leach beds and wetlands.

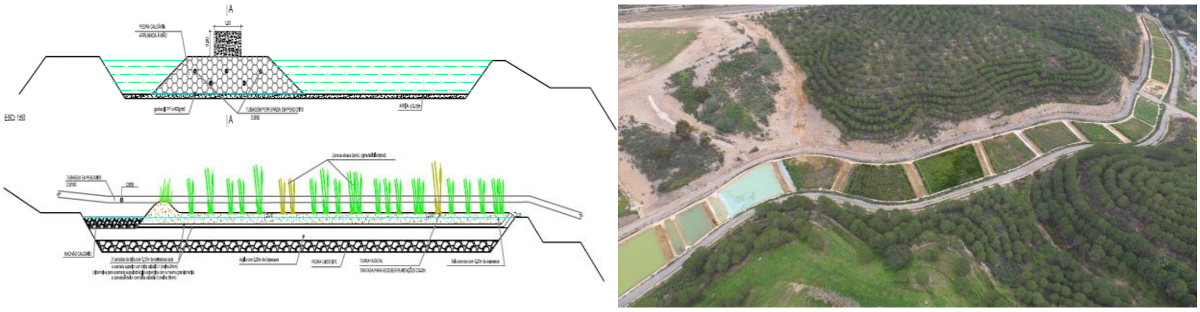

Figure 10 *Lousal passive treatment process with alkaline*

In case of passive treatment systems in general the most relevant regulatory limits is being complied, with some exceptions regarding iron and manganese. In case of Cunha Baixa and Lousal contaminants removal did not produced the excepted results and the existing passive system were recently improved and enhanced, and although the preliminary results are promising the period of operation is still not representative.

Conclusions and new perspectives

Since 2001 when the concession contract for the Environmental Remediation of Old Mining Areas was signed between the Portuguese State and EDM, 95 old mining areas were already recovered including most of the old mines with more significant negative environmental and public health impacts and the environmental liabilities.

Table 1 *Status of environmental remediation of the 175 old mining areas in Portugal in December 2015.*

Status	Polymetallic	Radioactive	Total
Concluded	61	34	95
Ongoing works	4	6	10
To be carried out	29	21	50
With constraints	20	0	20
Total	114	61	175

At the end of 2015 there were ongoing efforts to conclude the remediation of another 10 mining areas and there were 50 remaining areas with remediation works to be carried out until 2022, when the concession contract expires (Table 1). Overall, until 2015 a total of 86,4 million euros was invested in the remediation of old mining areas, 49,3 million euros in radioactive old mining areas and 37,2 in polymetallic massive sulphides old mining areas, and EDM estimates the need for around 89 million euros to conclude the remediation works in all old mining areas until 2022. Additionally, a post rehabilitation environmental monitoring and maintenance plan is ongoing in the old mining areas and should be continued after this period that could represent an annual expense of around 1,5 million euros.

The funding of this public service is ensured trough the royalties from Portuguese Mining Operators and EDM also benefited from significant co-funding from the European Cohesion Funds, which has been a critical factor for the realization of the implementation of the Old Mining Areas Remediation Plan in Portugal. Although the old mining areas represent a liability and a high cost in the environmental remediation, they can also be a source of income. In most of the 175 inventoried mining sites there are mining wastes that in light of the current rational of economic growth by the efficient use of the resources, should be regarded as secondary sources of raw materials.

A paradigm shift is needed allowing these wastes and mine waters to be considered not only as an environmental issue but mostly as possible stocks and sources of mineral raw materials. Given the current level of knowledge about the existing mining wastes in the Portuguese old mining areas, the first step to achieve this objective is the thorough characterization of the different mining waste deposits at each mine site, with particular emphasis on its particle size distribution and compositional features, and mine waters, including the demonstration that they can be reused. The mine sites already rehabilitated will have to be addressed without jeopardizing the interventions already undertaken. Only after a comprehensive analysis of the results to be obtained by such kind of approach it would be possible to separate the true wastes from residues and to search for new ways of reuse including the promotion of more powerful and environmentally friendly reprocessing technologies in order to recover additional by-products (Carvalho *et al.* 2016).

EDM is considering this new perspective not only in the on-going remediation projects, but also in the remediated mines, in order to assess the potential and feasibility for recovering value from old mining wastes and mine waters. It is also involved in international R&D projects to help new methods for extraction and exploration of secondary sources, like Project ENVIREE (ENVIronmentally friendly & efficient methods for extraction of REE from secondary sources), UNEXMIN (Autonomous Underwater Explorer for Flooded Mines) and VAMOS (Viable and Alternative Mine Operating System).

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Surface water monitoring in a mining impacted drainage basin with particular reference to bio-monitoring of protected species

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Abstract

The Weiße Elster river drains a watershed characterised by an intensive industrial use and the existence of historic as well as ongoing mining operations in Central Germany. Besides lignite mining major impacts result from uranium mining which was conducted between 1949 and 1990 in the watershed. Remediation of uranium mining legacies still requires the treatment of significant volumes of contaminated mine and seepage waters. The discharge of treated waters influences the hydrochemical conditions in the river system. The present monitoring includes the hydrochemical analysis of water and sediments in the small receiving streams close to the mining areas but also extends further into the Weiße Elster river. Limit values are not only to be met in the treated water outflow but also in the more distant river system. The controlled discharge of salinity and hardness proved to be a crucial element of the water management since the existing water treatment technology does not account for desalination. Changing flow conditions in the Weiße Elster river form a risk for the compliance with the limit values especially during periods of low flow. In addition to a number of other technical and management measures Wismut GmbH applied for a temporal increase of the limit value of hardness concentration in the Weiße Elster river. A higher limit value was granted but an additional biological monitoring was required due to the needs resulting from the Water Resources Act as well as the Habitat Directive. The relevant aspects, the methodology used and the main findings of the already conducted monitoring are outlined in the paper. According to the results of a 4-year monitoring period none of the indicator biota including benthic invertebrate fauna (i.e. mussels), fish (bitterling = *Rhodeus amarus*) and the green club-tailed dragonfly (*Ophiogomphus cecilia*) has been adversely affected.

Key words: Uranium mining remediation, surface water, biological and geochemical monitoring

Introduction

The Weiße Elster river drains a watershed of about 5,100 km² in Central Germany. It flows at a length of 257 km from the Elster mountains at the border of Czech Republic and Germany to the Saale river which is a tributary of the Elbe river. On its way it crosses areas which are densely populated, with intensive industrial and agricultural use as well as extensive historic and ongoing mining activities. While in its upper section the river has the characteristics of a stream in a mountainous area with respective flow velocities and river bed substrate (type 9.2 based on Annex II of the EU Water Framework Directive 2008/32/EC) the conditions change in the downstream area. Due to the reduced slope of the river bed the river was naturally characterized by meandering and braiding forming islands and oxbow lakes (type 17). For the respective river types a certain biocoenosis forms a general orientation as a target for a good condition of the surface water. Consequently, the present conditions are to be compared to this target. These natural flow conditions were partly destroyed in the river by flow regulation to use the fertile flood plains for agriculture and to realize open cast lignite mining during the past two centuries. Nevertheless, the natural conditions were conserved in sections of the river as e.g. a riparian forest around the town of Leipzig and therefore enjoy a distinct protection status.

In addition to extensive lignite extraction also large scale uranium mining and milling was conducted in the Weiße Elster watershed close to Ronneburg and Seelingstädt. The former joint Soviet-German

Wismut Company in charge of uranium mining and milling had started its activities in Eastern Germany right after the end of WW II. When uranium mining was stopped in 1990, about 50 % of the total mine extraction of about 230,000 metric tons of uranium had come from deep and open cast mines in the Ronneburg-Seelingstädt area. From 1960 to 1990 the vast majority of the mine production was processed at the Seelingstädt milling plant with a total output of 110,000 t of uranium (Barnekow et al. 2012). The residues were dumped in two tailings management facilities (TMF) located at former open cast mines close to the mill.

Remediation of the vast legacies is still ongoing at both sites. At Ronneburg the former open pit is already backfilled with about 131 million tonnes of mine waste rock which formerly had been dumped in 12 huge piles in the area. The presently realised flooding of the deep mine requires the management and treatment of contaminated mine waters which partly decant. However, for implementation of additional remediation measures the water level in the mine has to be managed in a given range to avoid uncontrolled outflow of the mine water to the surface.

At the Seelingstädt site stabilisation and contouring of the mill tailings is ongoing. The works at the Trünzig TMF are close to be finished. The regulation of the surface water discharge has to be finalised in the next years. The remediation of the Culmitzsch TMF containing about 85 million m³ of tailings is in progress with the present main focus on the stabilisation of the fine slime tailings at the bigger (61 million m³ tailings) of the two sub-impoundments. In addition to contaminated seepage, surface and ground waters from both sites a considerable volume of highly polluted pore waters have to be managed and treated during consolidation and contouring of the tailings.

Management of mine water discharge

At both remediation sites the treatment of collected waters is conducted by conventional lime precipitation which is effective for the removal of radioactive components such as U and accompanying metals from the water. On the other hand, salt concentrations especially sulphate, chloride and hardness are not decreased but even slightly increase due to the added lime and several pre- and post-treatment steps. The treated waters are discharged into small tributaries of the Weiße Elster river. The discharged maximum annual volume of treated mine waters reached 2.3 million m³ and 6.8 million m³ from Seelingstädt and Ronneburg, respectively. In the 5-year-periode between 2011 and 2015 the annual averages were 2.1 million m³ and 6.6 million m³. The composition of the mine waters to be treated at both remediation sites is characterised in Table 1 showing median and the 90percentile of the daily measured concentrations in 2015. While in the released treated water the annual average U-concentration is one order of magnitude lower (less than 0.1 mg/l) the released salt concentrations are at the same level as in Table 1.

***Table 1** Median/90Percentile concentration of selected parameters of treated water at remediation sites.*

Data for 2015	U [mg/l]	SO_4 [mg/l]	Cl [mg/l]	Ca [mg/l]	Mg [mg/l]	Hardness °German Hardness
Ronneburg (e-621)	0.74/0.81	2,660/2,870	59/62	458/496	409/447	160/171
Seelingstädt (E-306)	1.27/1.51	6,800/7,900	1,290/1,400	361/407	745/880	222/258

The permit for the discharge of the treated waters requires among others to meet limit values for hardness and salts in the Weiße Elster river downstream of the inflow of waters from the mining sites. Based on the composition of the mine waters especially hardness and sulphate are critical parameters, while metals and especially uranium concentrations are generally below the limit values set for the discharged treated waters due to the appropriate treatment technology.

Compared to the active mining period the remediation activities partly lead to a significantly increased quantity of contaminated waters resulting from mine water management and the water release during the consolidation of fine slime tailings. In this respect, remediation measures had to be delayed because certain limit values could not be met in considerable time periods even with a number of additional management measures as discussed in Metschies et al. (2013). One of the active management measures includes the amendment of the water discharge in the Weiße Elster river during periods of low flow from upstream storage reservoirs. This water management measure assures a minimum of 3.5 m³/s of river flow at an upstream stream gauge in Greiz used for management purposes. As a result the minimum discharge was temporarily increased on average by up to 50% compared to the unregulated conditions.

After reassuring that all technically feasible measures to manage the salt release were taken the permitting authority agreed to temporarily increase the limit of hardness to allow proceeding with the implementation of the remediation work. In the permitting procedure the relevant authorities of the Federal States of Saxony-Anhalt and Saxony responsible for the downstream river stretches were involved as well. In addition objections of individuals and legal entities exercising rights of water use downstream were considered. Special attention was paid to the aspect of environmental conservation. A number of areas protected by the EC Habitats Directive (Council Directive 92/43/EEC on the Conservation of natural habitats and of wild fauna and flora) are located downstream at the Weiße Elster river. Taking into account their special protection status WISMUT was required to plan and conduct a biological monitoring covering the protected areas as well as key species along about 100 km of the Weiße Elster river downstream the mining sites (Table 2).

Methods of applied biological monitoring

The procedures of the biological monitoring were agreed with the permitting authority and the involved nature conservation authorities responsible for various parts of the river downstream. The monitoring has to be conducted annually and focuses on fishes, mussels and macrozoobenthos including dragonflies.

Table 2 *Approximate distance of monitoring points from the river mouth and the mining sites.*

location	Distance from Weiße Elster river mouth [km]	Distance downstream the mining sites [km]	comment
Seelingstädt site	149	-15	Processing site
Ronneburg site	134	0	Mining site
e-423	124	10	Sampling point with MLC
5	82	52	Biological monitoring
6	81	53	Biological monitoring
9	70	64	Biological monitoring
7	65	69	Biological monitoring
1	48	86	Biological monitoring
2	46	88	Biological monitoring
3a+3b	27	107	Biological monitoring

The monitoring program has a specific focus on a cyprinid fish called bitterling (*Rhodeus amarus*) which is a short-lived species, generally surviving only for about five years. Their maximum size is 11 cm, but they are usually much shorter. The bitterling inhabits slow-flowing or standing waters, such as ponds, lakes, marshes, muddy and sandy pools as well as river backwaters requiring dense river bank vegetation. It has a remarkable reproduction strategy where parents transfer responsibility for the care of their young to various species of freshwater mussels. Therefore, the occurrence is restricted.

Rhodeus amarus is considered as endangered species being on the Red List of the Federal Republic of Germany (category 2: strongly endangered). It belongs to the species of annex II of the EC Habitats Directive which contain species whose core areas of their habitat are designated as Sites of Community Importance (SCIs) and are included in the Natura 2000 network. These sites must be managed in accordance with the ecological needs of the species.

Monitoring for fish is conducted by electrofishing of 300 to 500 m long river stretches at 3 locations each. The fish species are recorded and their number is counted and compared to an evaluation criterion based on Schnitter et al. (2006). This criterion relates the fish population to the area monitored and the distribution of the different age groups. Field work has to be conducted in late summer in order to also record juvenile individuals allowing to determine the state of preservation of the population.

At two locations in the river three transects of a total area of 12 m² each were monitored for the mussels needed for the reproduction of the bitterling. Here the river bottom is examined either using a rake, a sighting tube or screened by hand. At an additional location two riparian strips of 23 m² and 15 m² were intensively manually screened because of high turbidity and silt content of the river bed.

The evaluation of the macrozoobenthos considers organisms living at the bottom of the water column. Multi habitat sampling, collection by hand within the river water at relevant substrates such as stones, deadwood and detritus as well as brailer sampling along the beach vegetation are conducted to determine imagines. The abundance of the green club-tailed dragonfly (*Ophiogomphus cecilia*) is monitored at six locations along the river. In total 10 river stretches of 100 m length each are monitored along one or both river banks by collecting exuviae after the main emergence between mid of June and end of July at three dates and by visual observation of flying imagines. The determination of the state of preservation is done according to Schnitter et al. (2006). The determined status mainly depends on the number of exuviae counted in a section of 100 m or number of sections with more than five exuviae and is to a minor extend based on visual observation of imagines.

Monitoring results

Table 3 presents medians and 90 percentiles of daily measured sulphate, chloride and hardness concentrations at a key monitoring point in the Weiße Elster (e-423). The data are shown for time periods before and after the granted temporal increase of the hardness MCL. The data show the general tendency that the mean concentrations as well as the maximum concentrations increased between 2007-2011 and 2012-2015. While the existing limits for sulphate and chloride are still met the concentrations of hardness increased above the original limit value but remained well below the temporarily set limit of 24°dH. This also resulted from additional technical measures which were implemented to reduce the discharge of salt and hardness as outlined in Metschies et al. (2013).

***Table 3** Median/90 percentile concentration of parameters and resp. limits given in the Weiße Elster river (MCL ... Maximum concentration limit, °dH ... degrees German hardness).*

Time period	SO_4 [mg/l]	MCL SO_4 [mg/l]	Cl [mg/l]	MCL Cl [mg/l]	Hardness °dH	MCL Hardness °dH
2007 - 2011	168/312	450	77/109	250	13.1/19.0	19.0
2012 - 2015	217/322	450	88/115	250	15.0/19.7	24.0

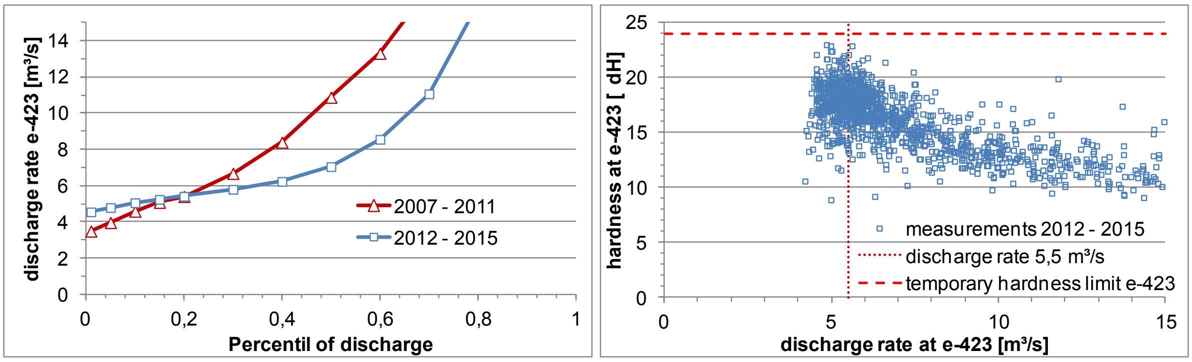

***Figure 1** Distribution of discharge before and after increase of limit (left) and the correlation of daily values of hardness measurements and discharge at measurement point e-423 in the Weiße Elster river.*

As shown in **Fehler! Verweisquelle konnte nicht gefunden werden.** the flow rate measured in the Weiße Elster river between 2012 and 2015 was in general considerably lower compared to the years before. Low discharge rates occurred significantly more often. The influence of the amendment of water from the upstream storage reservoirs is clearly visible for the discharge rates below 5.5 m³/s which account for more than 20% of the time period. Between 10 million m³ and 25 million m³ of water were added from the upstream storage reservoirs annually under low flow conditions affecting the concentrations of salt and hardness in the Weiße Elster river. As a consequence possible effects of the salt discharges on the biota in the downstream river could be significantly reduced. Except some days the measured hardness was less than 20 °dH in the monitored period (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

Table 4 summarises the results of the fish monitoring with respect to the occurrence of the bitterling (Figure 2). The number of bitterling was related to the area influenced by fishing to determine the status of preservation. An abundance of more than 2,500 individuals at 1 ha and a sufficient number of juveniles is considered as excellent (grade A).

***Table 4** Results of electrofishing at monitored location (grade A: excellent, B: good, C: average to bad).*

Location	Abundance of *Rhodeus amarus*	2012	2013	2014	2015
1	Number of individuals	363	398	274	229
	Individuals/ha	9,190	8,652	5,957	4,978
	grade	A	A	A	A
3b	Number of individuals	427	216	376	376
	Individuals/ha	9,085	4,596	8,000	13,383
	grade	A	A	A	A
9	Number of individuals	1	0	17	17
	Individuals/ha	33	0	486	171
	grade	C	C	C	C

***Figure 2** Bitterling (Rhodeus amarus) of 5 cm length.*

The duck mussel (*Anadonta anatina*) is an unpretentious species of freshwater mussel with a high adaptability. It becomes 10 to 15 years of age and has a length of up to 10 cm sometimes even 15 cm. It lives in standing as well as flowing waters but does not tolerate a strong oxygen depletion. **Fehler! Verweisquelle konnte nicht gefunden werden.** shows the number of mussels found along the monitored transects (3 times 12 m²) or beach stretches (23 m²). The transects had to be slightly moved at location 1 in 2014 because of high water level in the river and consequently worse conditions for the monitoring.

Table 5 *Results of mussel monitoring.*

Location	Area	Abundance of mussels	2012	2013	2014	2015
1	3 transects 12m^2 each	Vital individuals	12	26	35	32
		Distribution status	frequent	frequent	frequent	frequent
3b	Beach stretch 23 m^2 (2012: 15 m^2)	Vital individuals	8	12	15	39
		Distribution status	frequent	frequent	frequent	frequent
9	3 transects 12m^2 each	Vital individuals	82	49	62	37
		Distribution status	extensive	extensive	extensive	frequent

Evidence of sufficient juvenile mussels representing a good reproduction state is documented in the detailed monitoring results (Figure 3) where the mussels are grouped according to the length of the shells for location 1.

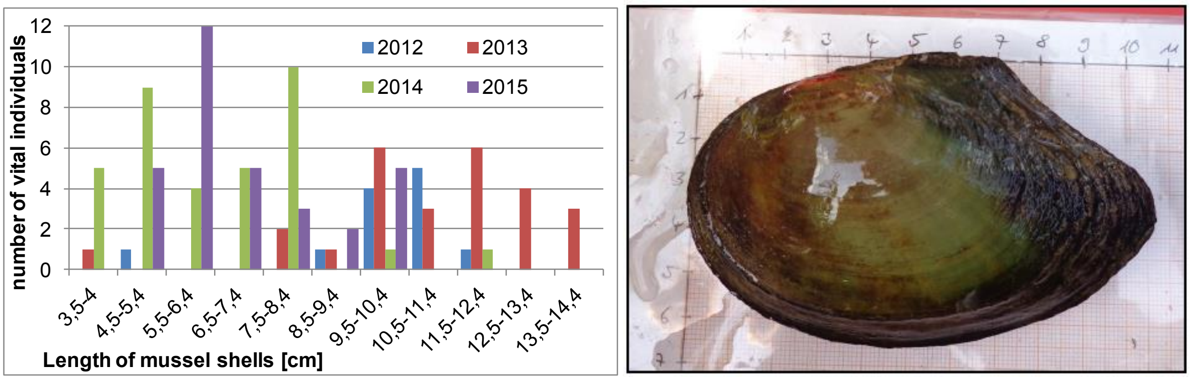

Figure 3 *Length distribution of the sampled mussels for the monitoring period at sampling location 1 (left) and a photograph of the Duck mussel (Anodonta anatina).*

Based on the monitoring of macrozoobenthos the ecological status of the water body is determined. The total number of individuals and of different taxa as well as the number of species of the orders commonly known as mayflies, stoneflies and caddisflies (*Ephemeroptera*, *Plecoptera Trichoptera* as EPT-taxa) are considered as important criteria. Table 6 shows the summarised results of the sampling campaigns during the past 4 years.

Table 6 *Results of macrozoobenthos monitoring.*

Location	Abundance of mussels	2012	2013	2014	2015
6	Number of taxa	44	24	49	50
	EPT-variety	21	16	22	23
	Ratio EPT/all individuals	48%	55%	44%	50%
7	Number of taxa	40	32	40	35
	EPT-variety	21	19	19	17
	Ratio EPT/taxa	51%	54%	49%	50%
2	Number of taxa	30	30	32	31
	EPT-variety	12	18	15	15
	Ratio EPT/taxa	41%	47%	43%	46%
3a	Number of taxa	28	25	24	33
	EPT-variety	3	5	3	9
	Ratio EPT/taxa	8%	7%	0%	22%

The registered evidence of the stonefly *Brachyptera braueri* was remarkable. This stonefly was considered nearly extinct but was found again in the last years in the federal states of Saxony and Thuringia. In March 2015 a number of larvae were found at the locations 6 and 7.

Between 100 and 200 exuviae of the green club-tailed dragonfly (*Ophiogomphus cecilia*) were found in each of four out of six locations during the annual three site visits between mid June and end of July throughout the monitoring period. At these locations the state of preservation of the dragonfly population is excellent without any significant trend. A good status was found for the location 7 with between 20 and 100 exuviae. At this location the river bank has eroded as well as rock stabilised bank sections. The natural eroded sections with overhanging roots represent a good dragonfly habitat. In contrast the remaining sections are less inhabited or even without any proof of evidence of the dragonflies. At one location (5) the results vary between average to bad and excellent with 2 exuviae (2012) and 98 (2013), respectively. At this location substantial morphodynamic relocations of the river bank material were found resulting in the great variability of the counted number of exuviae.

Discussion of results

In the Weiße Elster river at measurement point e-423 the increase of salt concentrations was on average about 15% compared to the time period before the temporal increase of the limit value for hardness. The elevated limit allowed a flexible water management at the remediation sites of Seelingstädt and Ronneburg ensuring an uninterrupted progress of the necessary physical works. In order to reduce the impact of the water discharge a number of additional technical measures had to be implemented in parallel. Nevertheless, changed chemical conditions were detected in the river at least during low flow conditions to which the monitored species have to adapt.

During the 4 year period 2012-2015 no change of the preservation status of the bitterling population was found in the monitored river stretches. The two areas with a high abundance of individuals are still in an excellent condition while at the other location only a small number of bitterling was encountered. This condition has been already reported for the first year of monitoring without influence of the higher hardness level. Structural deficits are the main reason for the limited fish population such as bank fixations and missing vegetation at the river banks.

The mussel population at the monitored transects was found to be frequent to extensive with a considerable amount of juveniles proving a stable population. Annual changes in the number of counted mussels can be attributed to different flow conditions which influence the effectiveness of the screening by hand. This could be the reason for the significant increase of the mussels counted at location 3b in 2015 (**Fehler! Verweisquelle konnte nicht gefunden werden.**). The variation of the number of mussels found at location 9 is mainly due to changes of the habitat conditions as a result of the flood in June 2013 when sediment such as sand bags was deposited in the river bed covering the mussels and forming a relevant migration obstacle.

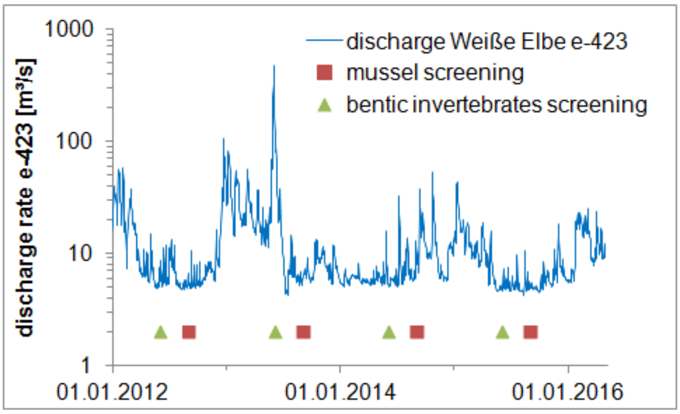

Figure 4 *Comparison of monitoring dates and flow in the Weiße Elster river (on logarithmic scale).*

The number of macrozoobenthos taxa was just slightly changing at the individual locations during the sampling campaigns in the past 4 years. The number of taxa was significantly lower at two locations only in 2013. This could be explained as an effect of an outstanding 2013 flood (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

A high percentage of the EPT-taxa among the collected individuals mark very good ecological conditions of the relevant river stretch. In near natural gravel dominated low land rivers (type 17) about 60% of all individuals belong to the EPT-taxa. At 3 out of 4 monitored locations this ratio was between 41% and 55% representing a good grade. This ratio varies from year to year in a range of up to 10% resulting from the variation of hydrological conditions. A bad to moderate rating is given based on the sampled macrozoobenthos at location 3a. This location is the farthest from the discharges at the WISMUT sites even downstream of the town of Leipzig. It is situated in an area with intensive agricultural use. The river has strong structural deficits in this stretch with silt deposition at the river bank and a lack of hard substrates as well as uniform flow conditions. There are also additional salt sources, such as sulphate resulting from mine water discharge from lignite open pits, which influence the chemical conditions in the Weiße Elster river.

Conclusions

The conducted biological monitoring along a 90 km long stretch of the Weiße Elster river gives a consistent long-term data base allowing to follow any systematic change of the biological conditions in the river. According to the results of a 4-year monitoring period none of the indicator biota including benthic invertebrates (i.e. mussels), fish (bitterling = *Rhodeus amarus*) and the green club-tailed dragonfly (*Ophiogomphus cecilia*) has been adversely affected while the average concentrations of salts and hardness increased. The increase of concentrations is more significant during the low flow conditions.

The average river discharge was more than 10% lower in the monitored 4-year period with more days with low flow conditions compared to the long-term average. The temporal increase of the hardness limit value in combination with additional water management measures such as the amendment of the river discharge at low flow conditions with water from the upstream storage reservoirs was important for an uninterrupted remediation work at the former mining and milling sites.

The biological monitoring shows that the fish and mussel populations are mostly in very good condition at the designated locations. No systematic influence of the temporarily increased limit value for hardness was found. Amount and number of taxa of the collected benthic invertebrates show a variability which is more likely to be caused by the annual changes of the discharge rather than the geochemical conditions. Flood events have a significant influence on the population due to the connected changes of the flow dynamics and the displacement of river bed substrate.

Biological monitoring will be continued at least till 2019 as long as the elevated hardness limit is in force. In the succeeding period additional activities would be necessary in case a deterioration of the monitored biological condition will be reported as an effect of the increased hardness.

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Innovative monitoring measures in the phase of post-mining

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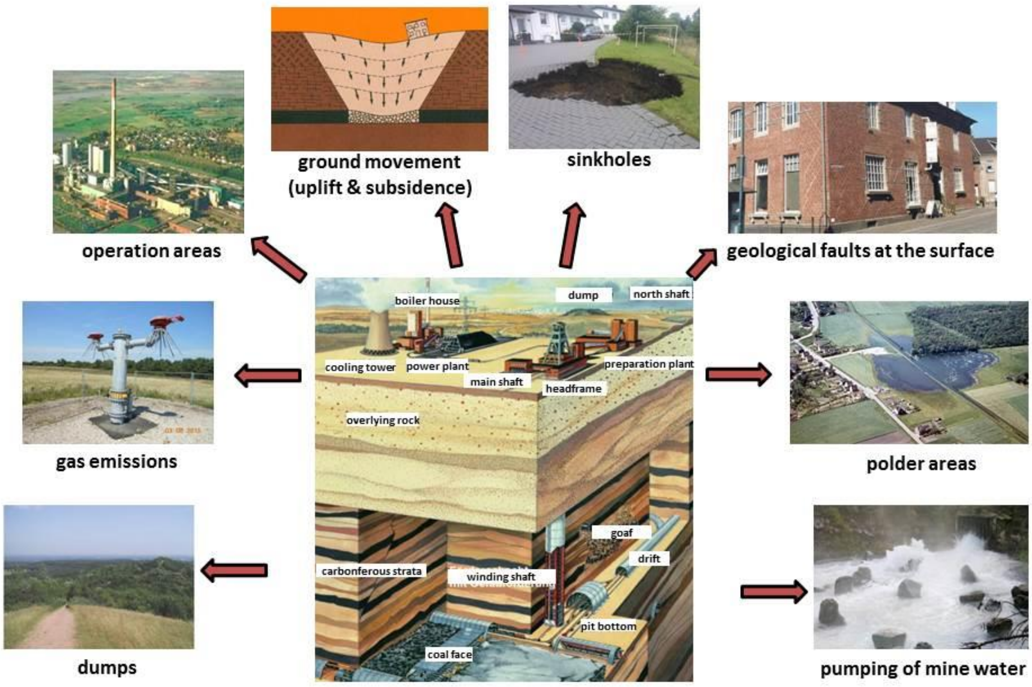
Abstract

Mining activities often influence huge areas, which can only be observed efficiently with remote sensing methods. Recently the European Programme of Earth Observation – called Copernicus – began to offer the opportunity to pursue this monitoring with innovative attempts in the production phase as well as in the post-mining phase. The combination of spatial data gained from satellite-supported sensors allows a precise verification of mining-induced environmental impacts with high resolution in time and space. This paper describes early experiences with innovative monitoring measures and discusses the perspectives of a sustainable mining process.

Key words: Ground movement, mine water, environmental impact, Copernicus programme

Introduction

Mining processes worldwide are a subject of a life cycle that begins with granting mining rights and licenses, then continues with the exploration and production stages, and ends with the closure of the mine. What follows is the stage of post-mining which stretches over a very long period of time depending on the complexity of the previous mining activities.



Action fields connected to post-mining (clockwise from bottom left): 1.) THGA, 2.) THGA, 3.) Boese & Farrenkopf, 4.) Kratzsch, 5.) DMT, 6.) Baglikow, 7.) EGLV, 8.) city of Bochum, 9.) GvSt

***Figure 1** Action fields connected to post-mining*

The challenges of post-mining involve factors of the environment, structural change, society and economy (Figure 1). In summary, we are facing impact on the elements of water, soil and air: the drainage of mine water affects the hydrochemistry of the receiving waters; shaft constructions, mining works close to the surface and large-scale underground cavities can cause instabilities at the ground surface; the air pathway at coal heaps and settling ponds is potentially polluted by dusting.

Such problems are international problems. They also encompass the conversion of former mine works surfaces, funding of the withdrawal and a successful management of structural change in the mining regions. In many cases, the challenges mentioned have already occurred during the production stage (Melchers et al. 2015).

Sustainable management of post-mining can only be successful if the future closure of a mine is already envisaged when planning mining activities. To achieve this, monitoring of the mining environment and the mining impact on its surroundings is required. The centre of the monitoring process is the element of water as this element is continuously changed in its mineralisation by the mining water drainage. Thus, the water bodies affected are facing changes in their plant and animal life. Ground movements at the surface lead to changes in the depth to water table and thus to changes in the vegetation. Pumping measures to keep open-pit mines dry have a similar effect.

Now, in Germany, the responsibility of the last mining company for how to cope with the closure and post-mining phases is clearly defined by German mining law and by rulings of our supreme court. But we can see that other nations too have developed an awareness of the necessity to properly organise the mining heritage and the opportunities and risks that emerge from that.

Such a responsible management with the opportunities and risks of (post-)mining requires a comprehensive understanding of the relevant processes where possible. In science and technology, it is common practice to observe, to measure, to develop models and to later compare the actual situation to the model; based on that, the models can and will be revised and improved.

The term monitoring has been established for such regulated cycles, not only in technology. Referring to the initial situation described, the question arises what mining objects and activities are concerned, what is their impact on the environment and what potential observation procedures can be applied.

A typical specific feature of mining processes is the fact that they eat up and impact large areas and that they are operated over long periods of time. Contrary to that, there are certain processes that happen on a small scale and in a short period of time. One example of such local impacts are the discontinuity zones at tectonic faults or subsidence at shaft constructions. The latter ones, looking at the speed at which they occurred, are similar to e.g. the breaks of dams at tailing lakes. Consequently, we need to search for methods and combine such methods that achieve a high score and reliability regarding the process to be monitored.

Copernicus Programme

At this point now, the space strategy of Germany’s federal government issued in 2010 gains new impetus. This strategy states explicitly that space travel has become an essential instrument for business, science, politics and society at large. Special emphasis is placed on the importance space travel has for innovation, growth, the job market, standard of living and environmental protection. One example of how this strategy is implemented is the Copernicus Programme launched by the European Union and the European Space Agency (ESA). Copernicus provides an up-to-date and high-performing infrastructure for earth observation and geo-information services. This project aims at supplying high-resolution data of remote sensing for both space and time. The Copernicus Programme provides free environmental data to its users.

Copernicus has seen the development of the Copernicus Sentinels – seven satellite missions that were especially developed for this programme and that monitor space. They are at the heart of the space component (Figure 2). The earth observation satellite Sentinel 1A has been in the orbit since April 2014 and supplies data on ground movements and parameters of soil physics. In June 2015 Sentinel 2A was launched according to schedule; this satellite is equipped with a multi-spectral sensor that generates images of the land surface. These images are used to analyse land coverage and land use. Sentinel 3 A has been in its orbit since February 2016; it carries a number of instruments to observe the surfaces of land mass and oceans.

Figure 2 *Sentinel 1A and Sentinel 2A (© ESA).*

The Sentinel satellites move in polar orbits at a height of approximately 700-800 km. Their observations cover nearly every point on the Earth's surface every five days. In their final stage, the satellites are supposed to be used in pairs. The Copernicus Programme is aimed at reliability and sustainability. Until 2018, another nine satellites are going to be launched and plans have already began to continue this programme far beyond the year 2027.

One major topic in this context is of course "Big Data". Indeed, the Sentinel satellites generate gigantic amounts of data that have to be processed, provided to users and, in particular, stored for a long period of time. By 2018 alone, the data volume will have risen to approx. 18 petabytes.

Together with EFTAS and other partners, the Research Institute of Post-Mining works on the use of satellite data for remote sensing and for monitoring actual processes of post-mining. The focus lies on the following aspects: the hydro-chemical balance of lakes and rivers; the ground water level; the land use; the land coverage, and the ground movements. Regarding the potential that is offered by the Copernicus Programme and the reliability of the data supply, monitoring can be innovated by linking the information generated by the satellite-supported sensors with terrestrial expertise, something that we call the in-situ component. This process can help to mitigate the risks of post-mining and to strengthen its opportunities, for example, providing new use and value to the old mining infrastructure to generate renewable energies.

Monitoring

As part of an ongoing research project, the Research Institute of Post-Mining is currently compiling an extensive catalogue of which monitoring methods are currently available for previous and new mining activities. Another objective is to utilise published information to describe how those individual methods can be used and how efficient they are. As a second step, selected methods shall be tested on practical examples. The third phase sees the development of recommendations for the selection and appropriate combination of such methods to meet specific requirements.

The Space Component

Now, which options are provided and what can we actually expect from those data that the satellite-supported earth observation provides us with?

The following examples are extracted from the R&D project GMES4Mining (www.gmes4mining.de) They demonstrate the potential of Copernicus for the monitoring of mining-induced environmental impacts.

The study site Kirchheller Heide, a heath located in the northern Part of the Ruhr area, was used in GMES4Mining to develop change detection methods for water bodies and soil moisture due to mining-related ground movement.

Mine-related flooding can be evaluated either directly by monitoring changes in water distribution or indirectly by observing changes in vegetation provoked by changes in soil moisture and water emergence. The sudden emergence of water in surface in a relative short time generates a unique pattern in the surrounding vegetation that can help in discriminating mine-related flooded areas from other types of water bodies. This information cannot be retrieved from the simple observation of changes in water distribution (Garcia Millan et al. 2014).

GMES4Mining evaluated the effects of emerging waters in vegetation. Plants around mine-related flooded areas often simply die, and rings of trees in different stages of decay can be observed (Figure 3)

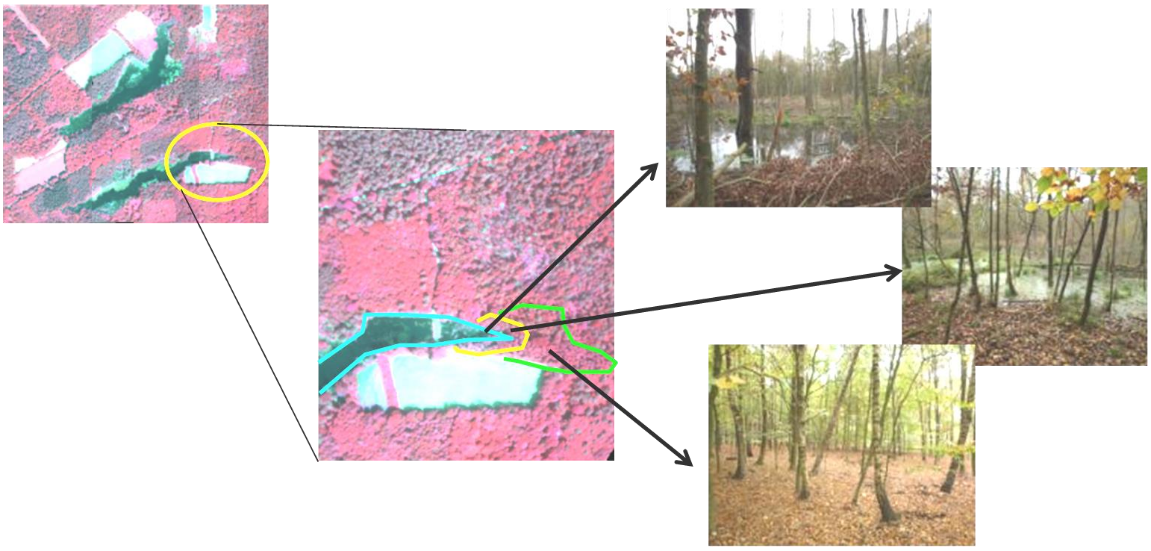


Figure 3 *Flooding stages in Kirchheller Heide. AISA-Eagle airborne sensor infrared composition. Photos taken in October 2012.*

Different stages of vegetation damage can be clearly differentiated by analysis of the hyperspectral dataset of the AISA-Eagle sensor (Figure 4). Nevertheless, an expensive aerial flight campaign can be replaced by the Copernicus Sentinel 2 mission data, which have been available free of charge since 2015. The vertical lines in Figure 4 represent the relevant infrared bands of Sentinel 2.

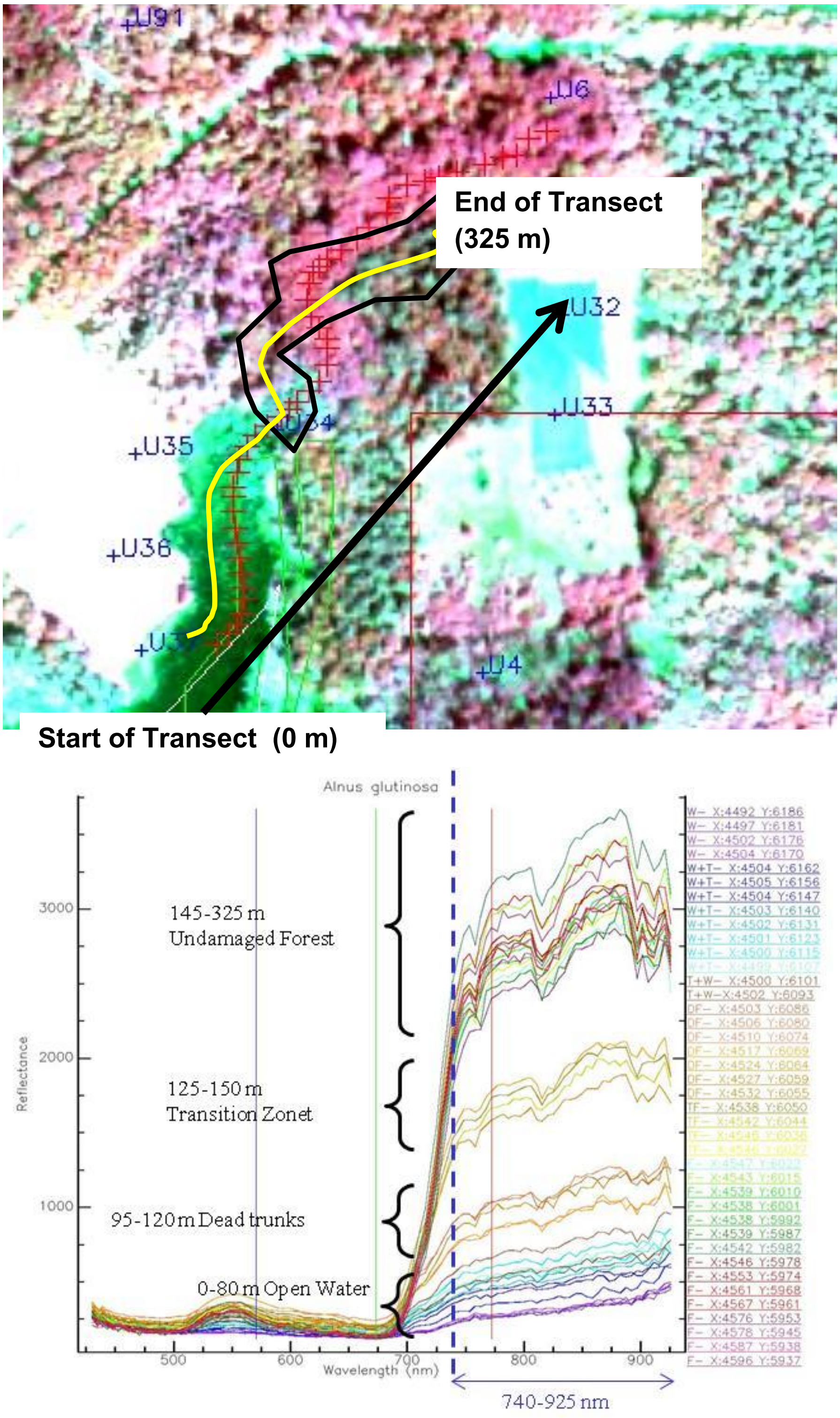


Figure 4 *Vegetation damage transect at study site Kirchheller Heide ranging from open water body to undamaged forest. AISA-Eagle airborne sensor data as graphs and Sentinel 2 bands as vertical lines.*

In addition to the analysis of vegetation damages, change detection of open water bodies can also be carried out with the help of Copernicus data. Water masks calculated with low albedo and using a threshold based on the data histogram can be summed up together in order to detect water bodies that experienced changes during the monitoring period. In low albedo water masks, water bodies are represented by a value of one, and everything else by a value of zero. Therefore, water bodies in this accumulated low albedo raster are represented by values different to zero. Water bodies which did not experience changes in the given time frame, independently of their nature (natural or human-made;

rivers, ports, lakes, etc.), present the maximum value (value 9 in Figure 5) and can be discarded. Water bodies that changed (including mine-related flooded areas) are represented in the intermediate values of Figure 5. The result of this exploration (accumulated low albedo masks) highlights not only mine-related flooding, but can be evaluated by experts in order to decide which areas are potential mine-related flooded areas and to discard other events (i.e. enlargement of a port, change of river beds).

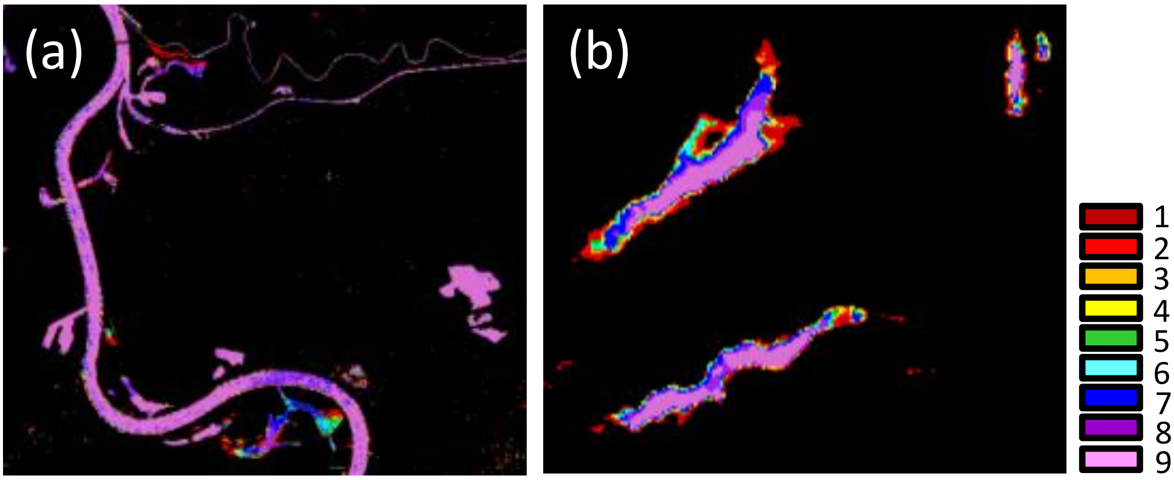


Figure 5 *Results of the change detection using nine RapidEye images between April 2009 and September 2012 for the Ruhr Valley, Germany (a). Known flooded area in Kirchheller Heide (b).*

Mining activities do cause ground movement. The use of satellite-supported remote sensing methods allows implementing monitoring of such ground movements without local installations being necessary. Since the TerraSAR-X radar satellites were launched in 2007, the ground resolution has been reduced to less than 1m.

Subsidences that are determined by radar interferometry receive the abbreviation PSInSAR. In urban areas, a sufficient number of reflectors, known as Persistent Scatterers (PS), are available. In rural regions, artificial radar reflectors, for example corner reflectors, can be erected.

Radar interferometry is an appropriate option for monitoring large-scale surfaces. As recent evaluations have shown, an accuracy of +/-1.5 mm can be assumed for subsidence/settlement monitoring of buildings and landscape formations where TerraSAR-X data are used.

Ground movement monitoring of larger areas, e.g. the entire Ruhr area, at high temporal frequencies is an option, not at least because of the higher intake capacity of the Copernicus radar mission Sentinel 1, which will enable a repeat rate of 1-5 days for radar interferometric measurements relying on two satellites of identical construction; the starting date is scheduled for mid-2016.

The In-situ Component

The Copernicus Programme provides a definition of in situ that is wider than that of other contexts. Here, the in-situ component refers to observation systems that are not operated in space.

Such systems are, for example, the following:

- Surveying results of geodesy and mine-surveying
- Air-based remote sensing instruments
- Site inspection
- Photography and photogrammetry
- Meteorological measuring facilities
- Probes at weather balloons
- Measuring buoys, stream gauging devices

Likewise, information products that are derived from such observations are part of the in-situ component. Those include, for example:

- Digital topographic maps
- Digital elevation models
- Ortho-photos
- Road networks
- Topical maps (e.g. forest areas, settlements, water bodies)
- Mining charts

The in-situ component is decisively shaped by the expertise of the specialists involved. The transparency of the available data is of importance, too. In this context, the information platforms of geo-data infrastructure play a special part. One example to be referred to here is the GEOportal.NRW. This platform allows all users simple research and visualisation of the geo-basis and specialist geo-data provided by the State Administration of North Rhine-Westphalia and also accommodates a specialist portal called "Hazardous underground potentials". This portal provides information on the spread of underground hazards that are caused by geological and mining factors.

Outlook

The Research Institute of Post-Mining at TH Georg Agricola in Bochum was founded as an initiative of the RAG Stiftung, a foundation set up by the legal successor of the German mining companies, RAG. The foundation also endowed a professorship to support both the research institute and the master study programme "Geo-Engineering and Post-Mining" (Melchers & Goerke-Mallet, 2015).

Against the background of the developments in the subsidised German hard-coal mining sector, the RAG Stiftung pursues the aim to ensure the qualification and availability of specialists who are needed to manage the perpetual tasks that mining has left us. Moreover, intensive work and research need to be done at the knowledge base of post-mining.

Mining processes help to supply people with resources – in other words, mining is as old as humankind itself. Facing the development of the world's population and of technological advancement there will be mining done in future around the world. Whereas the operation of any underground or opencast mine is necessarily time-bound, the impact the activities have on the environment can be of a much longer time period or even infinite.

Thus, it needs to be our aim to organise the post-mining process of former and current mine activities in an environmentally acceptable manner. The knowledge of how such mining processes impact the environment will enable us to plan, monitor and control processes so that they will become more and more sustainable.

In this context, monitoring is of particular importance. Only high-performance monitoring methods allow for a comprehensive understanding of processes and systems. Today, innumerable methods are available for observing mining facilities and operations as well as the environmental impact of those. Their efficiency has to be tested and developed further time and again. New methods have to be assessed for their applicability in (post-)mining. At the moment, this requirement holds especially true for the enormous potential that satellite-supported earth observation encompasses.

As initial examinations have shown, the data available from the Copernicus Programme can be put to value: the monitoring of ground movements caused by landslides, sinkholes, subsidence or fluctuations of (mine) water levels is almost ready for practical use. Changes in the depth to water tables and their impact on vegetation can also be observed and interpreted.

What needs to be done now is to purposefully bundle the numerous monitoring measures regarding the individual issues to be tackled and to combine those measures with the anthropogenic expertise: that is exactly what our innovative approach will focus on.

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Implementation of the Rehabilitation Operational Strategy for the flooded Opencast Mine Tamnava-West Field

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Abstract

Floods of opencast mines are relatively rare, but are more and more likely with changes in climatic conditions, when special and additional measures should be taken for the protection of mines against surface water. In the recent past, some of the coal opencast mines were flooded worldwide. It required, on average, about two years to reactivate these mines. In May 2014, catastrophic floods hit Serbia and the majority of the Kolubara coal basin. On that occasion, the largest opencast mine in this basin, Tamnava-West Field, was completely flooded with about 190 million m^3 of water, along with all continuous systems for production.

In order to repair the active opencast mine Tamnava-West Field completely, and to return it to the designed operations, early in June, just a fortnight after the floods, the authors have assembled an expert team who elaborated a plan for the rehabilitation of these opencast mines against consequences of the flooded waters. The expert team defined *Rehabilitation Strategy,* i.e. a scheduled document covering a wide range of synchronized and manageable processes and activities on the project for implementation of rehabilitation on this opencast mine.

Strategic objectives were implemented while respecting the rules of the profession and the world's best practice in realization of similar projects, with maximum consideration of the opencast mine overall reliability, as well as measures to protect the environment and ecology in general. Established strategic objectives are mainly implemented on schedule, with minor variations in investments realization. This project on the opencast mine Tamnava-West Field reconstruction presents a good example on how to react in an emergency, like this flood. The rehabilitation project foresees all the necessary activities, its scope and implementation dynamics in function for the safe rehabilitation by dewatering of the flooded mine, and reliable continuation of mining.

Key words: dewatering, rehabilitation, reliability, ecology, risks

Introduction

The largest producer of coal in the Mining Basin Kolubara is the opencast mine Tamnava-West Field. From the total of 30.7 million tons of coal produced in 2013, this mine has produced a record of 14.6 million of tons, which is 47% of the total production of the Kolubara basin. Along with all the produced coal, 33 million m^3 of overburden was excavated as well. Achieved production was implemented by nine continuous systems, from which eight are with bucket wheel excavators and one with a bucket chain excavator. According to the provided coal production information, opencast mine Tamnava-West Field is essential for the power generation in thermal power plant Nikola Tesla and overall energy stability in the country.

In mid-May 2014, the main parts of central and western Serbia were affected by catastrophic floods. These floods especially affected the western part of the Kolubara basin, where the Tamnava-West Field opencast mine is located. The opencast mine (OCM) was completely flooded, along with all continuous systems for production (Fig. 1).

Figure 1 *Flooded opencast mine Tamnava-West Field, view from the north and the south.*

Previous preliminary analysis show the following approximate flooded situation in the opencast mine Tamnava-West Field:

- Elevation of water table: 76.5 m
- Elevation of the deepest part of created lake: 10.2 m
- Surface of water table: 7,445,428 m^2
- Area of the opencast mine flooded part: 7,513,006 m^2
- Volume of the opencast mine flooded part: 190,586,345 m^3

The established expert team has developed an operational strategy as a planning document for the rehabilitation of the flooded opencast mine Tamnava-West Field. General objective of this document was to provide reliable and real dynamics for the gradual achievement of the designed production capacity in the opencast mine Tamnava-West Field. Strategic objectives of the project were, based on the analysis, to define the following:

- Optimal rehabilitation plan for the opencast mine in the function of equipment operation reliability and stability of the opencast mine;
- Dewatering dynamic of flooded opencast mine in the function of operating and final slopes stability, internal dumps and equipment and environmental protection;
- Dynamics of the opencast mine protection against surface water (river flows, retention, etc.);
- Dynamic, technology and equipment for mining on the flooded opencast mine.

Operational strategy for the opencast mine Tamnava-West Field rehabilitation

Project implementation of the rehabilitation strategy refers to a plan for the opencast mine rehabilitation (Pavlovic 2014), based on the previously conducted analysis on:

- Geometry of the flooded opencast mine, the internal dump site and location of the equipment under water;
- Stability of the opencast mine and internal dump site in the function of the flooded opencast mine dewatering dynamics;
- Stability of the opencast mine and internal dump site in the function of the mining technology and dynamics;
- Condition of river flows, retention basins and water reservoirs in the affected area on the opencast mine;
- The risk of coal mining continuation in the function of the opencast mine geometry, stability, dewatering and quality of pumped water;
- Direct and indirect damages on the opencast mine.

Since the opencast mine was completely flooded, for more reliable *situational analysis* it was necessary to perform mine, dump site and equipment geodetic underwater survey, as well as geodetic survey of river flows, retention basins and water reservoirs in the impact zone on the opencast mine, followed by an analysis of the stability of the flooded opencast mine and inside dump as well as deposit hydrodynamic model, at the end (Drebenstedt 2014).

SWOT analysis included the following factors:

- *Threats from the external environment:* climatic conditions during rehabilitation, impact on the environment and ecology in general, and funds.

- *Strong points of the project:* continuation of safe, reliable, efficient and effective production in the opencast mine and defined and manageable system of the opencast mine rehabilitation.
- *Weak points of the project*: insufficient reliability of the existing database for project development.

Risk assessment of project for the opencast mine Tamnava-West Field rehabilitation

Considering the importance of the opencast mine reconstruction project for the overall energy stability of the country, the high level of investments required for rehabilitation and the degree of uncertainties related to the project, the expert team has conducted an *ad-hock* risk analysis of the project (Pavlovic 2014).

Risk analysis covered the following aspects:

- Personnel;
- Mine and equipment:
    - Pumping of water and the amount of mud in the mine
    - Degree of machinery damaged and caused by flood and funds for repair
    - Preparation for mines rehabilitation;
- Environment Protection.

The risk analysis is based on the parameters shown in Table 1.

Table 1 *Risk Assessment.*

Result	**Consequences**			**Probability of an event - result**				
	P	**A**	**E**	**1**	**2**	**5**	**10**	**20**
	Personnel	**Mine and equipment**	**Environment protection**	**Hardly possible** (< 1 in 1000)	**Unlikely** very unlikely (1 in 100 > 1 in 1000)	**Probably** unusual but possible (1 in 10 > 1 in 100)	**Very likely** (certain > 1 in 10 cases)	**Almost certainly**
1	Without injury	No damage	No effects	(5) Low	(10) Low	(20) Low	(25) Medium	(50) Medium
2	Easy injuries	Small damages (< 10.000.000 €)	Smooth effects	(10) Low	(20) Low	(40) Medium	(50) Medium	(100) High
5	Lower injuries	Medium damages (10-50.000.000 €)	Low effects	(25) Low	(50) Medium	(60) Medium	(75) High	(250) Extreme
10	Major injuries	Serious damaged (50-100,000,000 €)	Localized effect	(50) Medium	(100) Medium	(200) High	(250) Extreme	(500) Extreme
20	Permanent disability	Very serious damaged (80-200,000,000 €)	Main effect	(100) Medium	(200) High	(400) Extreme	(500) Extreme	(1000) Extreme
40	Multiple deaths	Catastrophic damage (> 200,000,000 €)	Massive effect	(200) High	(400) Extreme	(800) Extreme	(1000) Extreme	(2000) Extreme

The following important results and conclusions of the risk analysis are provided:

Personnel

Slope stability. In case of slopes sliding, there can be fatal injuries. *Probability of the event - unlikely 40/2*.

Mine and equipment

Slope stability. If water pumping is not effective in accordance with the soil-mechanical characteristics of the material, it can lead to the collapse of slopes. In this case, three possible damages of equipment may occur:

- Complete dump site sliding with damage of the majority of equipment. The mine would be without production for minimum two years. Direct damage to the equipment and the indirect damage caused by the import of electricity are very high. *The risk is in the field 40/5, and the estimated damage is €800 million.*
- Partly dump site sliding (lowest benches - interburden). In this case, one spreader, one dragline and conveyor line (3 km) with two drive stations may be destroyed. *The risk is in the field 5/10, and the estimated additional damage is €75 million.*
- Partially sliding of excavated bench. In this case, bucket wheel excavator SchRs 1600 and part of the conveyor route with one drive station may be damaged. The damage is due to a complete refurbishment of the excavator, with longer downtime of excavation at overburden, as well as indirect damage by electricity imports. *The risk is in the field 10/10, and the estimated damage is €250 million.*

The amount of mud in the mine. If there is a lot of mud in the mine, and if it cannot be removed by pumping water, the following risks could happen:

- Complete line of coal is under the mud;
- Bottom line of coal is under the mud;
- Excavated area is under the mud.

Water pumping. If the water pumping is very slow it may cause the following risks:

- The equipment will be exposed to corrosion for a long time.

Degree of machinery damage caused by the flood. If the flood was very strong, it could cause damage on a part of the machinery. If this happens, it could cause the following risks:

- Complete two main coal conveyor lines are destroyed;
- Undermined area on which the bucket wheel is;
- Parts of frames are destroyed;
- All the equipment of Kolubara Metal Company is destroyed.

Funds for repair. If the amount of funds for the repair is small, a complete refurbishment of flooded machinery is not to be performed, which in the future will result in less availability and higher maintenance costs:

- Funds for repair are insufficient (less than €30 million), complete replacement of the electric is not performed;
- Funds for repair are insufficient (less than €50 million), complete replacement of the electric is performed, but without mechanical parts;
- Funds for repairs are €60 million, complete replacement of the electrical is performed, and mechanical parts.

Preparation for mines rehabilitation. If the time for recovery preparation is very long, i.e. if project documentation and equipment specification for the procurement is not done on time, if the tender procedures are being done too slowly, opencast mine may be out of operation for a longer period of time:

- Project documentation is not ready, i.e. takes a long time to prepare it, consequences of the inability to compile precise specifications for procurement, possible errors in the procurement and others. *The risk is in the field 10/5 unusual but possible, and the estimated direct and indirect damage is €200 million.*
- Tender procedure has been slow, consequences are that equipment was out of operation for a long time. *Risk is in the field 10/5 unusual but possible, and the estimated direct and indirect damage amounted to €200 million.*

Environment protection

Leaking of transformer oil, hydraulic oil and gear unit oil. If there is a leakage, direct pouring of water in the river Kolubara will be prohibited, and in this case, water must be cleaned. *Probability of the event is very likely, the risk in the field 1/10 with additional damage of €10 million*.

Detailed Project for rehabilitation of the opencast Tamnava-West Field implementation plan

Rehabilitation of the opencast Tamnava-West Field implementation plan is presented in Figure 2.

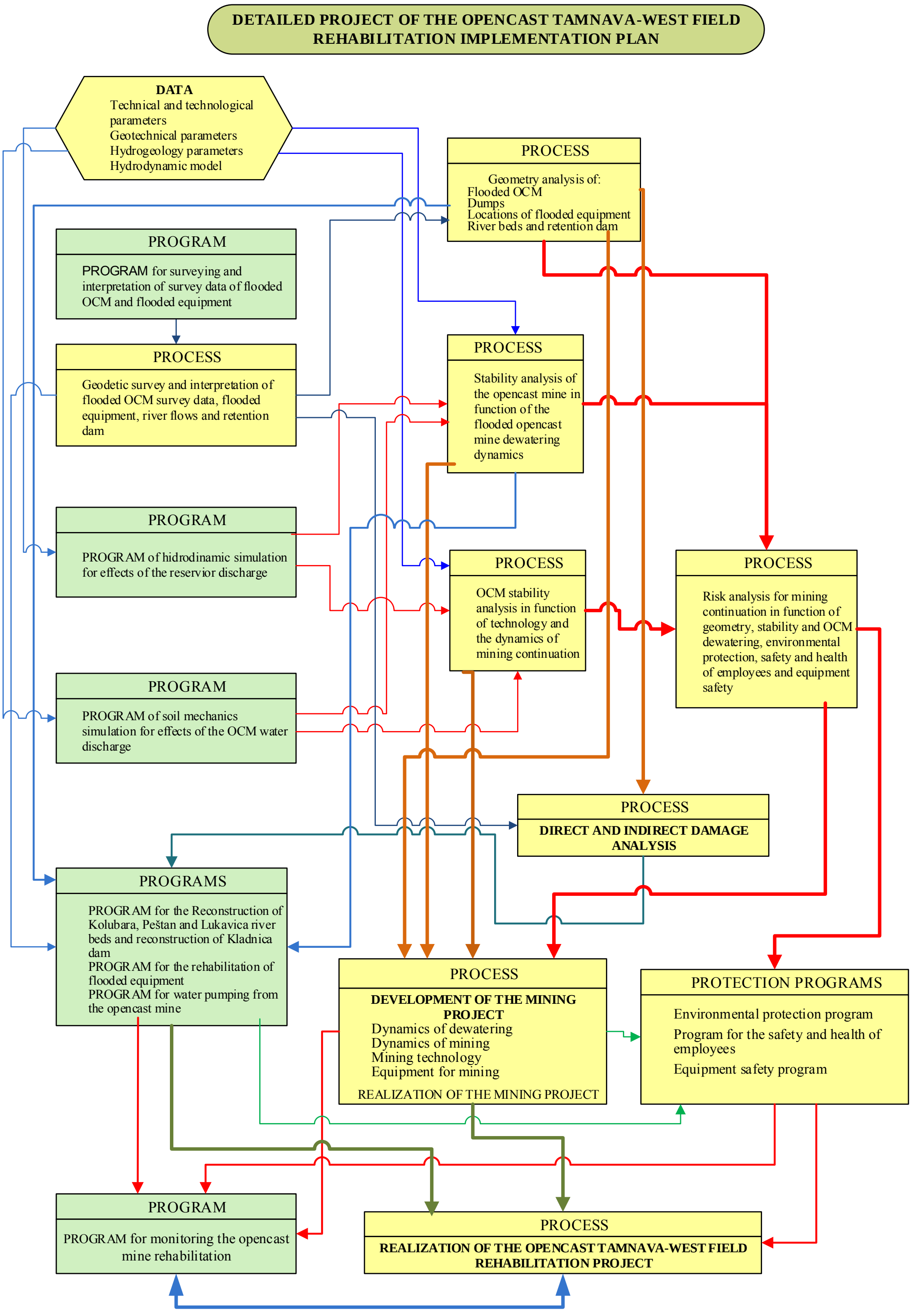
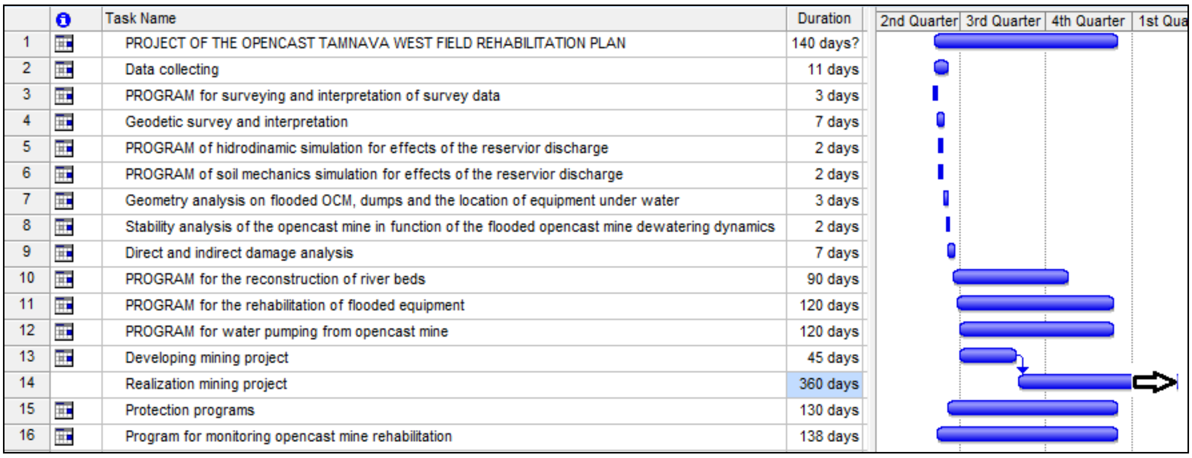


Figure 2 *The opencast Tamnava-West Field rehabilitation implementation plan.*

Dynamics of the project implementation

Dynamics of the project implementation includes development time and time for implementation, as presented in Figure 3.



	Task Name	Duration
1	PROJECT OF THE OPENCAST TAMNAVA WEST FIELD REHABILITATION PLAN	140 days?
2	Data collecting	11 days
3	PROGRAM for surveying and interpretation of survey data	3 days
4	Geodetic survey and interpretation	7 days
5	PROGRAM of hidrodinamic simulation for effects of the reservior discharge	2 days
6	PROGRAM of soil mechanics simulation for effects of the reservior discharge	2 days
7	Geometry analysis on flooded OCM, dumps and the location of equipment under water	3 days
8	Stability analysis of the opencast mine in function of the flooded opencast mine dewatering dynamics	2 days
9	Direct and indirect damage analysis	7 days
10	PROGRAM for the reconstruction of river beds	90 days
11	PROGRAM for the rehabilitation of flooded equipment	120 days
12	PROGRAM for water pumping from opencast mine	120 days
13	Developing mining project	45 days
14	Realization mining project	360 days
15	Protection programs	130 days
16	Program for monitoring opencast mine rehabilitation	138 days

Figure 3 *The opencast Tamnava-West Field dynamics of the project implementation.*

Measures and programs for the implementation of strategic objectives

To achieve the established strategic objectives, a series of hierarchically separated emergency measures were defined, with Implementation of the following programs:

Program of surveying and development of geodetic basis for all potential projects and rehabilitation works on the opencast mine Tamnava-West Field that are carried out in details, reliable and with high quality geodetic surveys, as well as the condition of the river flow, retention dam and water reservoirs in the impact zone of the opencast mine.

Program of hydrodynamic simulations for effects of the reservoir discharge for every 10 m of the water level being lowered in the opencast mine. This program includes innovation of a hydrodynamic model for the Tamnava-West Field deposit, with the purpose of simulation.

Program of soil-mechanics simulation for effects of the reservoir discharge from the accumulated amount of surface water in the condition of the opencast mine, soil-mechanics stability and internal dumps were analyzed each 10 m of lowering the water level in the opencast mine.

Program for the reconstruction of Kolubara, Peštan and Lukavica river beds and reconstruction of Kladnica dam includes all necessary activities on reconstruction, based on hydrologic and hydraulic analysis in accordance with new hydrological conditions, which are a result of flooding.

Program for water pumping from the opencast mine provided the reliability of pumping floodwaters by implementing the following activities:

- An analysis for determining possible dynamics of water pumping from the mine was carried out, taking into account the real technical possibilities, slope stability and the surrounding terrain and other factors of importance, while making sure pumping water in the shortest period is the primary objective.
- The conceptual design of a system for monitoring the elevation of groundwater modification in the area of the opencast mine is defined, depending on the dynamics of abstraction, the stability of the opencast mine and dump site and the quality of the water that is pumped into the recipients.

Program for the rehabilitation of flooded equipment provides defining of the investment in flooded equipment on the opencast mine with implementation time schedule. The following main and auxiliary equipment and machinery was flooded on the opencast mine: 3 overburden systems, 3 coal systems, an interburden system and 4 draglines.

Programs for the environmental protection, safety and health of employees and equipment safety are programs based on which analysis of impacts and risks are made, and that define protection measures and monitoring parameters for the following environment conditions, safety and health at work and protection of flooded equipment during the implementation of the flooded opencast mine rehabilitation.

Program for monitoring opencast mine rehabilitation is a program of continuous monitoring of the rehabilitation plan implementation for the flooded opencast mine. Monitoring program for implementation dynamic of individual activities is based on the designed approach, while monitoring of the environment, safety and health at work and protection of flooded equipment is based on the monitoring of key performance indicators (key indicators) by defined protection programs. As a part of the rehabilitation of the flooded opencast mine, it is planned to draft the mining design, which includes mining reclamation works and bringing the opencast mine geometry in designed condition.

Investment evaluation for the opencast mine rehabilitation

Defining the investment in flooded equipment in opencasts mines of the Kolubara mining basin is an extremely complex task, especially since the expert public had no previous experience in assessing the damage after such failures. According to the plan for the rehabilitation of the opencast mine Tamnava-West Field with dewatering, it was necessary to install 3 pump stations PS-1, PS-2 and PS-3, for the realization of the mentioned rehabilitation dewatering (Pavlovic 2014). Figure 4 shows the starting location of pumping stations. Capacity of the pump stations at the beginning of the operation is 23 m^3/s. Further water pumping is followed by increasing of lifting height and the length of the pressure pipeline, therefore the pump station capacity decreases.

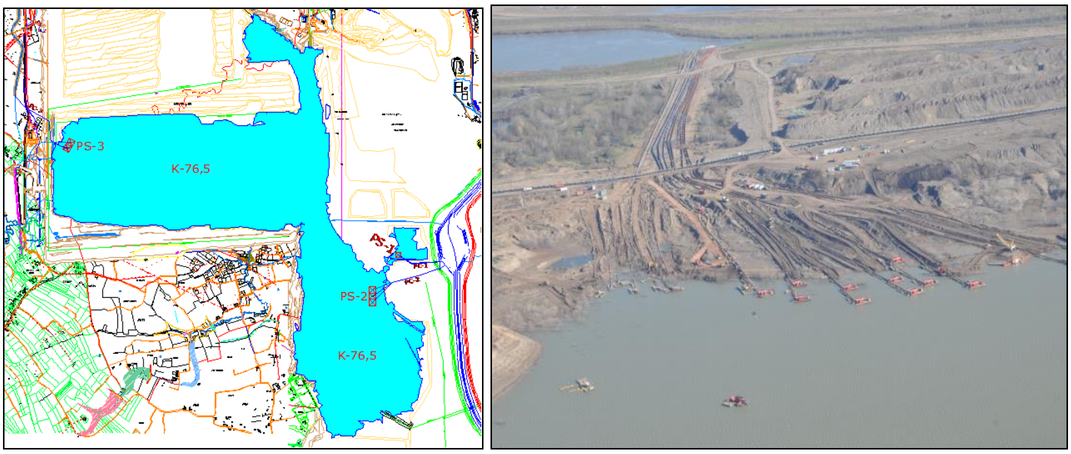


Figure 4 *Initial location of Pump Stations 2 on the flooded opencast mine.*

Investments include required equipment (procurement, transport, installation and commissioning of pumps, production of pontoons and procurement and installation of pipelines), materials and electricity for water pumping from the opencast mine Tamnava-West Field. Required investments amounted to €14.4 million. The value of the flooded equipment, if it would be procured as new, would amount to approx. €250 millions.

Discussions were focused on three levels of the repair works and revitalization of mining equipment according to the following criteria (Table 2):

- The minimum investment and minimum time for bringing mining machinery to operating condition; these imply activities such as dismantling only basic flooded equipment, washing and cleaning, the necessary replacement of critical parts, service for all parts of mining machinery, assembly of tested and cleaned equipment, as well as functional trials (Option 1);
- Investments that will eliminate all the negative effects of the flooded main and auxiliary mining machinery; these imply activities such as complete refurbishment/replacement of flooded segments, service for other machines parts, assembly of repaired and new equipment, as well as functional trials (Option 2);
- Investments that include complete refurbishment and modernization of the mining machinery; these imply activities in the overall revitalization and modernization of mining equipment, with functional trials after the assembly (Option 3).

For all the equipment, all three versions were considered. In all cases, investments in the electric part are the same. Table 2 provides comparative prices of investment for all three options. For the opencast mine Tamnava-West Field, repairs are carried out according to Option 2. Assessment of the investment or estimated direct damage caused by the opencast mine flooding was carried out on the basis of defined rehabilitation programs, presented in Table 2.

Table 2 *Assessment of investment for the rehabilitation of the opencast mine*

Description	**Amount €**
Program of geodetic surveying and geodetic database surveying	80,000
Hydrodynamic simulations program of the reservoir discharge effects	50,000
Soil-mechanical simulation program of the reservoir discharge effects	25,000
Program for pumping water from the opencast mine	14,400,000
Program for the reconstruction of Kolubara, Peštan and Lukavica river bed and reconstruction of Kladnica retension dam	5,600,000
Program for the rehabilitation of flooded equipment:	
- Option 1	32,360,000
- Option 2	45,698,000
- Option 3	46,858,000
- Kolubara Metal and Processing Plant	2,500,000

Total estimated investments required for the rehabilitation of the opencast mine Tamnava West Field, depending on the program selection for the rehabilitation of flooded equipment, range from €55 million to €69.5 million.

Conclusion

Flooding of the opencast mine Tamnava-West Field is a disaster caused by unprecedented floods and as such actualizes a number of issues related to emergency response in opencast mines and mining in general. On the example of the opencast Tamnava-West Field, the reconstruction project presents a good example on how to react in an emergency situation as it this flood was. Rehabilitation project foresees all the necessary activities, its scope and implementation dynamics in the function of safe rehabilitation by dewatering of the flooded mine and reliable continuation of mining.

Electric Power Industry of Serbia, and especially employees of the Mining Basin Kolubara, put in serious efforts so that the process of flood rehabilitation is done in a coordinated and more efficient manner, on the basis of the presented and accepted Operational Strategy Plan for dewatering and rehabilitation of the opencast mine. Dewatering and the reconstruction of rivers beds and retention dam were realized according to the Plan with costs that amounted to €20 million.

The plan anticipated that the complete electrical equipment is to be replaced by new one, which has been done. Estimated value of damaged electric equipment was €28.57 million, and the actual costs amounted to €28.43 million. Similar ratio of estimated and actual occurred damage at the mechanical equipment amounted to €17.5 million. When mechanical equipment is in question, Option 2 was applied. Established strategic objectives are mainly implemented on schedule, with minor variations in the realization of investments and mud extraction, with respecting the rules of the profession and the world's best practice in the implementation of similar projects and maximum consideration of overall operating reliability of opencast mines as well as measures to protect the environment and ecology in general.

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Bio-physical closure criteria without reference sites: realistic targets in modified rivers

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Abstract

The use of reference sites for establishing closure criteria in areas disturbed by mining activities is common practice. ‘Reference’ sites are those considered to be largely unimpacted by anthropogenic activity (retaining desirable natural characteristics), and occurring near disturbed sites. Sites are considered rehabilitated when their biophysical condition approximates that of the reference site. However, this approach often creates impossible or unrealistic targets for miners seeking to close rehabilitated lands. For example, reference sites are often limited in availability (or non-existent) due to impacts by other land uses. Further, any available reference sites might not be realistic matches for the rehabilitated sites – in many rivers (for example) it is questionable whether sites which superficially appear similar are actually ecologically similar.

We propose a more achievable approach to mine closure by comparing the bio-physical characteristics of rehabilitated sites to overall ecosystem variability, rather than specific target reference sites. Using multivariate ordination - a classic data clustering technique in ecology - as an applied management tool allows managers to measure how different their rehabilitated sites are from co-occurring sites, and how the rehabilitated sites are tracking over time. Our approach also identifies the key biological, physical, and chemical parameters that potentially differentiate a rehabilitated site and, therefore, the necessary actions to bring a rehabilitation site within range of normal river variability. Further, this conceptual paper introduces two unique case studies used to develop the model, involving microbes as indicators of rehabilitation progress and mine water impact in Australian rivers. The challenges and benefits associated with implementation of this approach from the practitioners’ perspectives are discussed. The outcome of this new approach to closure will allow miners to create realistic and definable targets for relinquishing rehabilitation land in already modified landscapes, potentially simplifying closure and project approvals.

Key words: multivariate ordination, river diversions, mining, rehabilitation, microbe

The problem with reference sites

The fundamental challenge in setting criteria for lease relinquishment or project approval is determining the rehabilitation objective. The use of reference sites for establishing closure criteria in areas disturbed by mining activities (e.g., river diversions, deforestation) is accepted by regulators across Australia (DITR 2006). However, this approach is flawed, often creating impossible or unrealistic targets for miners seeking to close rehabilitated lands.

The concept of an ecological “reference site” is broadly perceived as a location with a suite of desirable conditions, processes, and/or taxa with which to compare sites impacted by (most often) anthropogenic activities. Generally, reference sites co-occur with disturbed sites, yet are unimpacted and retain “naturalness” of the biota (Stoddard et al. 2006). However, many systems are so heavily modified that sites unimpacted by human activities do not exist and, therefore, it can be argued that the use of a reference site is inappropriate (Chessman and Royal 2004). In the instance where reference sites are nominated, a judgement call must be made as to the "desirable" traits of a reference site, which can include: pre-human ecosystem condition, the best of a suite of degraded sites, or an ideal condition that sites might achieve if they were properly managed (Stoddard et al. 2006).

After a site is identified as having reference attributes, comparison with the impacted site must then be made, requiring additional judgement about how similar impacted sites have to be to reference sites in order to meet rehabilitation objectives. Further, any available reference sites might not be realistic matches for the rehabilitated sites – in many rivers (for example) it is questionable whether sites which superficially appear similar are actually ecologically similar (Blanchette et al. 2014). Of particular note is the high level of natural seasonal ecological variability in the landscape, which can confound efforts to define reference sites. For example, Australian dryland rivers exhibit extreme temporal variability, where the drying river naturally contracts into a series of warm, turbid, isolated waterholes, mimicking an ecosystem under anthropogenic stress (Blanchette and Pearson 2013; Blanchette and Pearson 2012). While it is possible to design rehabilitation and monitoring programs in fairly stable ecosystems that account for broad seasonal variability, in the instance of seasonal rivers, their inter- and intra-annual condition changes so dramatically that it would be a challenge to describe, in detail, the characteristics of an ideal reference site. Essentially, reference sites are a human construct, resulting in restoration targets where changing ideals and natural spatial and temporal variability ensure the goalposts are constantly shifting and/or undefined.

River condition assessment programs that provide alternatives to reference sites can more realistically capture the natural variability of a river system, and provide clearer rehabilitation goals. The 'trend approach,' whereby expectations of condition occur along a natural gradient (Sheldon 2005) is one example of a monitoring program that has eliminated the need for reference sites. However, this approach still requires interpretation: where along the condition gradient is sufficient for rehabilitation and, therefore, lease relinquishment? Another approach that operates without reference sites is the 'trait approach,' which involves the characterisation of ecological traits to predict natural suites of taxa (Chessman et al. 2010). This method, which also captures natural variability, still requires judgements about which ecological traits are desirable, as well as significant effort to determine species' traits and the relationship between condition and assemblage characteristics in each river (a program impractical for environmental managers).

From a practitioner's perspective, when governments approve projects that deliver economic benefit, it is acknowledged that there will be some cost to the environment. Consequently, reference sites are only a guide and most likely can't be replicated. In order to increase stakeholder certainty, process transparency and environmental performance in mine closure, we propose moving away from the use of reference sites towards an approach that considers the variability of the entire system under study.

Towards 'system variability' as closure criteria

Evaluating rehabilitation success is based on measuring a combination of physical, chemical and biological criteria ('bio-physical' criteria). Our model compares the biophysical criteria in rehabilitated sites to the overall spatial and temporal bio-physical variability of the local environment (hereafter referred to as 'system variability'), rather than specific reference sites. We used riverine environments to develop and test the model (see below section), but the system variability approach can also be applied to terrestrial ecosystems disturbed by mining.

The system variability approach to developing closure criteria employs multivariate ordination - a data clustering technique traditionally used in ecology - as an applied management tool (see Fig. 1). Ordination (NMDS, non-metric multidimensional scaling for biological data; and PCA, principal components analysis for physico-chemical data) visually portrays similarity among locations based on multiple variables as a physical distance, with similar sites closer together and different sites further apart (Ramette 2007). We suggest that a successfully rehabilitated site would lie within the river's 'normal' variability (Figure 1), which is sustained (and can be tracked) over time, rather than a one-off comparison to an arbitrarily determined reference site. A rehabilitated site would be considered 'within' the variability of the system as determined by (for example) permutational MANOVA (PERMANOVA) in PRIMER (null hypothesis of no significant difference between sites/assemblages with *p* significant at < 0.05) (Clarke and Gorley 2006). Another advantage of the system variability approach is that the temporal trajectory of biological communities and physico-chemical variables of rehabilitated sites can be tracked over time allowing companies to potentially relinquish land that is not yet within the overall variability of the system, but is well on its way.

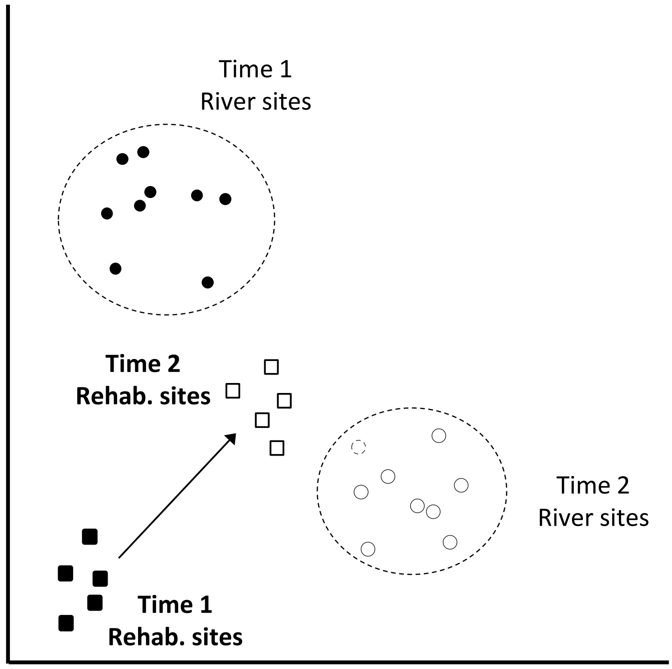

Figure 1 *Hypothetical non-metric multidimensional scaling (NMDS) ordination of biological community data from multiple sites along a river over two time periods (1 and 2). Diagram shows how rehabilitated river sites move from being distinctly different to the rest of the river to being more similar. Relative to closure, the aim is for the rehabilitated site to move within the cluster of river sites during the appropriate period of sampling (i.e, time 2 rehab. sites not significantly different from time 2 river sites, as determined by permutational ANOVA).*

Using BIOENV in PRIMER (Clarke and Gorley 2006), the system variability approach to closure can also identify the key biological, physical, and chemical parameters that potentially differentiate a rehabilitated site from the rest of the environment and, therefore, the actions necessary to bring a rehabilitation site within range of normal river variability (see Figure 2).

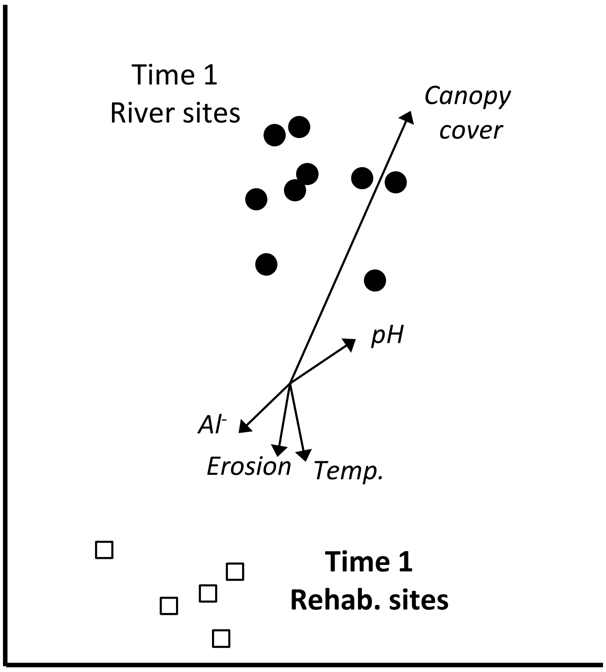

Figure 2 *Hypothetical ordination of biological community data from multiple sites along a river during one monitoring period. Diagram shows community assemblages at rehabilitated river sites (open squares), and at other river sites (black points). Vectors (as generated by BIOENV in PRIMER) indicate which environmental parameters are most influential on the variability in community assemblages (length of vector = importance). In this example, river sites have higher pH levels and more complete canopy cover, whereas the rehabilitated site is acidic with poor canopy cover. Variability in the assemblage at the rehabilitated site also appears to be influenced by higher levels of aluminium, erosion, and temperatures. Therefore, the company would be advised to increase bankside vegetation of canopy trees (decreasing water temperature and erosion), and pay particular attention to sources of acidity and aluminium. Over time, biological assemblages at rehabilitated sites would be expected to become more like those of the rest of the river.*

Developing the approach: river diversions as test beds

As a result of mining activities, rivers may be artificially diverted to allow resource extraction. Current Australian monitoring protocols facilitate comparison of diversion condition to undiverted river sites, but do not allow stakeholders to determine how well the diversion is tracking over time, or the measures necessary to place a diversion on the trajectory to license relinquishment (Alluvium 2014). There is need for a monitoring method that can assess progress towards attainment of a rehabilitation objective, because decades may be required to actually achieve rehabilitation goals. However, the fundamental challenges inherent in designing monitoring protocols (and, therefore, setting criteria for lease relinquishment) is determining the rehabilitation objective.

Case Study 1: Closure of river diversions in the Hunter Valley, New South Wales

Our current project in the Hunter Valley coal mining area of New South Wales aims to test the systems variability approach in regards to closure of two different river diversions. The systems variability approach can both set rehabilitation objectives and assess progress towards attainment of the objectives (e.g., whether diversions are similar or different to the rest of the river). Both these river diversions occur in seasonal tributaries of the Hunter River, which naturally experience little or no flows for much of the year, except during summer rainfall (but see below). In one tributary, the river diversion is a classic trapezoid channel, where no attempt was made to replicate the original river channel that it now replaces. Efforts have been made to stabilise and improve bankside vegetation along part of the channel length. Further complicating the scenario is mine water discharging just below the channel from the active mine, altering this once seasonally-flowing creek into a permanent river system. There is no requirement for this diversion to be modified before closure. The second tributary contains a more recent diversion where every effort has been made to match the characteristics of the river it replaces. Stringent monitoring requirements have been imposed by regulators to ensure diversions match reference sites.

Our sampling methods for this project combine classic ecological techniques with cutting-edge genome technology. Environmental genomics ('metagenomics' or 'community genomics') facilitates rapid identification of microbes by sequencing DNA directly from field samples, free from the selective effects of culturing that hampered previous attempts to understand microbial communities (Whiteley et al. 2012). Essentially, we now have potential bio-endpoints that can inform faster, cheaper, and more sensitive monitoring protocols than current bio-endpoints (e.g., fish, aquatic insects). Using microbial communities as our bio-endpoint, we will sample in, above and below the diversion in each river, measuring microbial communities in the waters and sediments, as well as physico-chemical and riparian parameters quarterly (as per the hydrological cycle) for one year.

Using the system variability approach, if (for example) the 'modern' diversion sites are not significantly different to the rest of the river, it would be considered a strong contender for closure and relinquishment. If the 'modern' diversion sites are significantly different from the rest of the river (and are in worse condition), we could determine what bio-physical parameters were driving this difference and intervene if necessary. Setting the criteria for future closure at this site could be based around the biota if considered important. For example, fish communities may be required to be similar to the rest of the river, even if the water quality remained outside this variability. Ongoing monitoring would demonstrate that the diversion site would remain similar to the other sites, as determined to the satisfaction of stakeholders. The trapezoid channel site will likely be distinct from the rest of the river, and downstream river permanency will likely have an impact on all the parameter groups measured. Further, any impacts of remediation works on the channel will be identifiable. Although closure is already permitted for the diversion, further remediation will be beneficial. The system variability approach can also be applied to closure of ongoing discharge to identify the consequences of permanency and set closure criteria.

Case Study 2: River diversion as a pit lake closure strategy in Collie, Western Australia – effects on the Collie River

Diverting a river through a former pit lake may carry beneficial nutrients, propagules, and pH-neutral water to an acidic hyper-oligotrophic lake, increasing lake water quality and biodiversity, potentially providing a closure strategy for companies. However, as the lake fills, the water will decant and flow downstream, which poses risks to catchments as potentially acidic and metalliferous run-off enters waterways. In Collie, Western Australia, the Collie River was diverted around an operation then subsequently redirected back through a pit lake (Lake Kepwari) as part of three-year trial to determine the effects on the lake and river. We sampled riverine macroinvertebrates, water quality, riparian condition, microbial communities (benthic and pelagic), and fish communities above and below the pit lake for a year (n.b. the lake was also extensively monitored but is not the focus of this case study).

We will compare multiple samples (macroinvertebrates, microbes, physico-chemical data) collected above and below the pit lake over five time points encompassing the Collie River's annual hydrograph. Using PERMANOVA in PRIMER, our null hypothesis is that there is no significant difference ($p < 0.05$) among *a priori* spatial groups (above and below the lake). Using the system variability approach, a result of no significant difference suggests no measurable impact of diverting the river through the pit lake on a particular variable. If groups above and below the lake were significantly different, the cost of the closure strategy may be quantified; further monitoring could be performed to determine if recovery occurred, or stakeholders could make an informed choice about whether the cost of this closure strategy was acceptable in light of the benefits to the pit lake and the original condition of the river. However, in this instance, statistics must be interpreted with care and accompanied by further data exploration, as results may be due to natural/background spatial variability rather than the effects of the lake.

Conclusion

The system variability approach to closure uses established analytical techniques and current monitoring strategies. It has many advantages over the use of reference sites (see Table 1), in that the criteria are likely to be more ecologically relevant by reflecting natural variability and existing land impacts, as well as having a clear endpoint. In essence, the outlined approach to setting completion criteria is simply an extension of commonly used ecological assessment methods, but applies the normal outputs of these methods to facilitate closure. Current ecological assessment techniques focus on using multivariate approaches to highlight differences in communities (i.e., demonstrating the impact of mining); we are simply suggesting that where there is no significant difference between the rehabilitated area and other parts of the ecosystem, closure has been achieved.

Table 1. *Summary of key elements of the reference site and system variability approaches to closure of mined lands. '+' indicates concept is an aspect of the method/approach, '-' indicates concept is not an aspect of the method/approach.*

	Reference site approach	**System variability approach**
Establishing the criteria		
Pre-disturbance/historical baseline data	+	-
Requires ideal sites in nature for comparison.	+	-
Can be used in heavily modified landscapes	-	+
Accounts for natural ecosystem temporal/spatial variability	-/+	++
Stakeholder consensus to design ideal rehabilitation characteristics	+	-
Stakeholder consensus that companies are 'allowed' to rehabilitate to the standard of the rest of the system.	-	+
The assessment		
Requires determination about how many sites represent 'variability' in a system.	-	+
Ongoing monitoring to establish success has been achieved	+	+
Deciding which bio-physical variables are important to measure	+	+
Visually tracks rehabilitated sites over time relative to overall ecosystem.	-	+
Successful closure		
Demonstrates when a site is sufficiently rehabilitated.	-	+

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Low Carbon After-Life – overview and first results of project LoCAL

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Abstract

The LoCAL Project "Sustainable Use of Flooded Coal Mine Voids as a Thermal Energy Source - a Baseline Activity for Minimising Post-Closure Environmental Risks" aims at providing bespoke tools for investigating flow and heat transfer in flooded mine workings. New tools for quantifying and modelling heat transfer in networks of flooded mine workings are under development Another aim of the LoCAL project is to overcome the hydrochemical barriers to effective heat transfer from raw and treated mine waters. Ochre clogging is a well-known phenomenon which affects a lot of mine water heating and cooling systems. The LoCAL project not only covers technical and engineering issues, but also provides economic and management models for efficient energy extraction and distribution. Technical, legal, managerial and cost-benefit analyses of various types of decentralised and centralised heat pump systems are being carried out. Project activities are being simultaneously undertaken in mining areas of the UK by research organizations in partnership with industrial enterprises (University of Glasgow in partnership with Alkane Energy Ltd.), Spain (University of Oviedo, with HUNOSA as the industrial partner) as well as in Poland (Central Mining Institute, in partnership with Armada Development). The current paper describes first project outcomes of the three areas mentioned above.

Key words: Mine water, heat recovery

Introduction

It has long been recognised that mine water can be used as a source of both heating and cooling. A flooded underground mine represents a huge thermal resource and store, with a temperature at (or somewhat above, in deep mines) the annual average air/soil temperature.

The concept of using mines as sources of heating and cooling is widely recognised and reviewed (Banks et al. 2003, 2004; Watzlaf & Ackman 2006; Banks et al. 2009, Hall et al. 2011; Preene & Younger 2014; Ramos et al. 2015 and Bracke & Bussmann, 2015, Banks 2016). MW scale mine water heating and cooling systems are operating at at Heerlen, Netherlands (Minewater Project, 2008; Ferket et al., 2011; Verhoeven et al., 2014) and in Mieres, northern Spain (Loredo et al., 2011; Ordóñez et al., 2012; Jardón et al., 2013).

Nevertheless, developers often appear reluctant to invest in mine water sourced heating and cooling. It is these barriers to concept uptake that the LoCAL project seeks to address. Five main barriers can be enumerated (Banks 2016):

1. Risk of ochre (ferric oxyhydroxide) clogging of heat exchangers. Many mine waters from coal and metal sulphide mines contain high concentrations of dissolved iron, manganese and other metals, which can form mineral scales under adverse hydrochemical conditions. This risk can potentially be mitigated by (a) maintaining reducing conditions in the mine water - heat exchange circuit, (b) managing pipeline pressures and dissolved gases and (c) utilising environmentally benign reducing agents (sodium bisulphite, sodium dithionite).
2. Risk of thermal breakthrough of thermally spent (e.g. cool) reinjected water, via open mine pathways, to the (e.g. warm) production well(s). This risk can be managed by conscientious mapping of underground workings, together with analytical modelling (Lauwerier 1955,

Pruess & Bodvarsson 1983, Rodríguez & Díaz 2009, Loredo et al. in press), possibly coupled to pipe network models such as EPANET (Ferket et al. 2011), or by numerical modelling.

3. Legal and licensing uncertainty. Can an abstraction licence be obtained and for how long can it be guaranteed? Does the operator accrue any liability for current or future discharge of contaminated mine water? Can a discharge consent be obtained? Will the water need to be treated prior to discharge? Will the water need to be reinjected to the mine via one or more costly reinjection boreholes?
4. Does a proven long term demand for heating and cooling exist in the local vicinity of the mine (given that heating and cooling can typically only be transferred over modest distances). Is there any new development planned - and, if so, is it still at an early enough planning stage that conventional heating and cooling solutions are not "locked in"? If existing demand is present, will new low-temperature heating systems need to be retrofitted?
5. What is the density of heating and cooling demand? If a dense heating / cooling demand is not present in the immediate vicinity of the mine, how extensive a district heating and cooling network will be required and what capital investment does this represent? Will there be a centralised heating / cooling plant room, or will distributed heat pump / heat exchange solutions be used?

The above-mentioned barriers were the inspiration to start an international project under the EU Research Fund For Coal and Steel, named: "*Low Carbon Afterlife: Sustainable Use of Flooded Coal Mine Voids as a Thermal Energy Source - a Baseline Activity for Minimising Post-Closure Environmental Risks*" (Acronym: LoCAL). One of the LoCAL Project's aims is the provision of bespoke tools for investigating flow and heat transfer in flooded mine workings. For this purpose a new tool for heat transfer modelling in flooded mine workings is under development within the LoCAL project. The tool combines flow modelling in the underground mine workings with an updated version of the heat transfer model proposed by Rodriguez and Diaz (Rodriguez R, Diaz MB, 2009). For the purpose of providing evidence required for calibration of this tool, monitoring of specific sites is being undertaken as part of the project, which provide evidence of important mixing processes at the system scale. Once the tools is fully developed and calibrated, the LoCAL project will demonstrate its use on a system in development.

Another aim of the LoCAL project is to overcome the hydrochemical barriers to effective heat transfer from raw and treated mine waters. Ochre clogging is a well-known phenomenon which affects a lot of mine water pipelines. It is particularly important in case of heat transfer from mine water, because ochre can not only affect flow, but also the heat transfer process itself, at least where the mine water used for heat transfer is rich in dissolved iron. Therefore, within LoCAL two types of strategies are being explored. The first comprises preventative methods for ochre clogging of subsurface pumps and pipework during open-loop heat-pump exploitation of mine waters. The second type comprises approaches suited to closed-loop strategies for oxidised, ochre-precipitating mine waters in treatment ponds.

The LoCAL project does not only cover technical and engineering issues, but also provides models for efficiency of energy extraction and distribution. For this purpose technical, legal, managerial and cost-benefit analyses of various types of decentralised heat pump system (as well as centralised plant room systems) is ongoing. Ownership, management and financial models are studied in order to assess the accessibility to subsidies with different ownership models. Responsibility for contamination and licensing aspects with different ownership models is being taken into consideration. Pathways to market uptake of mine water-sourced heat pump systems are also being investigated. As the mine water can potentially serve not only as a source for heating but also as a sink for cooling, models for incorporating cooling into delivery systems are in progress as well. Ultimately, the project is designed to provide a 'toolbox', to ensure application of the project results, comprising all models and tools developed by the LoCAL project.

LoCAL project pilot sites

UK sites

Two UK heat extraction operations are currently incorporated within the project- Caphouse Colliery in Overton, near Wakefield, Yorkshire, at 53.6416°N 1.6251°W, and Markham Colliery just north of Bolsover, Derbyshire, at (53.2424°N 1.3285°W). These sites, within 50km of one another, form part of the East Pennine Coal Field and during their lifetime worked numerous coal seams from Pennine Lower and Middle Coal Measures of the Westphalian (Pennsylvanian) Coal Measures Supergroup of the English East Midlands (Sheppard, 2005). Differing hydrological and hydrochemical scenarios have influenced the thermal extraction techniques utilised at each site.

Caphouse

Caphouse Colliery was in operation from the 1780's through to 1985. The site was converted and reopened as the Yorkshire Mining Museum in 1988 and eventually became the National Coal Mining Museum of England (NCMME) in 1995. Iron-rich waters were continually pumped from the Hope Shaft, sunk in 1827 to 197m bgl, until 1993 when it was intended for regional mine waters to be pumped and treated at the hydrologically connected Woolley Colliery (53.5961°N 1.5338°W). In 1996 a hydrological blockage between Caphouse and Woolley lead to locally rising water levels and so pumping at the Hope Shaft had to recommence in order to prevent uncontrolled break-outs of ferruginous mine water via the numerous other abandoned mine openings in the region.

The Hope Shaft is now pumped on a daily basis by a submersible pump at c. 170 m bgl to maintain mine water levels at 148-153 m bgl. Water is pumped at around 76 L/s for 12-16 hr/day, typically from 10-11 pm onwards, to take advantage of cheaper night-time electricity. A 10 kW heat pump was installed at Hope in April 2015 to provide space heating to a small building housing a museum exhibit. The heat pump can be coupled to either one of two heat exchangers; an 'open loop' shell-and-tube heat exchange system which can only be used when the Hope Shaft is being actively pumped (i.e. night-time and early morning) and a 'closed loop' heat exchange unit submerged in the first aeration pond of the treatment system that can be used throughout the day. Initial analytical results show little isotopic variation in the raw minewater and a recent rapid rise in salinity, suggesting possible breakthrough of deeper sourced waters to the pump interface (Figure 1; Burnside et al. In Press).

Markham

Markham Colliery operated from 1904 to 1993. Markham's Shafts 1, 2 and 4 were backfilled on abandonment, while Shaft No 3 was left largely open, in order to vent mine gas accumulation, with a hydraulically open plug set in the shaft at the level of the Ell seam (428.8 m bgl). The No. 3 shaft and the land surrounding it was acquired by Alkane Energy in 1998 in order to extract coal bed methane. As water levels continued to rise c. 2m/month following abandonment of the coalfield, methane-rich horizons were eventually submerged and methane extraction became uneconomic by 2006.

By May 2011, the water level in Shaft No. 3 was 239.5 m bgl. In 2012 a "standing column" heat pump arrangement was installed, complete with pump at 235 m bgl (extracting water at c. 15°C and 2-3 L/s), sealed shell-and-tube heat exchanger thermally coupled to a 20 kW heat pump, and return diffuser at 250 m bgl for the return of thermally spent (at 12°C) water (Athresh et al., 2015). On 28th January 2015, mine water levels had risen sufficiently to allow the entire standing column arrangement to be raised in the shaft, with the pump being positioned at 170 m bgl, below the reinjection diffuser at 153 m bgl. Initial analyses show little isotopic variation, suggest strong stratification in the water column and indicate a gradual increase in salinity of waters at the pump interface as the water table continues to rise (Figure 1; Burnside et al. In Prep).

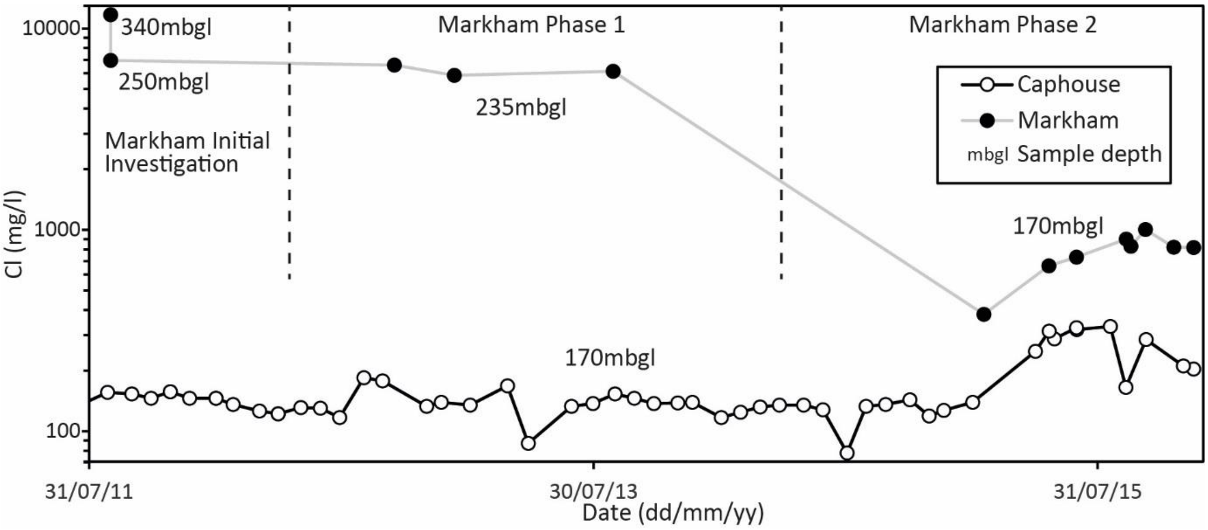

Figure 1*: Chloride plot for Caphouse and Markham sites (Burnside et al. In Press; In Prep).*

Spain site

HUNOSA has developed two geothermal projects in order to take advantage of the minewater supplying heating and cooling to the surrounding population and industrial districts by use of heat pump technologies. This activity aims at making pumping sustainable in economics and environmental terms. Barredo is a closed mine with an average discharge of 4Mm^3/year.

Both geothermal projects share the mine water pumping system. Installed in Barredo Shaft, the infrastructure uses a best quality self-supporting pipe, made of rubber and polyster. Four pumps Grundfos SP 215-4-AA (75 kW), with a nominal flow of 215m^3/h and a nominal height of 60 meters provide the necessary water flow for geothermal supply.

For the University buildings, that are sited around 300 meters far for the shaft, minewater is distributed directly the by gravity into the buildings with two pre-isolated pipes made of polypropylene (Ø 6” for the Research Centre and Ø 4” for the Hall of Residence). The exchanger of the energy to the secondary circuit of clean water and the heat pumps are placed directly on the buildings.

For the Hall of Residence, the generation scheme is simple because cooling is not required. A heat pump RTWB 207 produces hot water at 35 °C with a runback temperature of 30 °C.

At the Research Centre building, a compensated generation system, consisting of two chillers RTWB 210 (heating power of 362 kW each unit), was built. This design allows us to produce simultaneous heating and cooling. Both chillers produce hot water at 50 °C that returns at 45 °C after being used on the heat circuit and simultaneous cold water on the cold focus at 7 °C. When the water comes back from the cold circuit of the building it returns at 12 °C. Thus the heat pump can work steadily with a thermal gap of 5 °C on each focus. Should the thermal loads become unbalanced, mine water acts as a balancing fluid. When cold requirement exceeds the heat requirements the mine water decreases the temperature of the return water of the heating circuit through a plate heat exchanger (UFP 102/55). Furthermore, in winter time the minewater is used to dissipate the excess cold produced by the chillers ensuring that they can operate with an appropriate thermal gap. (Klinger et al., 2012).

In the case of the hospital, that is located 2 km far from the shaft, the minewater goes directly to heat exchanger placed on the mine installations. It is a tubular heat exchanger with a thermal exchanging power of 3500 kW. After the exchange, the minewater is discharged into a river. The heat is given to a secondary circuit that is a secondary close loop of clean water of 4 km made with polyethylene pipes, Ø 400 mm. Three Grundfos HS -150-125-381 320 5/1 FA pumps (3*55 Kw) are used to pump this clean water to the heat pumps in the hospital.

Hospital Vital Álvarez Buylla thermal installation includes two Carrier 30XWH-1.152 chillers, which can provide heat (1509 kW each one) or cold (1141,4 kW each one) to the building, depending on the climate conditions and the specific needs of the clima system. Another chiller, a CARRIER 30XWH-652, produce simultaneous heating and cooling in a compensated generation system, similar to the one of Research Center.

First data of the geothermal systems allow us to establish that use of minewater energy in these buildings has reduce emissions more than a 60%, comparing actual systems with conventional natural gas boilers and air chillers. Furthermore, even considering the pumping costs, geothermal mine water energy is truly competitive and can provide substantial savings to the final consumers.

Polish site

The Upper Silesian Coal Basin (USCB, southern Poland) is a heavy industrialized region and mining has formed the basis of its industrial development for several centuries (Janson et al. 2009). In 1990 there were 63 active coal mines; although subsequently, around half of them have been closed. In most cases, the abandoned mines are only partially flooded. Mine water levels are being kept down by permanent dewatering from several pumping stations in order to protect the remaining active mines from flooding.Polish pilot site for LoCAL project is located close to Ewa shaft from former Szombierki mine, in the city of Bytom. The amount of the water pumped from Szombierki mine is around 5 m^3/min (83 L/s), while the temperature varies from 24 to 28 degrees (Fig. 2). The team of Central Mining Institute is currently conducting monitoring of mine water from abandoned and active mines in Bytom (Janson et al. In Press). Szombierki mine has been closed for several years, but the Armada Development company (industrial partner in LoCAL project) is conducting land reclamation works at the site. Reclamation included the construction of a sports area (golf course) and housing development. The proximity of the minewater discharge from the former Szombierki is an argument for using renewable energy as the main source for heating and cooling at the planned residential area. First step of implementation of this assumption is an pilot installation that is being constructed within LoCAL project. Company has prepared an technical project for pilot installation, and its main assumption is to use water directly from Ewa shaft discharge pipeline.

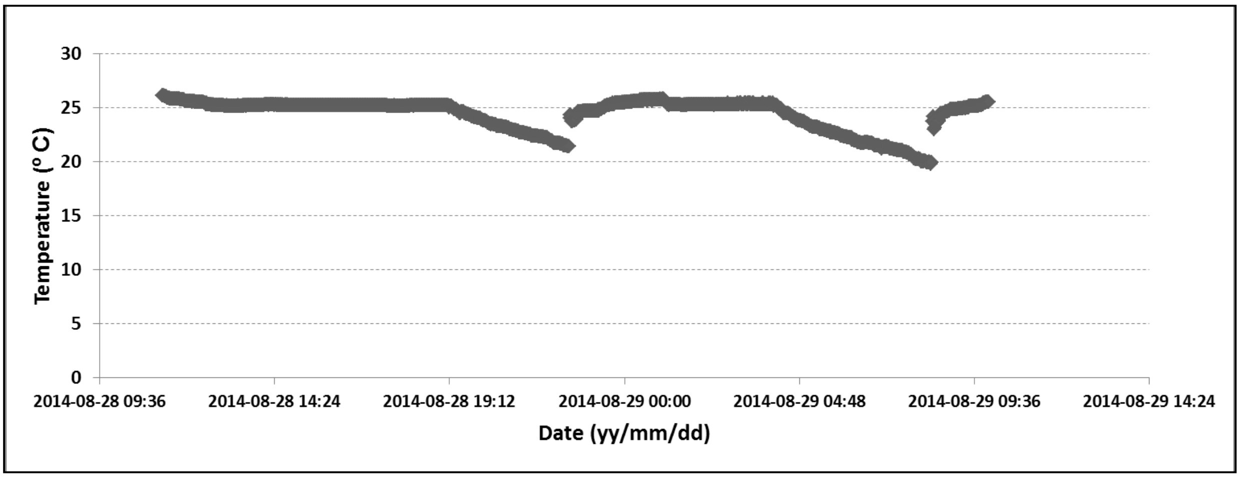

***Figure 2**: Temperature plot for mine water discharge from Szombierki Ewa shaft*

At the Armada pilot site mine water will be used for heating administrative buildings via 6 kW heat pump. It is planned to implement two circuits, mine water will flow through heat exchanger and than the 20% solution of plopylene glycol will support heat pump. The main problem at Polish site remains the proper ownership model, as Armada, being the party interested in the use of mine water for heating purposes, is not the owner of pumped mine water, although the pipeline crosses their lands.

Conclusions

The current paper describes the motivation, aims, concepts and some first project outcomes of the pilot project areas from UK, Spain and Poland included in joint international project LoCAL - "Sustainable Use of Flooded Coal Mine Voids as a Thermal Energy Source - a Baseline Activity for Minimising Post-Closure Environmental Risks". The project is ongoing, therefore no conclusive statements can be drawn yet, however the conditions seem to be appropriate for heat extraction at all LoCAL pilot sites. At UK test sites both closed and open loop systems are under tests and methods for prevention of ochre clogging are tested as well. In Spain the efficiency of heating system based on mine water seems to be proven as more effective compared to traditional gas boiler systems. In Poland the temperature, quantity and proximity of pumped mine water is very promising for the installation of mine water based heating system; the main problem there remains the proper ownership model.

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Risk-based Regional Scale Screening of Groundwater Contamination from Abandoned Mining Sites in Serbia - Initial Results

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Abstract

Mineral mining is recognized as one of the main human activities that influences groundwater and can lead to changes in quantity and quality of groundwater resources. The impact of ongoing and abandoned mining operations on groundwater resources has largely been assessed on a local scale and such assessments have generally been site-specific. However, a number of recent studies of the impact of mining operations on surface water and groundwater resources address the entire catchment area. Apart from the guidelines for the inspection of closed and abandoned mining waste facilities, arising from the "Mining Waste Directive", several methods have been developed to characterize the environmental impact of mining on a regional or national scale

This paper describes methodology focused on screening of groundwater pollution risk induced by abandoned mining sites on a regional scale. The presented methodology is based on a concept developed for groundwater pollution risk mapping, with suitable modifications to highlight and quantify the processes and factors related to the interaction between mining operations/mine wastes and groundwater. Risk screening methodology was undertaken on the basis of an assessment of groundwater pollution potential expressed via groundwater vulnerability, which was followed by characterization of abandoned mining sites as potential hazards. In preliminary groundwater pollution risk screening, the value of the hazard index was multiplied by the groundwater vulnerability index, resulting in the risk index.

Presented methodology was applied on the example of 59 abandoned mining sites across Serbia, related to various types of ore deposits. Initial results show that this methodology can be successfully applied to identify mining sites that pose a high risk of groundwater pollution, as well as to pinpoint catchments and groundwater bodies that are potentially at risk.

Key words: Abandoned mines, risk assessment, mine water, groundwater contamination, Serbia

Introduction

Analysis of interaction between mine facilities and mining wastes with the environment if often based on the risk assessment approach. According to their targets, two types of risk assessment methodologies are recognized (Tiruta-Barna 2007): human health risk assessment and ecological risk assessment. Within the framework of ecological risk assessment, three main phases were separated (EPA 1998): problem formulation, analysis and risk characterization. When assessing pollution related risks, source-pathway-receptor concept is usually applied. Related to groundwater resources, most of the existing approaches for assessing weather contaminated site constitute a risk to groundwater focus on a local scale (Troldborg 2010). Ketelaere et al. (2004) proposed a risk mapping methodology for summarizing the result of risk assessment with regard to the risk spatial distribution that can be applied on catchment or regional scale.

Mining heritage, from small scale mines to large industrial mining complexes, adversely affects natural resources and the environment. Abandoned mining sites, along with associated facilities for the preparation and processing of ores, waste rock disposal sites and tailings, constitute potential hazards and can have a negative effect on the quality of water resources. In order to decide which sites should be given the highest priority and to rationalize future remedial activities, risk assessment is shown to be very useful. Within the European Union this issue is addressed through so-called "Mining Waste Directive", adopted in 2006 (European Commission 2006), which requires development of an inventory of closed and abandoned waste facilities. In this framework, a preliminary risk assessment and prioritization of abandoned mining sites for future remedial activities need to be undertaken.

With regard to water resources, the impact of ongoing and abandoned mining operations on surface water and groundwater has largely been assessed on a catchment scale (Zobrist et al 2009; Sima et al. 2008; Younger and Wolkersdorfer 2004). Apart from guidelines for the inspection of closed and abandoned mining waste facilities, arising from the Mining Waste Directive, several methods have been developed to characterize the environmental impact of mining on a regional or national scale (Raptanova et al. 2012; Mayes et al. 2009; Hudson-Edwards et al. 2008; Davis et al. 1997; Turner et al. 2011).

This paper describes a GIS-based methodology for preliminary risk assessment of groundwater pollution caused by abandoned mining operations. The presented methodology for preliminary risk assessment is based on a concept developed for groundwater pollution risk mapping (Ketelaere et al. 2004), with suitable modifications to highlight and quantify the processes and factors related to the interaction between mining operations/mine wastes and groundwater. Proposed methodology was tested on a regional scale and this exercise encompassed the territory of Serbia south of the Sava and Danube rivers. The study included 59 abandoned metallic (Cu, Pb-Zn, Au, Fe, Sb, Mo, Bi, Hg), non-metallic mines (coal, Mg, F, B) and closed uranium mines across Serbia.

Methods

Risk screening methodology of groundwater pollution as a result of abandoned mining operations was undertaken on the basis of an assessment of groundwater pollution potential expressed via groundwater vulnerability and level of hazard. As a first step, intrinsic groundwater vulnerability was assessed with the GOD method (Foster 1987), on the basis of readily available data, which was followed by characterization of abandoned mining sites as potential polluters. To assess groundwater vulnerability with the use of GOD method, the following parameters were analyzed: groundwater occurrence, overall aquifer class and depth to groundwater.

The hazard identification process comprised physical characterization of mining sites, related to various types of ore deposits, and hydrochemical assessment of mine water originating from those sites, through development of a simple indexing method for hazard and risk quantification. Abandoned mining sites were classified as hazards on the basis of eight criteria divided into two main groups of factors: Factor S (Source) and Factor T (Transport). Factor S was assessed by means of five criteria: hydrochemistry of mine water, ore type, geological environment, the size of waste rock dump, and the existence of a tailings storage facility. Factor T was assessed trough following criteria: mine water discharge, distance from the nearest watercourse and stream order of the receiving water body.

In preliminary groundwater pollution risk screening, the value of the hazard index was multiplied by the groundwater vulnerability index obtained by the GOD method, resulting in the risk index. Workflow with necessary steps for the implementation of the methodology is shown in Figure 1.

Filed work comprised of collecting data on the extent of mining, the presence of tailings and flotation agents, the mining method (underground or open-cast), presence of mine water discharge and sampling of mine water. Along with the filed work, assessment of each potential hazard was based on the use of topographic and satellite maps, and published and fond documentation from archives and relevant agencies.

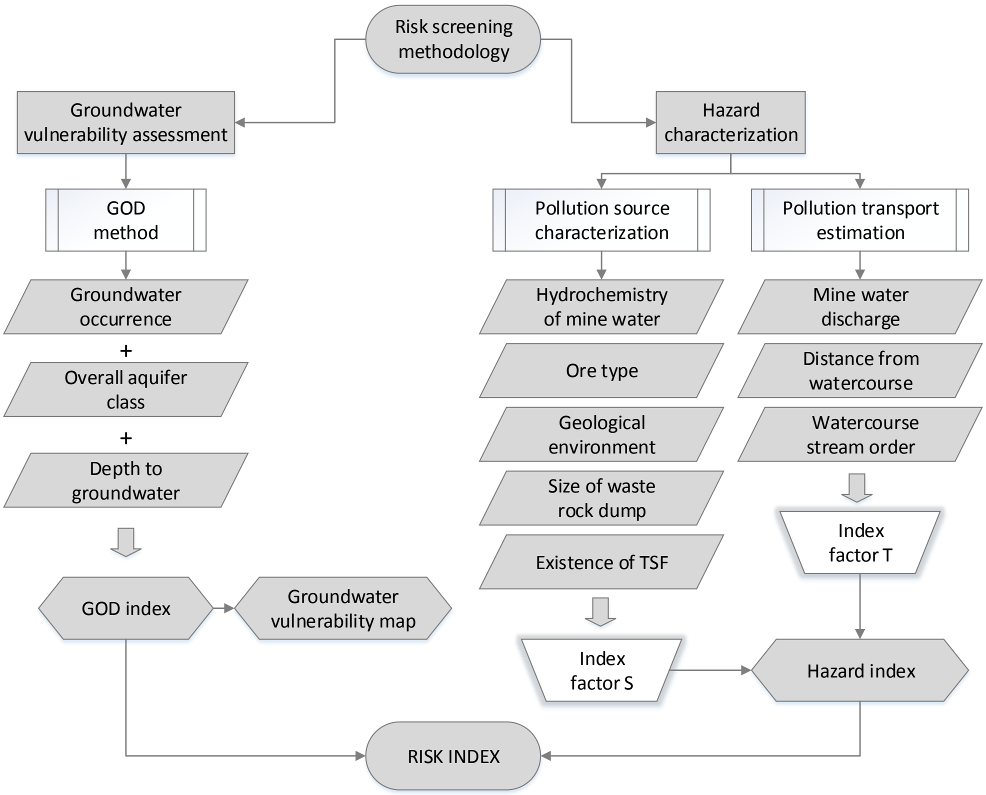


***Figure 1** Workflow of groundwater pollution risk screening induced by mining activities.*

Sampling and chemical analyses

The study included 80 mine water samples from 59 abandoned mining sites. Measurements of pH, electrical conductivity (EC) and temperature were performed in the field with an Mi805 instrument fitted with an MA851D/1 multiparameter probe. To prevent precipitation of metals, a portion of each sample was acidified with an HNO_3 solution at pH<2. Dry residue (after drying at 180ºC), total hardness and $KMnO_4$ demand were tested in the laboratory. Gravimetry was used to determine TDS and volumetry to test for hardness and $KMnO_4$ demand. With regard to macrocomponents, Na^+, Ca^{2+}, Mg^{2+}, K^+ were determined by AAS (Atomic Adsorption Spectrometry), CO_3^{2-}, HCO_3^-, Cl^- by the volumetric method, and SO_4^{2-} by the turbidimetric method. The concentrations of NH_4^+, NO_3^-, NO_2^- and P were established by means of UV-VIS spectrophotometry, and silica concentrations by ICP-OES spectrometry. The concentrations of metals and metalloids (Fe total, Mn total, Cr total Al, Zn total, Cu total, Pb total, Cd total, Ni total, As total) were determined by AAS, as were the specific elements depending on the types of ore deposits (Mo total, F, Sb total, U total).

Hierarchical Cluster Analysis

In view of the fact that the research encompassed abandoned mines of several types of mineral resources, originating from diverse deposits in very different geological and hydrogeological settings, the hydrochemical characteristics of the tested mine water samples varied to a considerable extent. Given the specific chemical compositions, a multivariate statistical method, or more precisely the Hierarchical Cluster Analysis (HCA), was used to group and classify mine waters. To produce data that could be used in an environmental study, HCA was applied to parameters indicative of pollution, such as pH, TDS, SO_4^{2-}, Fe and As (Atanacković et al. 2013). IBM SPSS Statistics 19.0 software was used for statistical analysis. Based on the selected parameters, the mine water samples were grouped into three primary clusters and six sub-clusters.

Groundwater vulnerability assessment

Groundwater vulnerability was assessed on a regional scale, including the eastern, western, central and southern parts of Serbia. Given the size of this area, the GOD method (Foster 1987) was applied. The main criteria for the selection of this method were their relative simplicity, applicability to different types of aquifers and availability of input data. The vulnerability index was based on three parameters: groundwater occurrence, overall aquifer class and depth-to-groundwater. A modified scheme (Živanović 2011) was used to quantify these parameters. The reference document was the geological map of Serbia (S = 1:300,000).

Risk screening methodology

The preliminary characterization of the groundwater pollution risk from abandoned mining sites was based on a comparison of the intrinsic groundwater vulnerability and the potential pollution sources (hazards), which were abandoned mines in the present case. This risk characterization approach is based on a concept developed and used for groundwater pollution risk mapping (Ketelaere et al. 2004). First the intrinsic groundwater vulnerability was assessed with the use of GOD method, which was followed by characterization of the potential hazards. A calculation model was developed for these purposes, based on the parameters/characteristics of abandoned mines, which might have an effect on groundwater quality.

Abandoned mining sites were classified as hazards on the basis of eight criteria divided into two main groups of factors: Factor S (Source) and Factor T (Transport). Factor S relates to the characterization of the abandoned mining sites themselves, as direct sources of pollution, assessed by means of five criteria: physicochemical properties of mine waters identified by the relevant HCA cluster, ore type, geological environment, size of waste rock dump, and existence of a tailings storage facility. The criteria were selected so as to be relatively simple and readily available but, on the other hand, to also be hydrogeologically relevant to the assessment of the groundwater pollution potential.

Within the Factor S, a weight was assigned to each criterion. The criteria were compared and the weights determined by means of Pair-wise Comparison Matrices (Saaty 1994; Turner et al. 2011). The value of Factor S for each of the studied mines was obtained by adding up the product of the values of each criterion and the associated weight, according to the formula:

$$Factor\ S = \sum_{i=1}^{n} Si * wi$$

With regard to Factor T, parameters that affect the pollutant transport potential were assessed, including: the amount of mine water discharged by the abandoned mine, distance to the nearest surface stream and stream order of the recipient. The value of Factor T was determined based on the assumption that the pollutant transport potential increases as the distance to the nearest surface stream decreases and as the amount of water discharged by the abandoned mine increases, and that it is inversely proportional to the flow rate of the receiving watercourse. Given that flow data on a large number of affected streams were not available, the amount of water was expressed in relative terms, via the stream order (the higher the stream order, the higher the flow rate, and, consequently, the higher the pollution attenuation potential). Factor T was the quotient of the sum of nearest-stream distance indexes (T1), water quantity indexes (T2), and stream order indexes (T3), according to the following formula:

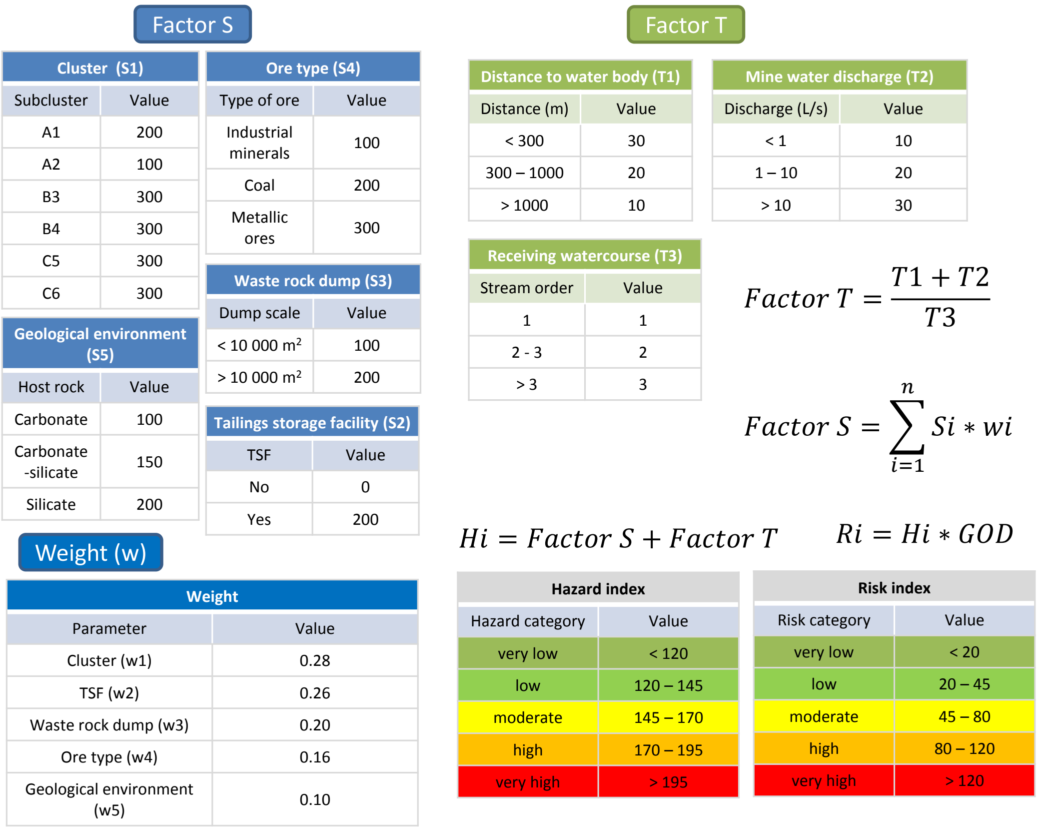
$$Factor\ T = \frac{T1+T2}{T3}$$

The hazard assessment parameter (Hi) was quantified by simply adding up the values of Factors S and T. In preliminary groundwater pollution risk screening, the value of the hazard index was multiplied by the groundwater vulnerability index obtained by the GOD method, resulting in the risk index Ri:

$$Ri = Hi * GOD$$

The values of Factors T and S were calculated and the hazards and risks classified using the calculation model shown in Figure 2.

In view of the fact that preliminary risk screening was performed on a regional scale, the abandoned mining sites were depicted as point futures. The highest value of the GOD index over a 1 km radius from the point feature was the representative vulnerability index to be included in the estimation of the risk index. The presented methodology for regional scale screening of the groundwater pollution risk was developed for implementation in a GIS environment. Neutral local thresholds based on the classification of natural breaks were used to arrive at cut-off values that served as a basis for determining classes with different indexes for the applied hazard quantification criteria.



Factor S

Cluster (S1)	
Subcluster	Value
A1	200
A2	100
B3	300
B4	300
C5	300
C6	300

Geological environment (S5)	
Host rock	Value
Carbonate	100
Carbonate -silicate	150
Silicate	200

Ore type (S4)	
Type of ore	Value
Industrial minerals	100
Coal	200
Metallic ores	300

Waste rock dump (S3)	
Dump scale	Value
< 10 000 m^2	100
> 10 000 m^2	200

Tailings storage facility (S2)	
TSF	Value
No	0
Yes	200

Weight (w)

Weight	
Parameter	Value
Cluster (w1)	0.28
TSF (w2)	0.26
Waste rock dump (w3)	0.20
Ore type (w4)	0.16
Geological environment (w5)	0.10

Factor T

Distance to water body (T1)	
Distance (m)	Value
< 300	30
300 – 1000	20
> 1000	10

Mine water discharge (T2)	
Discharge (L/s)	Value
< 1	10
1 – 10	20
> 10	30

Receiving watercourse (T3)	
Stream order	Value
1	1
2 - 3	2
> 3	3

$$Factor\ T = \frac{T1 + T2}{T3}$$

$$Factor\ S = \sum_{i=1}^{n} Si * wi$$

$$Hi = Factor\ S + Factor\ T$$

$$Ri = Hi * GOD$$

Hazard index	
Hazard category	Value
very low	< 120
low	120 – 145
moderate	145 – 170
high	170 – 195
very high	> 195

Risk index	
Risk category	Value
very low	< 20
low	20 – 45
moderate	45 – 80
high	80 – 120
very high	> 120

***Figure 2** Calculation model applied for screening of regional-scale groundwater pollution risk*

Results and discussion

Groundwater vulnerability

Regional groundwater vulnerability was assessed applying the GOD method. The study region was comprised of hilly and hilly-and-mountainous areas south of the Sava and Danube rivers, while the area that falls within the Pannonian Plain (the Province of Vojvodina) was not considered because its geology is such that there are no substantial deposits of metallic minerals or coal. In terms of land area, more than 50% of the terrain belongs to the class of negligible-to-low vulnerability, 25% to moderate vulnerability, and 20% to high-to-extreme vulnerability (comprised of karst terrains and alluviums of large rivers) (fig. 3).

In Serbia, 153 groundwater bodies have been identified (Official Gazette RS, 2010), 129 of which are located in the study region. Abandoned mining sites potentially affect 26 of them. The spatial distribution of groundwater vulnerability was assessed relative to the groundwater bodies and the presence of abandoned mines. The assessment showed that the vulnerability index of most water bodies associated with abandoned mines was from 0.2 to 0.32, while in the case of groundwater bodies in areas where there were no abandoned mining sites the range was slightly wider (0.2 - 0.45). With regard to potentially affected groundwater bodies, the low groundwater vulnerability class was found to be dominant. High-to-extreme vulnerability exists to a much lesser extent and is generally associated with carbonate formations.

Hazard identification

Slightly less than 30% of the study cases exhibited a hazard index of less than 145 (i.e. they belonged to the hazard class with a low pollution source potential). The largest number of abandoned mining sites (40%) belonged to the moderate hazard category, while the remaining 30% had a hazard index greater than 170 and constituted significant pollution sources (fig. 4 - left).

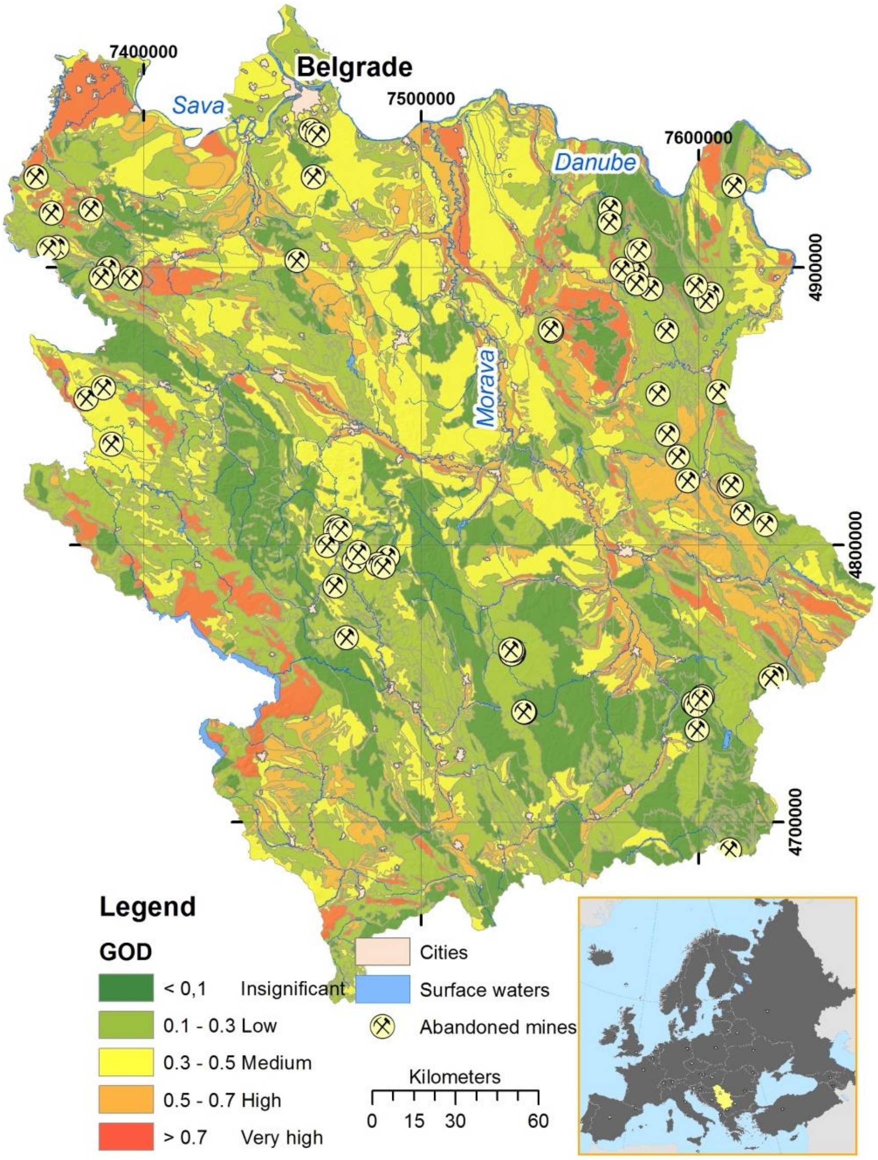


***Figure 3** Groundwater vulnerability map (GOD method)*

With regard to the types of minerals, abandoned copper, lead, zinc, mercury and antimony mines were classified into the highest hazard category. Abandoned mining sites affect the natural water environment, mostly through uncontrolled discharge of mine water into surface water bodies. In such circumstances, the mine water impact needs to be assessed and quantified not only at the point of discharge, but also in terms of the downstream transport and attenuation of water pollutants along the different water pathways and environments (Younger and Wolkersdorfer 2004). In this regard, apart from the characterization of hazards, a preliminary impact assessment for catchment areas was undertaken. Depending on the number and classes of hazards, the level to which associated catchments are potentially impacted was described using three categories (low, moderate and high). Catchments characterized as moderate or high require a detailed assessment of the impact of abandoned mining sites on a catchment scale.

Risk screening

The risk screening methodology applied in this research resulted in the identification of abandoned mining sites according to their potential for causing an adverse impact on groundwater resources. Most of the studied cases (two-thirds) belonged to the group that exhibited no risk or a very low risk of groundwater pollution. Some 17% of the abandoned mining sites were characterized as posing a moderate risk, while 15% of the studied mines were found to pose a high or very high risk (fig. 4 - right).

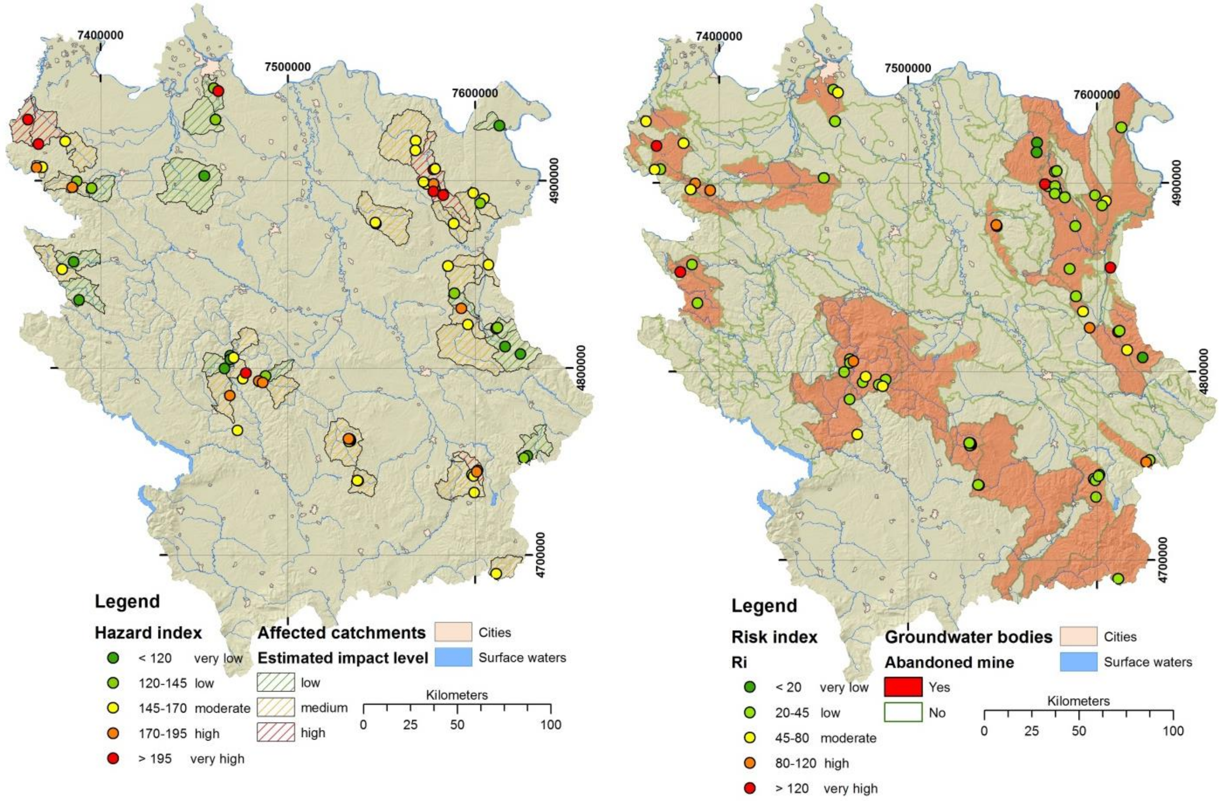


Figure 4 *Map of studied region showing abandoned mining sites.*
Left - hazards and estimated impact level within associated catchments.
Right - categorized according to risk index, and potentially affected groundwater bodies

The spatial distribution of the abandoned mines is such that they are associated with 26 groundwater bodies. The level of impact of these mines on groundwater quality needs to be studied in detail, primarily within the zones of abandoned mines classified as posing a high or very high risk. The screening showed that the highest risk to groundwater quality exists in western Serbia. Although the largest number of abandoned mining sites, which constitute significant hazards, are located in eastern Serbia, they were found to pose a low risk of groundwater pollution. The primary reason for this is that most of these mines are situated within the Timok igneous rock complex, which is a significant metallogenic zone but exhibits a low hydrogeological potential for groundwater circulation and storage.

Conclusion

Risk screening of groundwater pollution as a result of abandoned mining operations was undertaken on the basis of an assessment of groundwater pollution potential expressed via groundwater vulnerability and level of hazard. Groundwater vulnerability was assessed applying the GOD method, while the hazards were characterized and quantified by a specially-developed calculation model based on the physical characteristics of the abandoned mining sites and the hydrochemistry of the mine waters. Approach described above was successfully applied to identify mining sites that pose a high risk of groundwater pollution, as well as to pinpoint catchments and groundwater bodies potentially at risk, where monitoring needs to be established. It was the first step toward the development of this method. Further efforts will focus on the inclusion of additional parameters, more detailed analysis of pollutant transport and uncertainty analysis and prioritization between contaminated sites. Given that groundwater monitoring and protection constitute mandatory but also very challenging tasks, which require substantial resources, the above-described methodology can be used in the initial stages of the development of national groundwater monitoring programs, as well as to improve resource management in groundwater protection and remediation.

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UNITED NATIONS DEVELOPMENT PROGRAMME (UNDP); Detailed technical design for acid mine water treatment in Novo Brdo Mine, Artana / KOSOSVO

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Abstract

In the past, Trepça Mining & Metallurgical Complex was the backbone of the economy of Kosovo with mining being Kosovo's premier industry. One of the mines belonging to the Trepça Group of Mines is the lead (Pb) and zinc (Zn) mine at Artana/Novo Brdo, located 22 km (38 km by car) east of Prishtina. Some mining operations still continue. There are large amounts of tailings and mine waste heaps at the site, and thus, acidic waters contaminated with hazardous substances are discharged into the Krivareka (aka Marevc) River (Aikaterini 2012).

The purpose of this project was to prepare the detailed technical design for the treatment of this acid mine drainage to neutralize the acidity and to eliminate the flow of heavy metals and other contaminants into the river. Thus, a significant source of heavy metal pollution in the area was to be eliminated.

GEOtest a.s. and Fichtner Water & Transportation GmbH, Department Mining & Environment were contracted by UNDP Kosovo as engineering consultants for the project. In a first phase, the Consultants collected and analyzed available data on geology, geography, hydrology, hydrogeology, land use etc., collected new data and performed all necessary surveys, laboratory tests, sampling and site investigations necessary to prepare a detailed technical design for an acid mine waters treatment plant.

The results of this first phase were crucial in order to determine the sources and the scale of the pollutants as well as the flow regime of contaminated water. This information was important to determine the remediation method, the most suitable location and the water treatment technology.

On the basis of these data, the Consultant made recommendations on the choice of the appropriate water treatment technology to assure the proper treatment of the acid mine drainage. Following the selection of the treatment technology in cooperation with the Client and Beneficiaries, the Detailed Technical Design for an active treatment technology was developed.

Key words: former mining, ecological improvement, dewatering, acid mine drainage

Introduction: location, relief, climate, AMD situation

In the past, Trepça Mining & Metallurgical Complex was the backbone of the economy of Kosovo with mining being Kosovo's premier industry. Today, with most processing plants being closed and limited exploitation of minerals taking place, Trepça Complex represents both Kosovo's greatest potential for economic recovery and the country's big environmental challenges resulting from former mining operations in Northern and Eastern Kosovo that have left toxic mining waste threatening tens of thousands of human beings in the area.

Artana mine complex is located in the eastern part of Kosovo, in the municipality of Novo Brdo (see Figure 1). It neighbors the municipalities of Gjilan, Kamenica, Prishtina and Lipjan. The municipality of Novo Brdo includes 33 villages (settlements) within an area of 204 km². Semi-urban settlements are

Novo Brdo, Bostana, Llabjan, Koretishte, Pasjak, Kufce and Stanishor; other settlements are scattered in hilly-mountainous areas.

Figure 1 *Borderline KOSOVO and location of the municipality of Novo Brdo (Helvetas 2012)*

The relief in the area surrounding the mine complex is quite steep. The mine is located in a mountainous area under the highest peak with an altitude of 1,250 m a.s.l. The mine is situated in close vicinity to a valley, which leads to the Krivareka River valley. The highest elevation has adit V of the mine at 805 m a.s.l. The lowest point in the project area is the Krivareka River with an elevation of 664 m a.s.l.

The territory of the municipality of Novo Brdo is dominated by typical continental climate. However, due to the high altitude, some parts of the municipality are dominated by mountainous climate. The temperatures are lowest in January and highest during July and August. During the last 20 years, the average annual rainfall has been between 910 mm in 2002 and 540 mm in 2008.

The Novo Brdo Mine was currently reopened with small-scale mining activities and has four open adits. Two of the adits –adits V and VI - show outflows of acidic mine waters. The situation is shown in figure 2 and can be described in detail as follows: The outflow of acid mine waters from adit VI (figure 2 upper left) and the natural run-off from adit V partly contain acidic mine water from the upper mining levels (figure 2 upper right). The conflux of these two outflows as well as the discharge into a channel pipeline leading towards the main valley and discharging finally into the Krivareka River show the characteristic red colors of acidic mine waters.

The objective of the project was the treatment of the acidic streams from the adits V + VI in Novo Brdo Mine, Artana, in order to neutralize acidity and remove dissolved contaminants so as to comply with prevailing environmental standards. It had to be taken into consideration that the Trepça Group plans to increase the mining activities in the Novo Brdo area.

Scope of work

Fichtner and GEOtest were contracted as Consultant by UNDP Kosovo to evaluate the current situation and the requirements of an appropriate technical solution for the acid mine water treatment including a technical design for a water treatment plant. During the project, the Consultants evaluated all available geological, hydrogeological, meteorological and hydrological data, the spatial planning and the geology of the deposit as well as former and current mining operations.

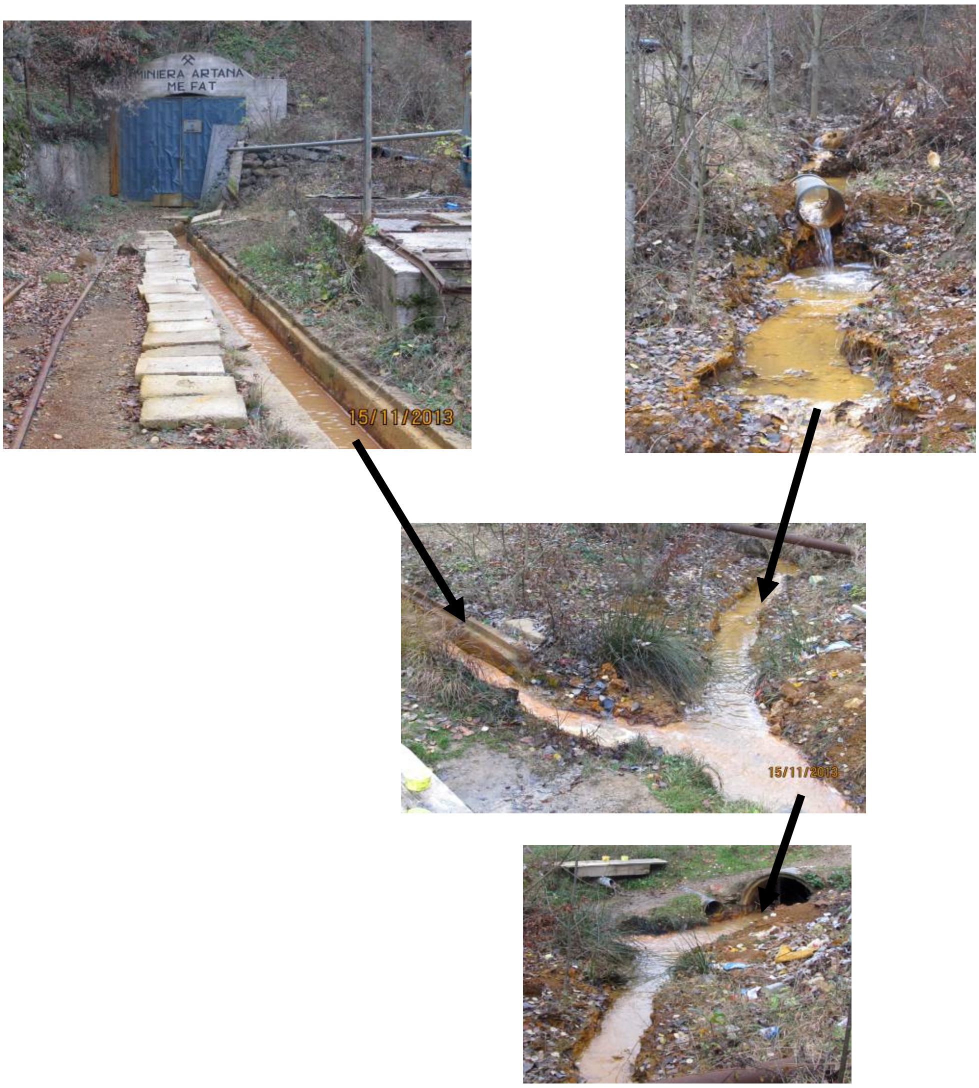


Figure 2 *Outflows and open creeks with acid mine waters*

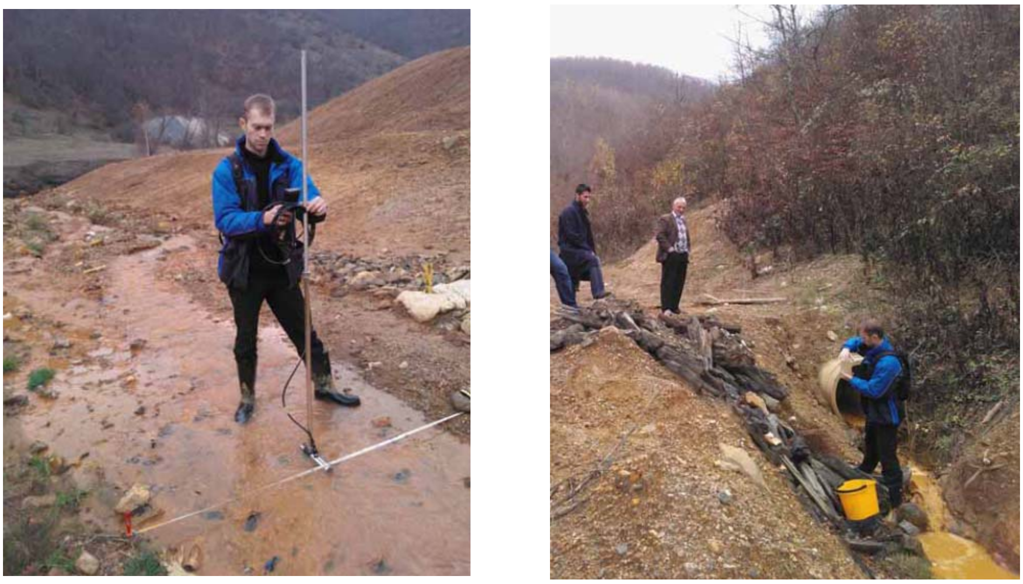


Figure 3 *Flow measurements with Acoustic Digital Current Meter OTT and sampling*

The team carried out a site visit with the following activities:

- Mapping of the mining area with all outflows of the mine, geology etc.
- Flow measurements of all surface water streams with Acoustic Digital Current Meter OTT (see figure 3)
- Water sampling (see figures 3 and 4)
- Investigations to identify an appropriate location for the treatment plant
- Discussion with the local authorities regarding planning and approval of a new treatment plant

Figure 4 shows the mining area with the sites for water sampling (red dots) and flow measurement (blue dots).

Source: WMS Server http://goto.arcgisonline.com/maps/World_Imagery

Figure 4 *Sampling and flow measurement locations*

All results of the first investigations as well as the water treatment scenarios were presented and discussed with the Client, different Ministries and Authorities, relevant stakeholders and the Trepça Enterprise Company as possible operator.

Results of the investigations

Flow measurements

The outflow from adit VI was measured at 11.8 l/s (pH 2.82). The outflow from adit V was approximately 0.05 l/s. From the point of discharge at adit V towards the confluence with water from adit VI, the water flows through a narrow valley of a length of about 630 m. Along this flow path, two small creeks additionally discharge into the stream. Close to the confluence of mine water outflow from shaft VI, this stream was measured with a total flow rate of 0.2 l/s (pH 3.17).

After the confluence of these two outflows, the stream of acid mine water continues on a flow rate of 12 l /s or 43.2 m³/h towards the Krivareka River. No additional discharge of acidic mine water into the stream could be observed.

The Consultants expect that the flow rate of contaminated mine water will be relatively constant, reflecting the main climatic trends during the year as well as former studies (MONTEC 2007 and Aikaterini 2012) that measured 35 to 50 m³/h for the mine water outflows in the same range. Outflow of acid mine water from adit VI is about 98% (11.8 l/s) of the total flow rate; from adit V it is about 2% (0.2 l/s).

The Krivareka River was measured downstream of the current discharge of acid mine waters with a flow rate of 69 l/s (250 m³/h).

Chemical content

The following table shows a short summary of the assay of the chemical contents of adit VI and the conflux of adits V+VI. Furthermore, the limits to be considered for discharge into the Krivareka River are listed:

***Table 1** Summarization of chemical contents available*

Parameter	VI*	VI**	V+VI*	V+VI**	Limits***
pH	2.82	2.9-5.6	2.85	2.86-5.6	6.0 – 8.5
suspended solids [mg/l]	245.0	152-362	179.0	140-252	-
Q [l/s]	11.8	9.98-14.05	12.0	-	-
Pb [mg/l]	< 0.05	0.05-0.23	0.103	0.01-0.34	0.2 – 1.0
Zn [mg/l]	72.07	65.3-110.0	66.74	28.6-85.0	0.5 – 2.0
Cu [mg/l]	0.961	0.01-1.0	0.267	0.01-0.75	0.1 – 0.5
Cd [mg/l]	0.15	0.01-0.16	0.141	0.01-0.18	0.01 – 0.2
Mn [mg/l]	54.6	47.8-86.0	44.3	14.0-61.0	1.5 – 2.5
Fe [mg/l]	222.0	44.4-306.5	175.0	23.3-224.8	2.0 – 5.0
As [mg/l]	0.47	0.62-0.67	0.358	0.25-0.51	0.05 – 0.2
SO_4 [mg/l]	1,670	604-1,622	1,437	400-1,310	150 – 250

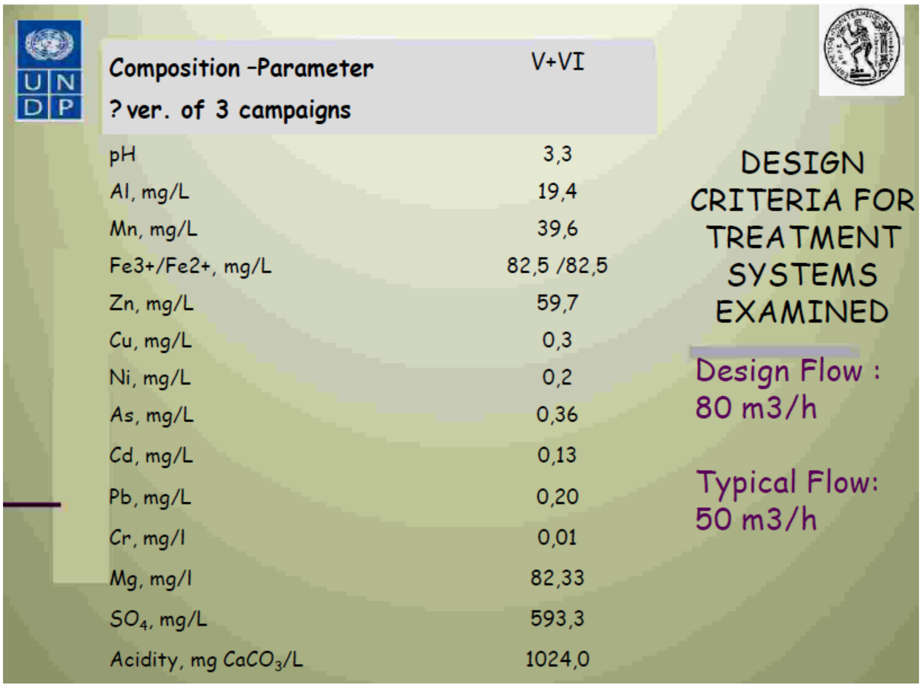
*: result GEOtest a.s.

**: min-max former investigations (MONTEC 2007, Aikaterini 2012)

***: Limits of discharge Category II – Category V (Kosovo 2008)

Methodology of the treatment plant

The UNDP and the former study elaborated by Aikaterini (2012) developed design criteria for the treatment system on the basis of the results of former investigations (see figure 5). Most of the former studies preferred a passive treatment system such as wetlands to reduce the technical effort and the OPEX for the treatment plant.



Composition -Parameter ? ver. of 3 campaigns	V+VI
pH	3,3
Al, mg/L	19,4
Mn, mg/L	39,6
Fe3+/Fe2+, mg/L	82,5 /82,5
Zn, mg/L	59,7
Cu, mg/L	0,3
Ni, mg/L	0,2
As, mg/L	0,36
Cd, mg/L	0,13
Pb, mg/L	0,20
Cr, mg/l	0,01
Mg, mg/l	82,33
SO_4, mg/L	593,3
Acidity, mg $CaCO_3$/L	1024,0

DESIGN CRITERIA FOR TREATMENT SYSTEMS EXAMINED

Design Flow : 80 m3/h

Typical Flow: 50 m3/h

Figure 5 *Design criteria required by the Client*

On the basis of the results of the Consultants' investigation and the assessed quality of the acid mine water, resulting in increased acidity and heavy metal content, a passive treatment technology was not considered a sustainable solution. For a design flow rate of 80 m^3/h and considering the criteria for chemical content, an area of about 80,000 m^2 would be required for the implementation of a passive treatment system. Such an area is not available in the vicinity of the location. The only suitable area is close to the former flotation and processing plant in the main valley of Krivareka River (see figure 4) with an extension of approx. 30,000 m^2.

According to the limitation of space, the Consultants recommended a semi-passive or active treatment technology at an early phase of the project. The following parameters need to be considered when making a decision for semi-passive or active water treatment technology:

- Topography
- Available and useable hydraulic potential
- Range of flow rates in quality and quantity (Trepça Enterprise is planning further mining activities at the level adit VI. This could result in a quantitative and qualitative change of the outflows.)

Finally, the Consultants recommended an active water treatment technology. It is highly expected that the quantity and quality of the outflows will change in future. In that case, a semi-passive treatment technology is not as flexible as necessary. The beneficiary and the stakeholders of the project followed this recommendation. Therefore, the detailed technical design considered an active treatment system.

Conclusions and recommendations

All activities, investigations and discussions suggest an Active Treatment Plant (see figure 7). The objective of the water treatment process is the purification of the acid mine water outflow of Novo

Brdo Mine, Artana, to fulfill the requirements applying to the discharge values (see table 1) and to follow the rules and regulations of the Government of Kosovo. On the basis of the results of the preliminary design, the following active treatment procedure was chosen:

- Step 1: Adjustment of pH-value for oxidation (target pH-value: 4 to5)
- Step 2: Oxidation basin (oxidation of iron, manganese, heavy metals, arsenic, sulfides)
- Depending on the specific water conditions, oxidation by atmospheric oxygen may not be sufficient. In this case, oxidation needs to be promoted by adding hydrogen peroxide (H2O2).
- Step 3: Pre-settling (suspended solids)
- Step 4: Flocculation / coagulation / pH-adjustment up to 8.5 to 9.5 (colloids, metals, arsenic, colloids, carbonate hardness) and sedimentation
- Step 5: Neutralization to pH 6.5 to 8.5 (discharge into river); this step includes an ion exchanger in series for polishing.
- Step 6: Sludge dewatering (thickener; dewatering)

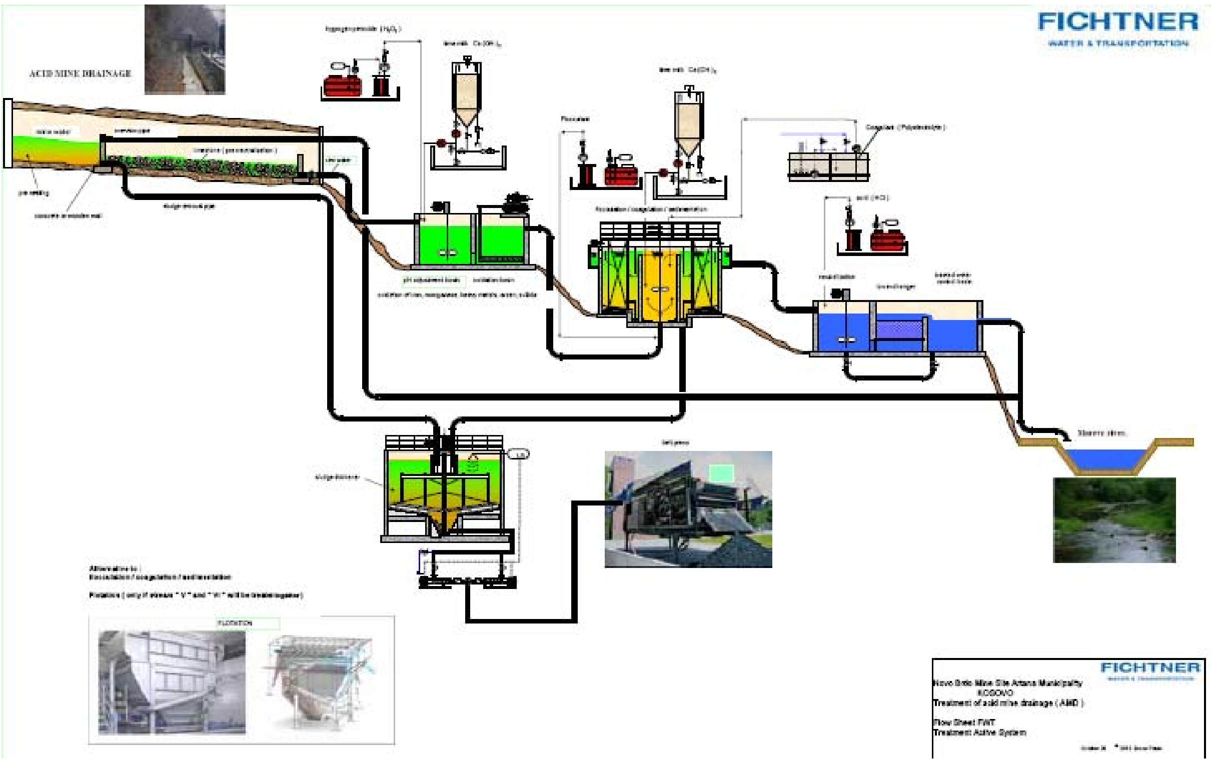


Figure 7 *Technical design of an Active Treatment Plant*

It is recommended that the operator of the water treatment plant controls the treatment process on different stages of the process. Accordingly, it is proposed that an indicative analysis of the treated water is included at step 4. Monitoring of the final quality before final discharge could be added at step 5 to assess the performance of the system and to prove the successful removal of contaminants.

The dewatered sludge is a waste-product of the water treatment and contains heavy metals and other contaminants. Hence, the sludge must be safely transported and deposited on a proper waste disposal site.

The Consultant thus made the following recommendations:

- The requirements, permission and conditions of the final deposition of the dewatered sludge should be clarified by the Client prior to the tendering procedure for the water treatment plant.
- A contract between the operator of the water treatment plant and an operator of an appropriate deposit could be prepared by the Client.

Acknowledgements

We thank the United Nations Development Programme UNDP and the involved authorities of Kosovo as well as Trepça Enterprise for the good cooperation in the project.

Thanks to all colleagues at GEOtest a.s. and Fichtner Water & Transportation GmbH, who have contributed to the success of this project.

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Detection of iron-rich groundwater "hot spots" entering streams in Lusatia

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Abstract

In the German Lusatian Lignite Mining Region, high iron concentrations occur in the groundwater, which discharges to natural streams and brings about unfavourable conditions. It was suspected that the iron load to streams varies greatly in space, and that the contamination originates from discrete point sources (hot spots). Water quality analyses of the few local monitoring wells were found to be insufficient to characterise the problem. A direct push technique for exploring iron hot spots was therefore developed to better identify the areas of high priority for remediation. The developed method was tested at a 700-m-long section of the stream "Kleine Spree", where the presence of hot spots was expected and the planning of remedial measures is already underway. Along that section several samples have been taken from the stream bank and a large spatial variation of iron concentrations was found. While the highest detected dissolved iron concentration in the groundwater beneath the stream bank was about 400 mg/L, 50 m downstream the concentration was only about 240 mg/L and 100 m further it decreased to 50 mg/L. Temperature measurements were conducted to qualitatively characterize the groundwater influxes along the studied section of the stream.

Key words: river, groundwater, iron, hot spots, Kleine Spree

Introduction

In the German Lusatian Lignite Mining Region, acid mine drainage causes high iron and sulphate concentration in the groundwater. With the rising groundwater table that follows closure of open pit mines the iron-rich water discharges into natural streams, oxidizes and settles into a thick layer of iron sludge, bringing about unfavourable conditions for organisms and for commercial and recreational use.

Areas of iron-rich water discharge can be roughly located using flow measurements and water sampling in the stream. Explorations of shallow groundwater quality in these areas have shown that the local iron concentrations differ greatly. This implies that high concentrations appear in the form of so-called "hot spots" (IWB 2012). Due to their linear structure and high cost, remedial measures such as subterranean barriers, injection of oxidizing agents or pump-and-treat should be limited only to areas of high priority. It is therefore imperative to locate these hot spots as accurately as possible.

The use of existing observation wells is not suitable for this purpose, because the information they provide about the spatially differentiated groundwater conditions is limited due to their low spatial density, permanently fixed locations and the positions and lengths of their filter sections. It is difficult to make sure that the water sampled is the same as the water entering the stream, and thus difficult to reliably quantify the iron load to the stream. To understand the interactions between groundwater and surface water and to identify contamination caused by mining leachate or natural hot spots, a characterization of geochemical characteristics at high spatial resolution is essential (Cirmo and McDonell 1997, Nimick and von Guerard 1998). In several studies, the direct push water sampling method was used to gain depth-specific groundwater quality results (Pitkin et al. 1999, Edge and Cordry 1989). Schulmeister et al. (2003) discovered that this method is suitable for the measurement of inorganic parameters like iron. The simplified direct push technique offers the benefits of no drill cuttings, minimal purge water generation and efficient sampling for a large number of points.

To explore the hot spots in the study area, a direct push method for water sampling was developed and tested. An abstraction element is rammed into the stream bed or bank to the desired depth and the water abstracted using a hand vacuum pump. This technique requires only two people and results can be gained fast and flexibly while on site. Challenges included the thick sludge deposit of iron hydroxide in the stream and fine soil material in the aquifer, which can clog the filter of the abstraction element and lead to turbid water samples and falsified lab results.

The method was tested along a section of a stream in Lusatia. In designing the sampling device and conducting all measurements simplicity and efficiency had the highest priority after the quality of data. In this way this method can be easily applied at any similar sites to obtain good results in a short period of time.

Study area

The "Kleine Spree" is a tributary of the Spree River with a total length of 40 km and a catchment area of 175 km² within the German state of Saxony. The long-term mean discharge of the Kleine Spree is 2,500 L/s. In previous investigations areas of significant interaction with iron-rich groundwater were detected by using flow measurements and water sampling at intervals of several kilometres along the river. Furthermore, a groundwater inflow rate of 200 - 300 L/s with a total iron concentration of 60 - 80 mg/L was determined. Explorations of shallow groundwater quality within these areas have shown that the local iron concentrations vary greatly (IWB 2012).

A 700-m-long section of the Kleine Spree was selected to test the developed direct push method. The section is about 2 km upstream from the confluence with the Spree River and lies to the south of the village Spreewitz (Fig. 1). It stretches from the Railway Bridge (St. 1+000) in the Southwest over the area of the Old Cloth Factory (St. 1+200) to the bottleneck to the Spree (St. 1+700) in the Northeast. The closed and flooded open pit mine "Burghammer" and its overburden stockpile are located to the south of the study area, which affect the groundwater dynamics and chemistry and therefore the Kleine Spree. In addition to the closed pit mine Burghammer the most significant source of pollution (75 %) is supposed to be in the Pleistocene aquifer of the "Spreewitzer Rinne", caused by pyrite oxidation (acid mine drainage) (IWB 2012).

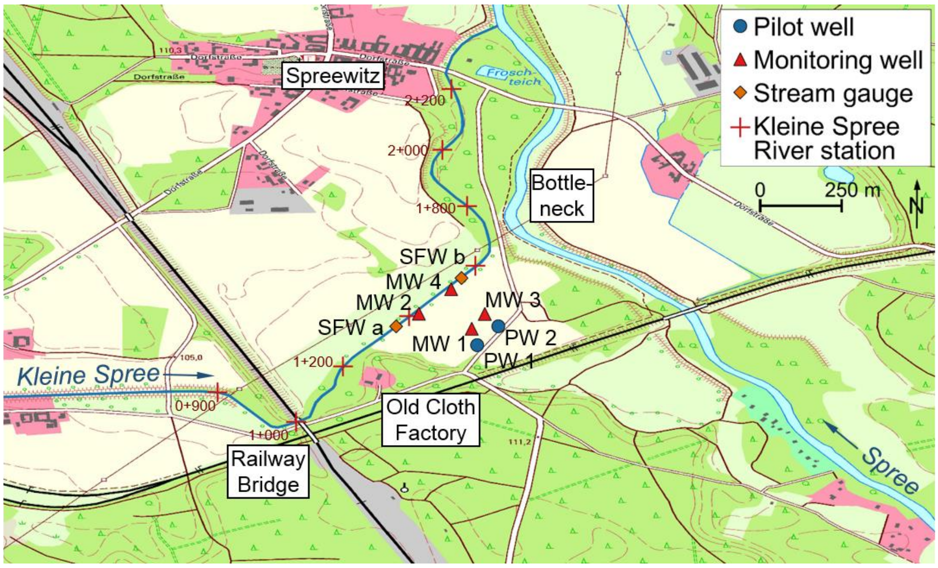

Figure 1 *Overview map of the study area.*

Downstream of the Railway Bridge the Kleine Spree gently meanders for 300 m with deciduous forest on the right and agricultural fields on the left, before running straight down to the bottleneck. The stream has a natural bed and gradient and the banks are host to dense vegetation. As the groundwater generally flows in a northwesterly direction with a shallow groundwater table, the right stream bank of the Kleine Spree was the focus of the investigations.

Planning and construction of remedial measures in the study area are already underway. A gallery of remediation wells is intended to capture the iron-rich water, which needs to be treated after abstraction. Two pilot wells were already constructed and tested. Four monitoring wells and two additional gauges in the stream were used to observe the groundwater and surface water levels and to determine the flow direction.

Materials and Methods

Water sampling probe

For testing purposes a water sampling probe (WaSP) was designed and manufactured with tool steel. The total length of the WaSP is about 200 mm, consisting of a 30-mm-diameter drive point (Fig. 2) and the 75-mm-long abstraction unit, which is reduced to a diameter of 25 mm. A total of 64 inlet ports with an opening width of 3 mm were placed all around the abstraction unit, to enable the groundwater to enter. A Prestolok® Push-In fitting is used to allow a quick and air tight connection to the polyethylene (PE) tubing (d= 4 mm). The WaSP screws into regular drill rods (d= 36 mm) to extend the tool as needed.

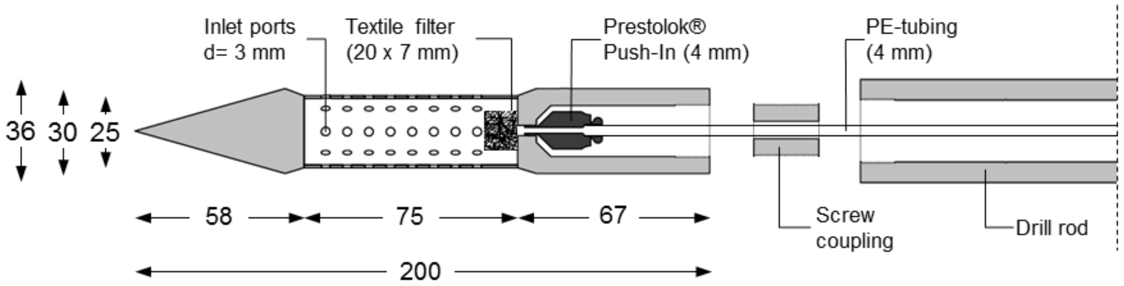

***Figure 2** Drawing of the WaSP and its components (not to scale).*

Initially a fine-mesh stainless steel screen was installed behind the inlet ports to prevent fine-grained sediment from entering to reduce the turbidity of the water sample. During the first tests, the screen became clogged by the thick sludge deposit of iron hydroxide in the stream. Furthermore the screen was damaged after just a few uses and needed to be changed out. Therefore the stainless steel screen was replaced by a modified geotextile filter, which can be easily installed inside the abstraction unit. Fine-grained sediment entering through the inlet ports now settled to the bottom of the abstraction unit after installation of the WaSP or was held back by the geotextile filter. After use, the abstraction unit can be purged by reverse flow.

In the design and operation of the WaSP there are three main criteria that need to be fulfilled to ensure a high-quality sample:

- Do not clog the WaSP with fine sediment or sludge,
- Do not contaminate or falsify the sample through unwanted influence from the soil layers above, for instance the sludge layer on the river bank, and
- Minimize destruction of the soil matrix and the consequent risk of adsorption of dissolved iron in the groundwater to be sampled.

Between August and December 2015, five sampling campaigns were carried out using the WaSP. To obtain as many samples as possible using comparable methods and detect variations in iron concentrations along the river, groundwater quality on the right-hand bank of the Kleine Spree was the primary measurement focus. Initially, two sampling points were envisioned for every cross-section to be investigated, one in the centre of the river (a) and one on the bank (b) (Fig. 3). The ground entry point for sampling at location (b) was chosen at a horizontal distance less than 0.5 m above the water line at the bank (Fig. 4). This ensured that no short-circuit flow occurred along the WaSP's drill rod between the surface water and the sampling point. For this reason, sampling point (b) was ultimately preferred, and only a smaller number of comparison measurements were taken at sampling point (a) for the cross-sections visited.

Iron hydroxide sludge deposits up to 0.3 m thick can be found along the banks of the Kleine Spree. As these posed a threat through contamination of water samples or clogging of the WaSP, a 0.5 to 1-m-deep hole was first created using a percussion core sampler (d_{outer} = 360 mm). The WaSP was lowered to the bottom of the hole and rammed in 0.2 to 0.4 m further using a sledge hammer. Prior to the design improvement using the geotextile filter, the WaSP was repeatedly clogged by fine-grained sediment. To combat this, 50 to 100 mL of bottled tap water was infiltrated through the WaSP's PE tubing using a sealed 100-mL laboratory syringe.

Upon reaching the desired sampling depth, at least twice the volume of water infiltrated in this way was pumped out before the actual sample was taken. The entire sampling apparatus including the syringe can be seen in Fig. 5.

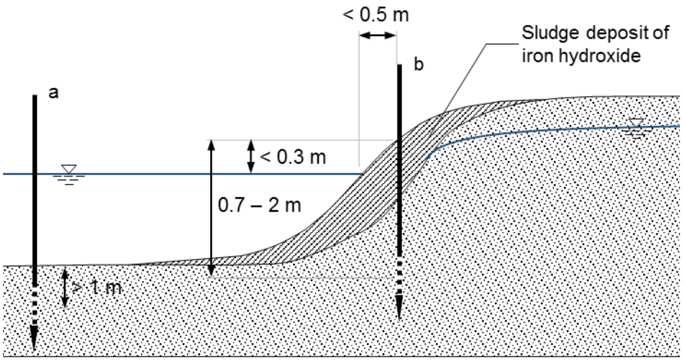

Figure 3 *Typical cross-section of the Kleine Spree with two planned measuring points.*

Figure 4 *Typical ramming installation of the WaSP on the bank at sampling point (b), using a hammer.*

Ramming the WaSP partially destroyed the soil matrix, which led to a visible increase in turbidity of the water sample. This can lead to the undesired effect that dissolved iron is adsorbed to the exposed grains of the freshly destroyed soil matrix or reversely, adsorbed or deposited iron is released from destroyed surfaces and conglomerates (Grischek et al. 2005). The turbid water was pumped out using a hand-vacuum pump at the lowest possible suction pressure and collected in a collection bottle (Fig. 5). The extraction flow rate ranged from 50 to 100 mL/min. Between 150 and 900 mL (300 mL on average) was pumped out before taking the sample.

The air-tight collection bottle was attached to the sampling tube, separated by a three-way valve with the Luer-Lock Connection System. A sampling syringe (V = 50 mL/ 100 mL) was attached to the last remaining valve port. The water sample was collected by closing off the tube to the collection bottle and drawing the water out of the ground under slight suction pressure. In this way, it was ensured that the water samples at no point came into contact with oxygen, until they were deposited into the sample bottles prepared with nitric acid. Syringe filters with a pore size of 0.45 µm were used to filter the samples before entering the sample bottles. At each sampling point a total of 5 sample bottles were filled (V_{tot} = 135 mL).

Water quality analysis

Field parameters electrical conductivity and pH were measured in a glass beaker using a MultiLine® Multi 3430 (WTW). To gain first information in the field, two field test kits from Merck (MColortest and MQuant) to determine iron have been used. The analysis of total iron (Fe_{tot}), dissolved iron and major cations and anions was performed parallel in two independent laboratories (HTW and ERGO). Cations were determined by ICP-OES (Spektrometer Optima 4300 DV, Perkin Elmer). Anions were determined using ion chromatography (ICS 900, Dionex).

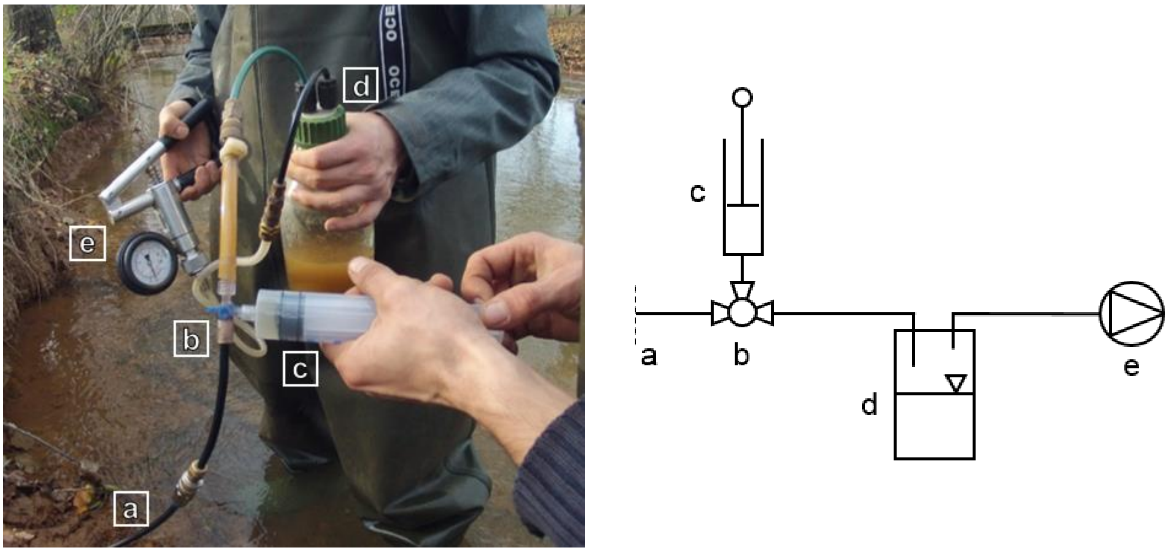

Figure 5 *Sampling equipment with the tube from the WaSP (a), a three-way valve (b), the connection to the sampling syringe (c) and the air-tight collection bottle (d) with the vacuum pump (e).*

Temperature measurements

Temperature measurements were conducted in the Kleine Spree to gain qualitative results in December 2015. The temperature in the river bed was measured at a depth of about 15 cm using a probe thermometer (FLUKE 561). Each cross-section was measured at 5 points in the river bed and one in the river water, at intervals of about 10 m along the river. The background groundwater temperature was measured in the 2 monitoring wells close to the river.

Results

During the site visits along the river it was possible to visually identify points of groundwater inflow, especially when the river water level was low. These were especially apparent near the Old Cloth Factory (St. 1+200), on the right side of the river. They were identifiable through a very wet bank with terraced pools and recognizable runoff channels in the sludge layer (Fig. 6).

Figure 6 *Evidence of groundwater influx on the right bank..*

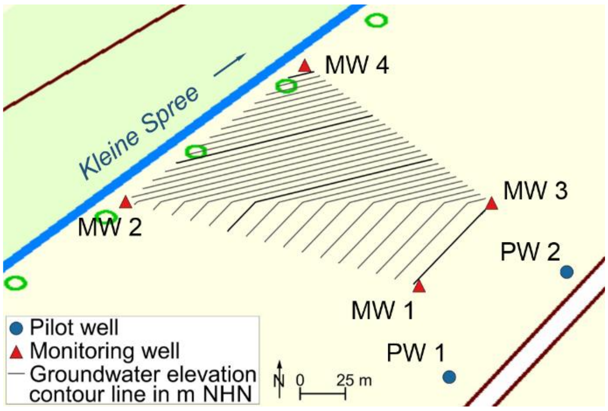

Figure 7 *Evaluation of the groundwater flow direction on the right side of the Kleine Spree.*

Water level measurements over the entire measurement period showed a groundwater flow direction uniformly towards the river. The water level in the river was always lower than the groundwater level in the two riverside monitoring wells, with a steadily rising gradient up to the two monitoring wells closest to the pilot remediation wells. As it can be assumed that there is a hydraulic connection between the groundwater and surface water, the section of the Kleine Spree studied acted as a gaining river during the entire measurement period, being fed by the groundwater from at least the right side (Fig. 7).

In total, 24 water samples were collected from the groundwater aquifer along the right-hand bank between St. 0+870 and St. 1+510, and several areas were sampled multiple times (Fig. 8).

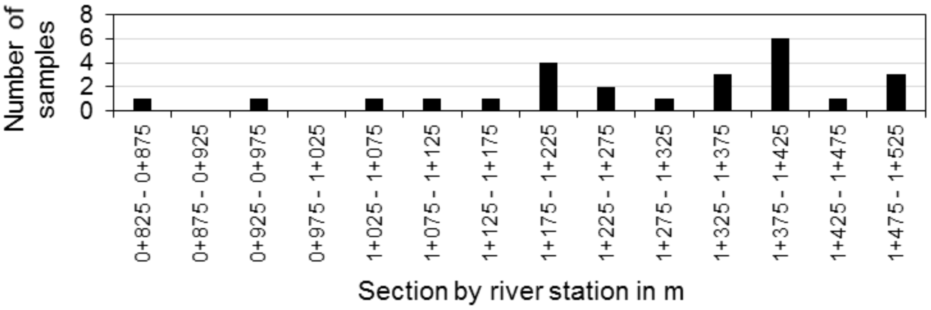

Figure 8 *Overview of samples taken and their locations.*

Within the study area, a large spatial variation of iron concentrations was found (Fig. 9). The independent analyses of the HTW and ERGO showed similar results, with an average difference of 11 %. The results from the different sampling days showed a consistent tendency at each location.

The highest detected dissolved iron concentration in the groundwater beneath the stream bank was about 400 mg/L at the Station 1+250 close to the Old Cloth Factory. Just 50 m further downstream the concentration was only about 240 mg/L and 100 m further still it decreased to 50 mg/L. In the actual area of influence of the pilot remediation wells the concentration of dissolved iron in the shallow groundwater is less than 40 mg/L. Upstream of the Old Cloth Factory, the progression of iron concentrations was less dramatic. At the Railway Bridge the concentration was about 200 mg/L and 100 mg/L was still measured 120 m upstream of the bridge.

Between St. 1+375 and St. 1+425 a total of 6 samples were taken, some on different days. The results from the different sampling dates showed a good agreement for specific stations and fit well within the overall progression of iron concentrations along the investigated section of river. Between St. +175 and St. 1+225 a total of 4 samples were taken. The result from Dec. 4th is likely an outlier, as all other results confirm the high iron concentrations along that part of the river (Fig. 9).

In general, the results from different days reflect the same overall pattern of iron concentrations along the 700-m-long section of the Kleine Spree. This could indicate the likelihood of a long-term stable condition, resulting from the fixed locations of hot spots in this area.

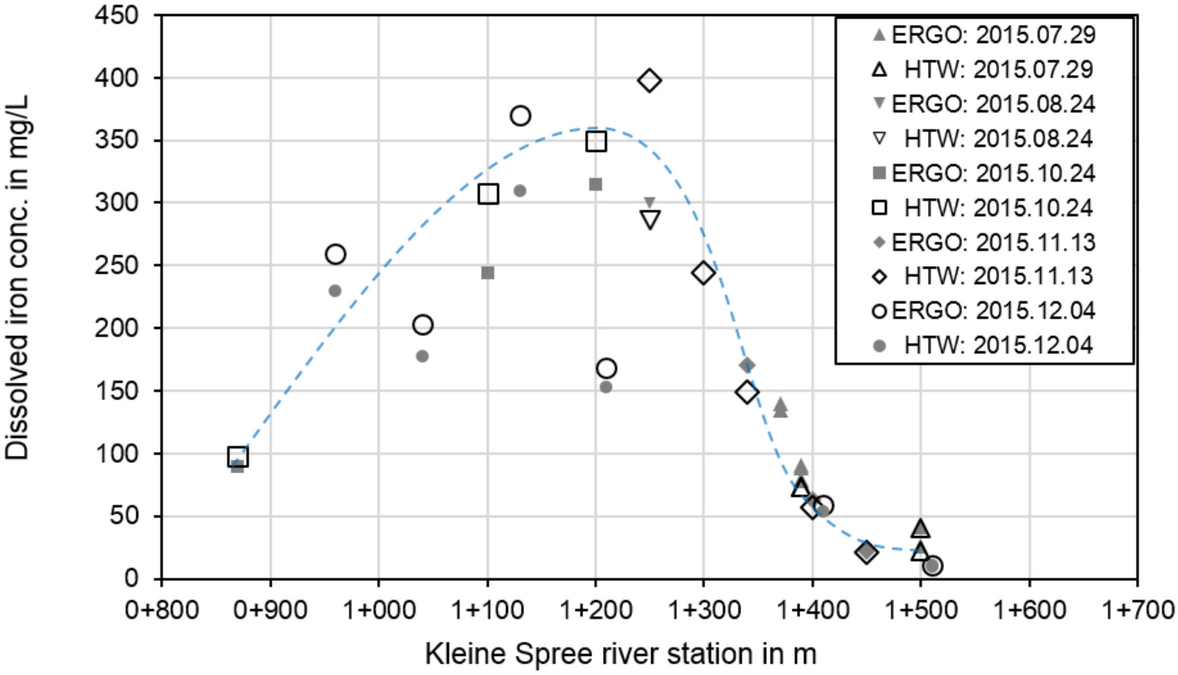

Figure 9 *Dissolved iron concentration in groundwater feeding the Kleine Spree.*

The investigated 700 m-long part of the stream has been classified into three classes with different ranges of iron concentrations in groundwater (Fig. 10): A – hot spot with highest iron concentration (> 300 mg/L), B – high iron concentration (100 – 300 mg/L), and C – lower iron concentration (< 100 mg/L).

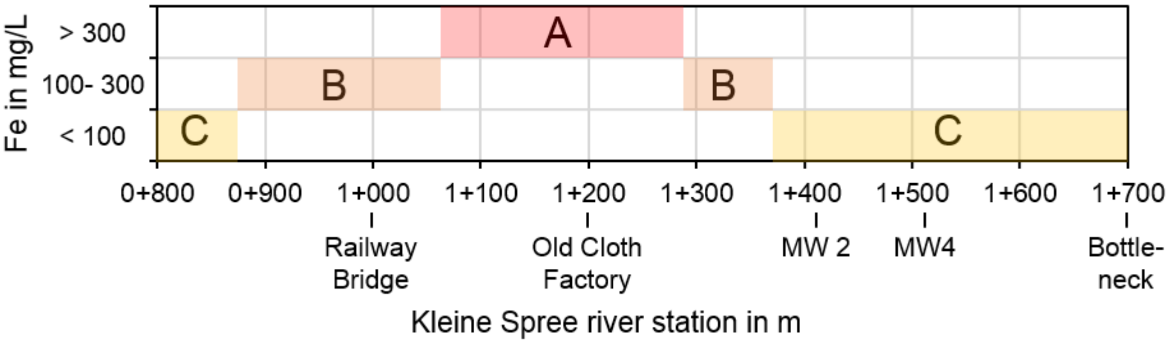

Figure 10 *Classification of the investigated river stretch.*

During the sampling period, the mean river water temperature was 6.4 °C and always lower than the temperatures measured in the river bed of the Kleine Spree ranging from 8 – 12 C (Fig. 11). This indicates that warmer groundwater was feeding the river. Along the investigated stretch of the river a change in temperature was observed downstream of St. 1+350. There, lower temperature in the river bed may be a result of lower discharge and flow velocity of groundwater entering the river. During hammer probing before application the WaSP at the right river bank, aquifer material was identified as medium to coarse sand, whereas downstream of St. 1+400 a higher portion of fine sand was found. Thus, a resulting lower hydraulic conductivity would support the assumption of lower discharge of groundwater into this river section. But different temperatures in the river bed may also be a result of entrance of groundwater from different depths of the aquifer.

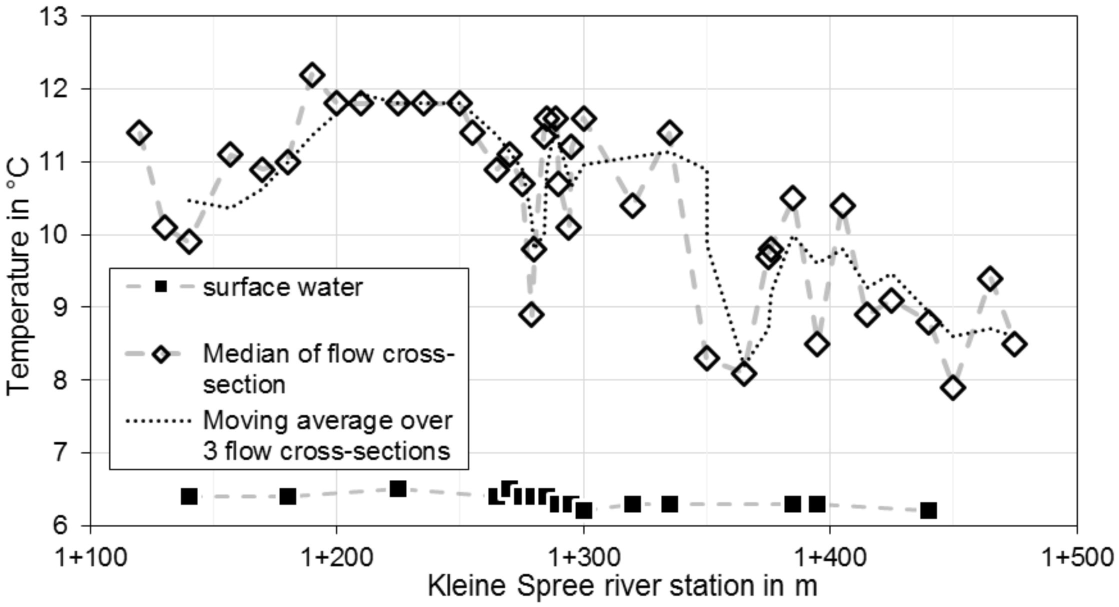

Figure 11 *Temperature of river water and within the river bed fed by groundwater.*

Conclusions

Based on experiences with direct push techniques for groundwater sampling, a method has been developed to investigate groundwater quality beneath rivers in mining regions, which are strongly affected by iron-rich groundwater and iron sludge deposits. Sampling campaigns to determine the iron concentration of groundwater entering the river by using the developed probe resulted in an acceptable agreement of the results from different dates.

Highly different iron concentrations can be found even along a 700 m-long river stretch. To determine the iron discharge rates, water quality data need to be combined with discharge measurements. As flow velocity and discharge measurements in the river itself will rarely allow to determine changes in the range of 0.1 – 1 L/s along a 100 m-long river section, other methods are required, e.g. temperature measurements to identify river sections of strong interaction with groundwater and higher groundwater entrance velocity. Therefor further investigations with have to be conducted. In future a multi-depth measurement of the stream bed temperature could be used to gain more accurate results of the groundwater influx rate.

The identification of hot spots of iron or classification of sections with different iron load is useful for the planning of remediation measures. For example, the highest effect will be achieved if groundwater inflow of class A would be treated or limited. On the other hand, injection techniques using air, oxygen or other oxidants to oxidise the iron in the subsurface as well as pump-and-treat techniques have specific limitations and may be not be applicable at such high iron concentrations as in class A.

Acknowledgements

The authors are grateful to the Saxon State Ministry for Science and Arts for funding the project “INTERDIS-1, WP Development of a monitoring technique to quantify the iron input into rivers in post-mining regions”. The authors also thank J. Feller for iron analyses in the HTW laboratory.

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Water drainage in the German coal mining after the close-down in 2018

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Abstract

As from 2018, coal mining in the Federal Republic of Germany will be terminated. The last mine will stop coal extraction. Nevertheless, for the operators an important task remains:

Rain water still continues to accumulate in the depths of the mines. This may enrich with minerals and reach a high salinity. In order to avoid contaminating the groundwater, this mine water needs to be pumped above ground.

In conventional water drainage, this task is done by underground dry-installed pumps. Which means ventilation, transport, and personnel must be maintained and the annual operating costs are quite substantial.

A new concept involves replacing the underground dry-installed pumps with floodable submersible pumps. The mine water can be allowed to rise to a level that would still be below the groundwater horizons so that mixing would definitely not be possible.

This concept’s benefits are obvious. Ventilation and transport are no longer required when using submersible pumps. Along with the now lowered power consumption of the pumping system, this leads to a significant reduction of the total operating costs.

For its technical implementation, cladding tubes, into which the submersible pumps can be lowered, will be introduced into existing mine shafts. In the former Walsum mine, for instance, two double-suction, and thus axial thrust free, submersible motor pumps are installed to pump the highly saline mine water at a depth of 800m.

Because changing the pump could be extremely complex and expensive because of the installation depth, highest operational safety, a long service life and ease of use – even under the harshest conditions – must be imperative.

Key words: Water management in disused mines, mine water drainage, water management, ground water level in mining

Introduction

Germany belongs to the classical European Mining Countries. Mining in Germany started already in the 12th and 13th century. With the beginning of the industrialization in the mid of the 19th century the stone coal became a very important resource for the production of the necessary energy. For this reason more and more mines were installed to meet the requirements.

Based on this the mines had to go deeper and deeper to reach the seams with the rich deposit of coal. This also was the time when pumping in the mining sector got more and more important.

Today in Germany there is a huge amount of abandoned mines mainly in the Ruhr and Saar area. These mines are partly used to handle the water balance for the still active mines. This is enabled because of the connections by the drifts in-between the different mines.

Actually around 13 mine drainage stations in the Ruhr area are active. After 2018 when the last active coal mine will be closed some of these stations still need to be in operation due to the fact that the mine water should not reach the ground water level because the ground water is used for the production of drinking water.

The mining area around the River Saar shows more or less similar picture of the situation. There actually 5 pumping stations are active. One of the differences there is that an electricity supplier is using submersible pumps to keep the water level in a specific depth for using the natural gas in place for power and heat production.

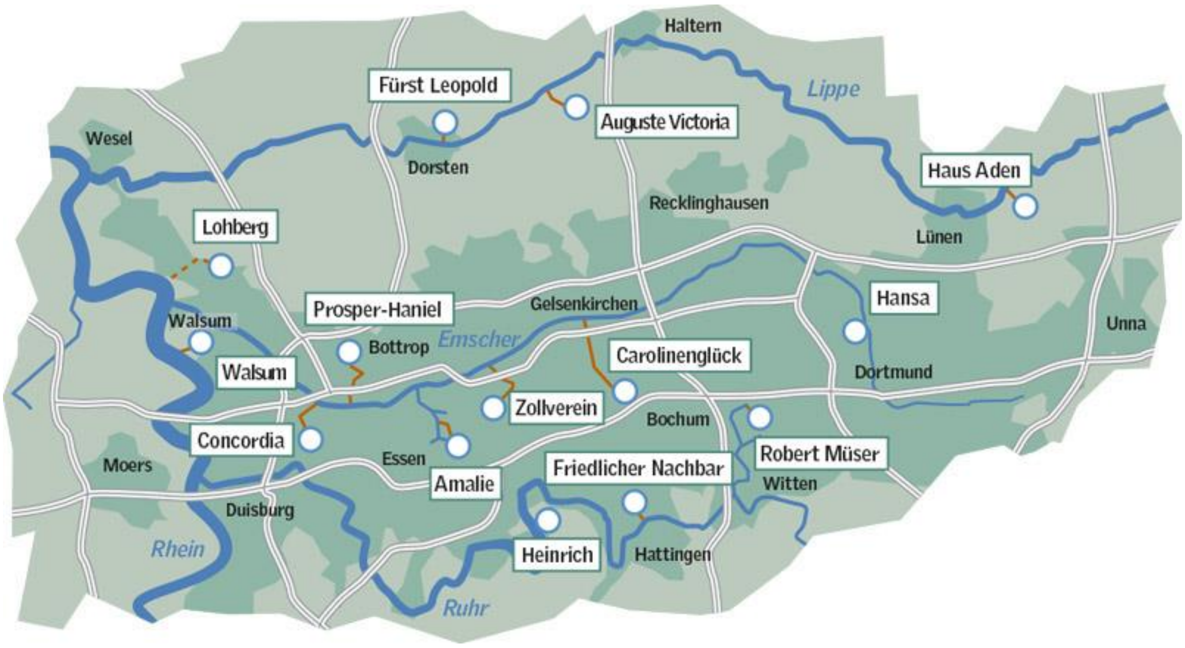


Figure 1. Map of the actually active mine drainage stations in the Ruhr Area.

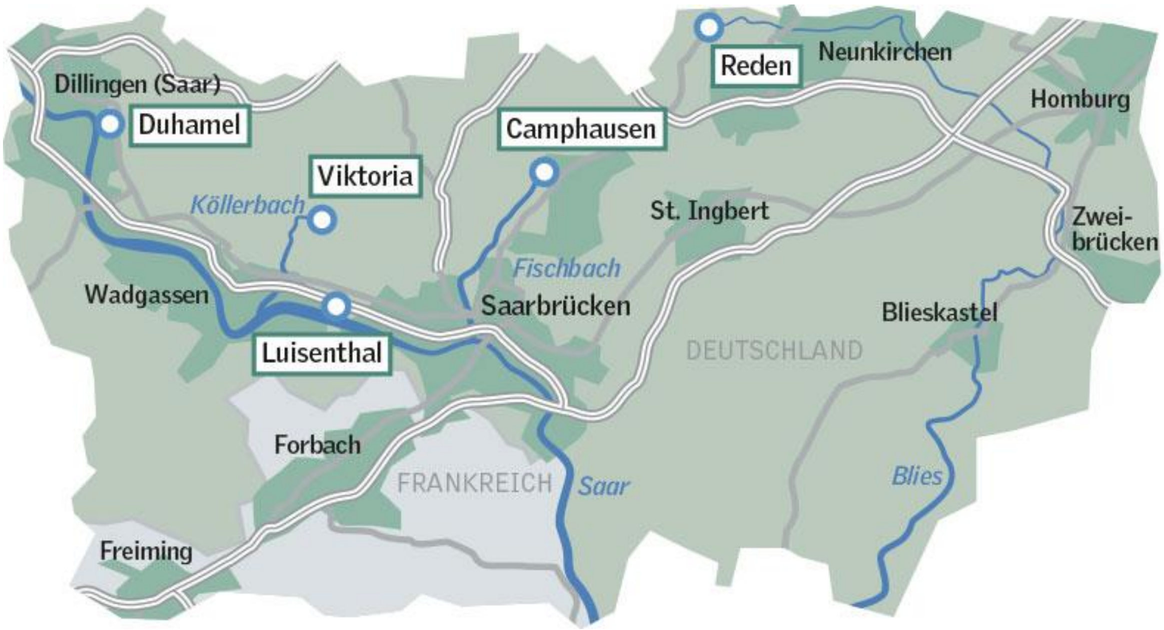


Figure 2. Map of the actually active mine drainage stations in the Saar Area

Recommended Measurements

Pumping out underground mine water to prevent reaching the environmentally critical level, controlling the ingress of water into mine shafts and to find a long term solution that allows keeping the costs in the ballpark.

Challenge – pump solution

A pumping solution does not only belong to the pump and motor unit itself. In fact it is also very important to develop and design pumping stations that can be operated from the surface level. The installation of the necessary equipment should be possible from the surface. This allows the company which is responsible for the water handling to decommission the conveying systems and also the ventilation systems are not necessary anymore.

From this point of view the Experts in the RAG company decided to close the vertical mine shafts with concrete and to implement so called cladding tubes through which the pumps and the necessary sensor (for example to measure the water levels) can be installed. Also it is important that the gas can be dealt which is coming out of the mines.

Solution

The responsible technical experts looked for a long term draining solution to face the problem. Related to the pumps and motors two main challenges had to be matched in this issue.

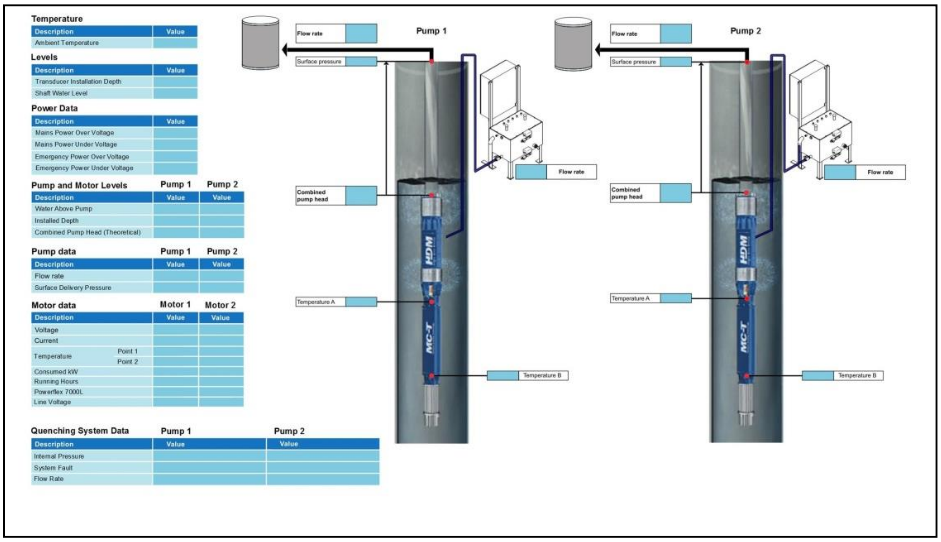
The materials which are in contact with the mine water – metals and elastomers – have to resist the medium for a long time. Therefore, the best material to face the medium and the mechanical properties had to be chosen. Multiple material options were taken into account and qualifying tests were necessary. Therefore, the renowned institute FEM (Forschungsinstitut für Edelmetalle) rebuilt artificial mine water based on the chemical analysis out of the mine and put test materials for a term of three months into this medium. Additionally by using higher temperatures, the reaction time gets faster and a longer period of time could be simulated to get findings of the long-term behavior of the materials.

As a result of these tests, the material selection was refined. Out of the remaining materials the materials with the best mechanical properties for the parts of the pump unit were chosen to enable a compact design of the pump unit.

The used duplex steels combine the features of stainless chromium steels (ferritic or martensitic) and stainless chromium-nickel steels (austenitic). They have those rust and acid resistant properties which are necessary to resist the medium influences. Further they have the required mechanical properties.

Nevertheless, the water analysis may always only be counted as a snapshot of the current situation. As caused by environmental influences the water composition may change. But due to the selected high value materials absolute safety and resistance in operation can be expected.

As a further step and in order to protect the motor of the pump unit against the entrance of the contaminated medium it has been designed encapsulated. That means that the motor is packed into an additional casing to protect the motor materials against the acid medium. The motor itself is filled with drinking water.



Temperature

Description	Value
Ambient Temperature	

Levels

Description	Value
Transducer Installation Depth	
Shaft Water Level	

Power Data

Description	Value
Mains Power Over Voltage	
Mains Power Under Voltage	
Emergency Power Over Voltage	
Emergency Power Under Voltage	

Pump and Motor Levels

	Pump 1	Pump 2
Description	Value	Value
Water Above Pump		
Installed Depth		
Combined Pump Head (Theoretical)		

Pump data

	Pump 1	Pump 2
Description	Value	Value
Flow rate		
Surface Delivery Pressure		

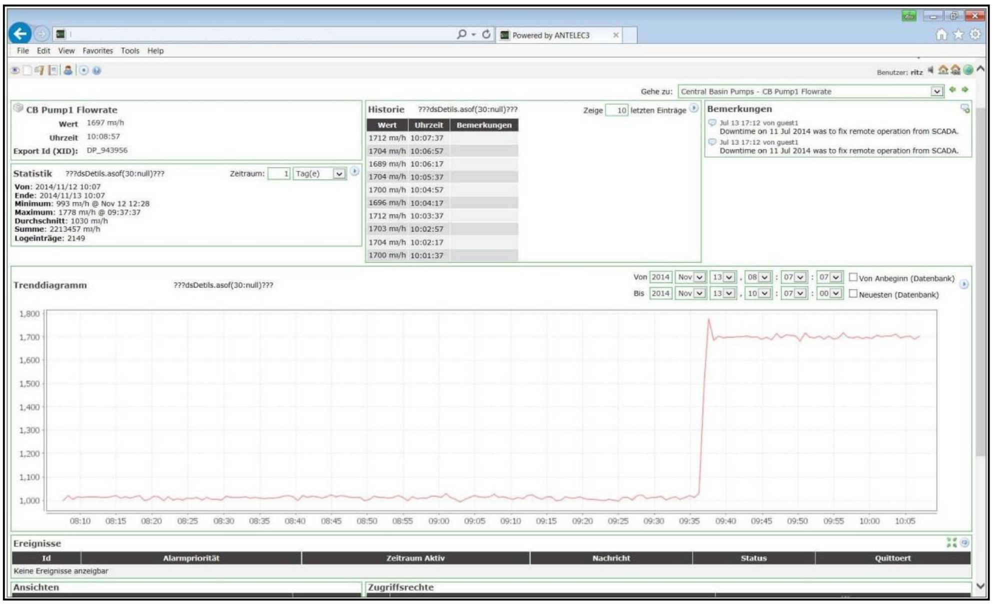
Motor data

		Motor 1	Motor 2
Description		Value	Value
Voltage			
Current			
Temperature	Point 1		
	Point 2		
Consumed kW			
Running Hours			
Powerflex 7000L			
Line Voltage			

Quenching System Data

	Pump 1	Pump 2
Description	Value	Value
Internal Pressure		
System Fault		
Flow Rate		

Figure 3. *Example for a monitoring scheme*



Gehe zu: Central Basin Pumps - CB Pump1 Flowrate

CB Pump1 Flowrate

Wert 1697 m^3/h

Uhrzeit 10:08:57

Export Id (XID): DP_943956

Statistik ???dsDetils.asof(30:null)??? Zeitraum: 1 Tag(e)

Von: 2014/11/12 10:07
Ende: 2014/11/13 10:07
Minimum: 993 m^3/h @ Nov 12 12:28
Maximum: 1778 m^3/h @ 09:37:37
Durchschnitt: 1030 m^3/h
Summe: 2213457 m^3/h
Logeinträge: 2149

Historie ???dsDetils.asof(30:null)??? Zeige 10 letzten Einträge

Wert	Uhrzeit	Bemerkungen
1712 m^3/h	10:07:37	
1704 m^3/h	10:06:57	
1689 m^3/h	10:06:17	
1704 m^3/h	10:05:37	
1700 m^3/h	10:04:57	
1696 m^3/h	10:04:17	
1712 m^3/h	10:03:37	
1703 m^3/h	10:02:57	
1704 m^3/h	10:02:17	
1700 m^3/h	10:01:37	

Bemerkungen

Jul 13 17:12 von guest1
Downtime on 11 Jul 2014 was to fix remote operation from SCADA.

Jul 13 17:12 von guest1
Downtime on 11 Jul 2014 was to fix remote operation from SCADA.

Trenddiagramm ???dsDetils.asof(30:null)???

Von 2014 Nov 13 , 08 : 07 : 07 ☐ Von Anbeginn (Datenbank)
Bis 2014 Nov 13 , 10 : 07 : 00 ☐ Neuesten (Datenbank)

Ereignisse

Id	Alarmpriorität	Zeitraum Aktiv	Nachricht	Status	Quittoert
Keine Ereignisse anzeigbar					

***Figure 4**. Example for a remote monitoring display*

The mechanical seal is tailored to the requirements of that special application. The sliding surfaces of the mechanical seal are specialized and all components are also matched up to the medium. A special construction of the mechanical seal guarantees absolute reliability and best operational characteristics. It is also charged with the inner pressure from a quench.

Weather conditions like rain influence the medium level as experienced with ground water all over the world. The changing water level requires a specific pump hydraulic to drain the water. Additionally, the level gets more or less steadily lower because of the dewatering. The more medium is pumped the lower is the level of the contaminated mine water. So the pump has to have a widely spread operation range until the calculated level is reached and to be kept stable.

The pump is submerged up to 70 m below the level of the mine water. When the level has reached the next lower marking, the pipe is enlarged with another pipe part. For the planning team it was important that the column pipe can be enlarged easily and without loss of time. Therefore, quick snaps are used. Additionally to the quick assembly they score with their compact design, low weight and less effort in comparison to conventional screw connections.

With every step down, the pump has to manage a higher pumping head. This has also been considered in pump selection. Furthermore, the pump is equipped with a cooling shroud to guarantee the necessary cooling flow. In future planning it is thought about operating the pumps within the cladding tubes. This way the cooling shroud is not needed anymore.

The used double-suction design of the pumps reduces any axial thrust nearly to zero. As a result, the pumps are extremely persistent and nearly maintenance free. Some pumps of that type had run in best performance up to 25 years without the need of maintenance. But considering the critical medium the terms of maintenance are shorter in this case. In case of maintenance the use of the quick snaps show their advantages. The pumps can be pulled out, maintained and re-installed in a comparably short time.

All pump units are especially designed for each location. This ensures an ideal use of electrical power and prevents the environment as much as anyhow possible.

Also belonging to the power absorbed by the motors the voltage of those is adapted to the electrical equipment, so that this can be sourced for esay handling and as cost effective as anyhow possible.

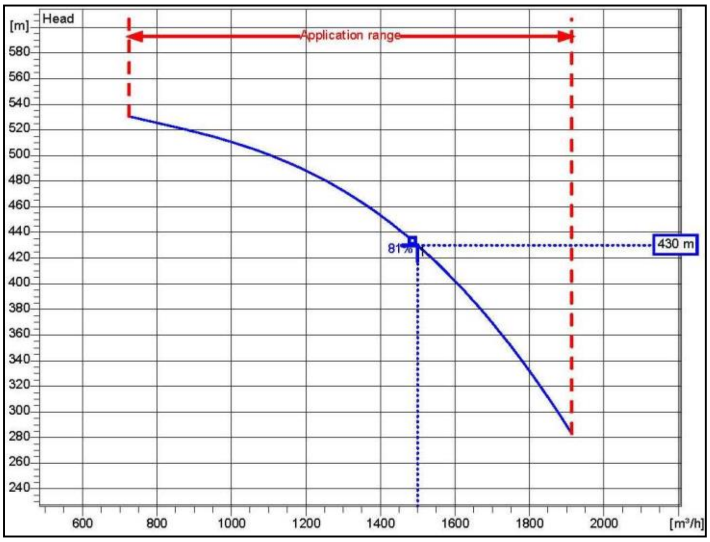


Figure 5. *Example of a performance curve of a pump*

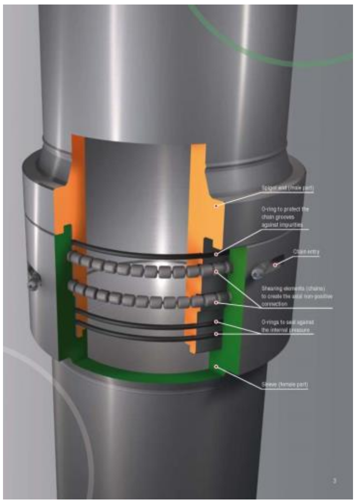


Figure 6. *Quick snap connection (from Carl Hamm Pipesystems; ZSM-Connection Brochure English; issue 07/13)*

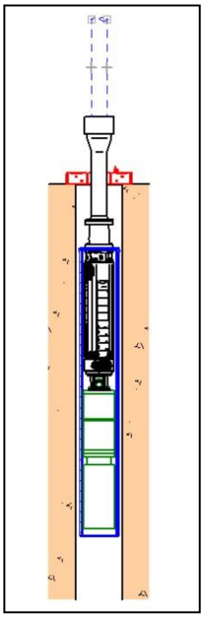


Figure 7*. Assembly scheme*

Figure 8. *Assembly*

Conclusion – Ecological Aspect

The mine water is being transported to the surface and onwards into an adjacent treatment plant. There, through the addition of lime, the pH value is raised, the acid is neutralised and the dissolved metals in the water are (co-)precipitated as hydroxides.

The South African authorities are planning a total of three pumping stations, which will each be developed at the mines' disused extraction shafts. In addition to the Central Basin in Johannesburg's city centre, pumping plants for the Eastern Basin and the Western Basin are currently in progress. The long term measurement is to force the water level in the flooded mines back from its current level of approx. 200 metres to a depth of 1000 metres and to keep it there, to then be able to begin mining gold and gold ore in the drained upper layers of the mines once again.

References

Carl Hamm Pipesystems; ZSM-Connection Brochure English; issue 07/13http://superiormining.com;Wikipedia.

Management of water levels in the flooded mines of the Witwatersrand, South Africa

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Abstract

Following the cessation of underground mining in the three original mining complexes in South Africa's Witwatersrand Gold Field, mines started to flood with no control measures in place. In 2002, acidic water began to discharge from the West Rand Gold Field's underground workings, negatively impacting on the downstream environment, with impacts identified in both surface and underground water. In the years following this, underground operations ceased in the Central Rand and East Rand Gold Fields and the underground workings were allowed to flood.

Three approaches have been identified for the management of the flooded underground workings:

- Flooding and management of the discharge at surface.
- Maintaining the water level at a pre-determined safe level, locally referred to as an "environmental critical level" by pumping.
- Controlling the water level in the underground workings by means of a discharge tunnel.

Currently, pump and treat programmes are at various stages of development and implementation in the three original gold fields. Planning for these has been severely hampered by a lack of reliable historical data on volumes pumped. The absence of supporting data also led to the selection of conservative environmental critical levels, which will be extremely costly to maintain.

Adjustment of the environmental critical levels in the Witwatersrand Mines would require a good understanding of both the hydrodynamics of the relevant underground mine workings and the local hydrology and hydrogeology in the areas likely to be impacted, but would reduce pumping costs and could allow the implementation of gravity-driven drainage in some areas. It may also have a positive impact on the rate of flow into the underground workings and on the water quality in the longer-term.

Key words: Witwatersrand, Acid mine drainage, pumping, prediction

Introduction

Gold was discovered in what is now the City of Johannesburg in an outcropping conglomerate of the Witwatersrand Supergroup in 1886. Since the initial discovery, the Witwatersrand Basin, including the early discoveries in and around Johannesburg and the entire "Golden Arc" extending along a strike length of more than 300 km has yielded over 2 billion ounces of gold (Chamber of Mines of South Africa Accessed 2016) and more than 150 thousand tons of uranium (Nuclear Energy Agency 2014). Mining commenced almost immediately, extending rapidly along the outcrop to the West and the East. Three gold fields - The East Rand, West Rand and Central Rand (**Figure 1**) - were defined, based on zones of contiguous outcrop and suboutcrop of the gold bearing strata. These conglomerate layers were mined down-dip to depths of as much as 3 000 m in these areas. Soon after the commencement of surface mining in 1886, the surface workings intersected the local water table, necessitating the pumping of water from the workings (pers. comm. N Lane). As the early surface workings gave way to larger-scale underground workings, the need to pump water increased. At the same time, the underground workings of adjacent mines were connected to each other, allowing mines to share infrastructure as well as providing emergency access to the workings. This trend continued until the three large complexes of interconnected underground mines had developed.

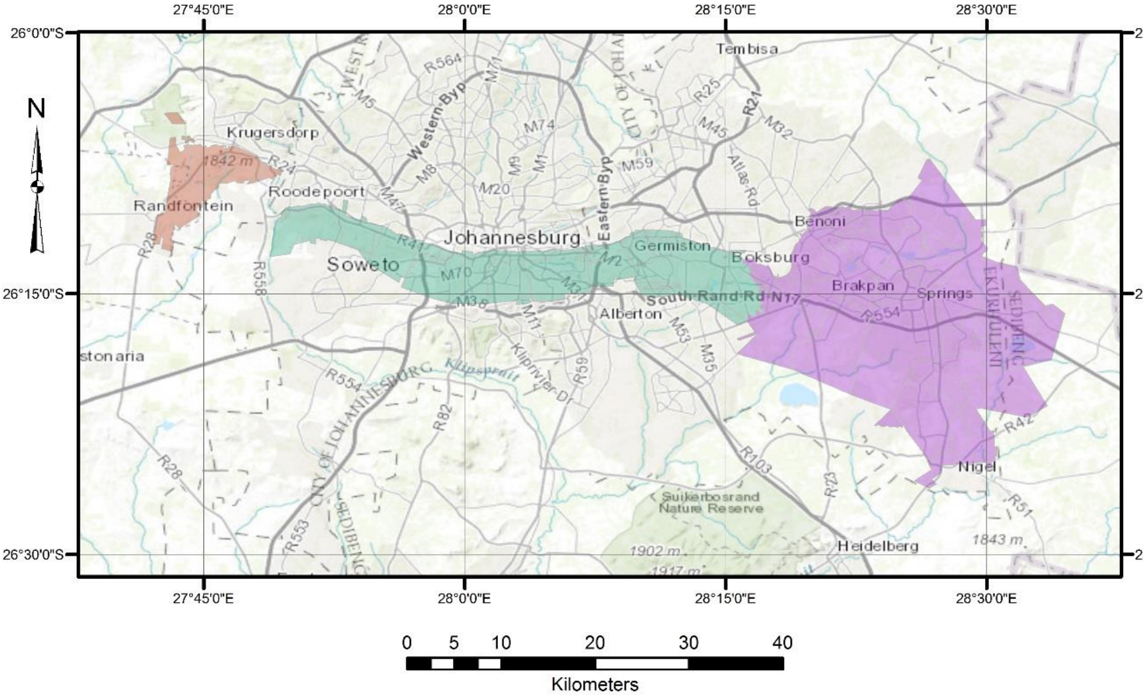

Figure 1. *Locality of the three original Witwatersrand Gold Fields, in and around the City of Johannesburg.*

Closure and flooding of mines

During the second half of the 20th Century, a combination of resource depletion and economic factors led to the successive closure of the mines in these three gold fields. The interconnection, which had optimised pumping when all mines were operational now began to count against the remaining mines, with adjacent mines discharging into each other via the inter-mine openings. As more and more mines closed, the responsibility for pumping fell onto fewer and fewer mines until the last operating mines – Randfontein Estates in the West Rand, East Rand Proprietary Mines in the Central Rand and Grootvlei in the East Rand ceased pumping in the late 1990s, 2010 and 2011, respectively. In all three cases, the mines were allowed to flood.

In September 2002, water began to discharge to surface from the underground workings of the West Rand. Owing to interactions with sulfides and other minerals in the ore, the water was acidic with substantial concentrations of sulfate and metals (Coetzee et al. 2002; Coetzee et al. 2005; Hobbs and Cobbing 2007). Plans were presented to lower the water level in the mine void to below an environmental critical level (ECL), initially looking only at surface discharge from low-lying shafts and adjacent springs and later revised to prevent contamination of groundwater. Pumping to achieve this objective commenced in April 2012 (Borralho 2014).

The prediction of the likely discharge rate from the underground workings in each of the gold fields is hampered by the limited historical records of volumes pumped which are available. Estimates of the volumes pumped during periods of active mining in the Central Rand and East Rand have been presented by Scott (1995), while Coetzee (2008) highlights the lack of reliable information to predict a discharge or required pumping volume for the West Rand.

Definition and establishment of Environmental Critical Levels

In 2010, following the impacts of the discharges in the West Rand and with the cessation of pumping imminent in the Central Rand and East Rand, an Inter-Ministerial Committee was established to assess the situation and recommend measures to manage the impacts of mine water in the Witwatersrand. A Team of Experts was appointed which delivered a report early in 2011 (Ramontja et al. 2011). This report recommended that water be pumped from the underground workings and that the water level be maintained at a level which will not lead to any surface discharge or groundwater contamination (Lin and Hansen 2010; van Biljon 2011).

Conservatively determined levels were identified, allowing for the prevention of surface discharge and the maintenance of the water level below any potentially useful aquifers as well as providing a buffer to allow for high recharge levels during particularly wet years. These levels, along with the historical water levels and likely surface discharge levels are shown on Figures **2** to **4** and **Table 1**.

Table 1. *Environmental Critical Levels for the three original Witwatersrand Gold Fields (Lin and Hansen 2010; Ramontja et al. 2011; van Biljon 2011)*

Gold field	ECL (m a.m.s.l.)	Rationale
West Rand	1530 m	Prevent discharge to surface and adjacent dolomite aquifer.
Central Rand	1503 m	Prevent discharge to surface and groundwater in lowest-lying portions
East Rand	1150 m	Maintain water level below dolomite where this overlies the mines and could have potential for groundwater supply

These levels were set conservatively, *i.e.* it may be possible to adjust them to shallower depths, saving pumping costs. However, this would require additional information regarding shallow groundwater levels and qualities to set a baseline and monitoring of the effect of mine flooding on the surrounding aquifers. Monitoring boreholes would be required to provide an early warning capacity to detect discharge from the mine voids to adjacent aquifers. Sufficient pumping capacity would also be required to lower the water level in response to indications of discharge or increased recharge during periods of high rainfall and above-average recharge.

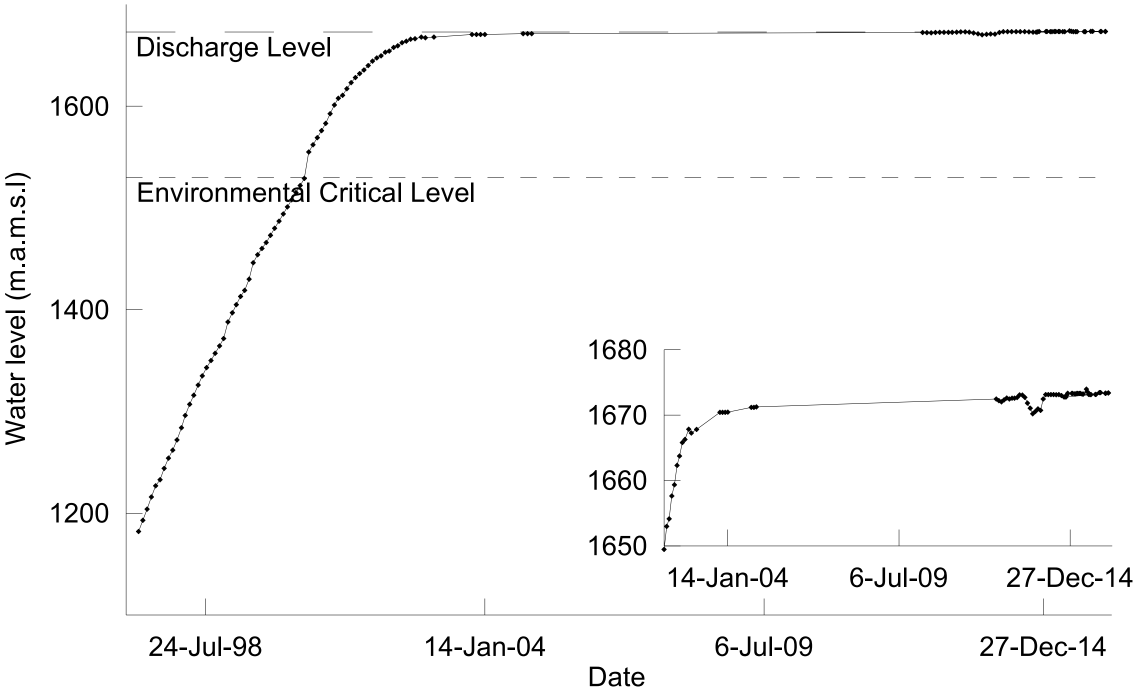

Figure 2. *Flooding of the underground workings of the West Rand Gold Field, 1997-2016 (Data compiled from monitoring of Randfontein Estates: Central Vent Shaft, Randfontein Estates: 18 Winze and Randfontein Estates No. 8 Shaft. Monthly average levels are presented for data collected since 2002). Inset graph shows recent data, since the first surface discharge and after the commencement of pumping.*

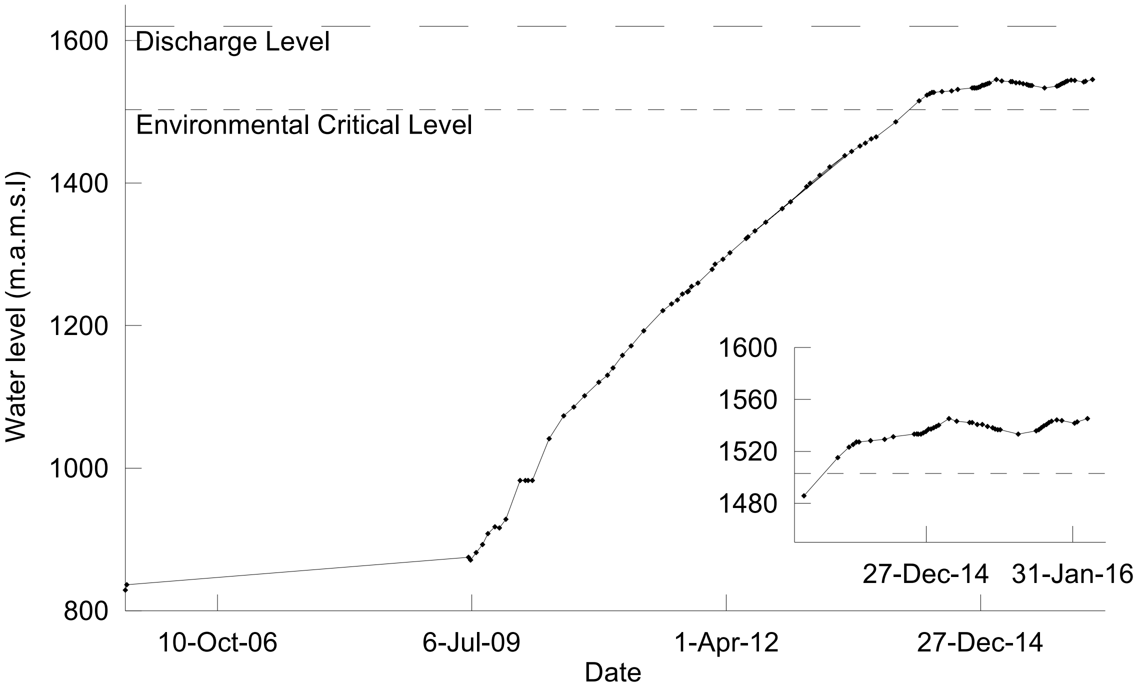

Figure 3. *Flooding of the underground workings of the Central Rand Gold Field, 2005-2016 (Data from Crown Mines No. 14 Shaft). Inset graph shows recent data, after the commencement of pumping.*

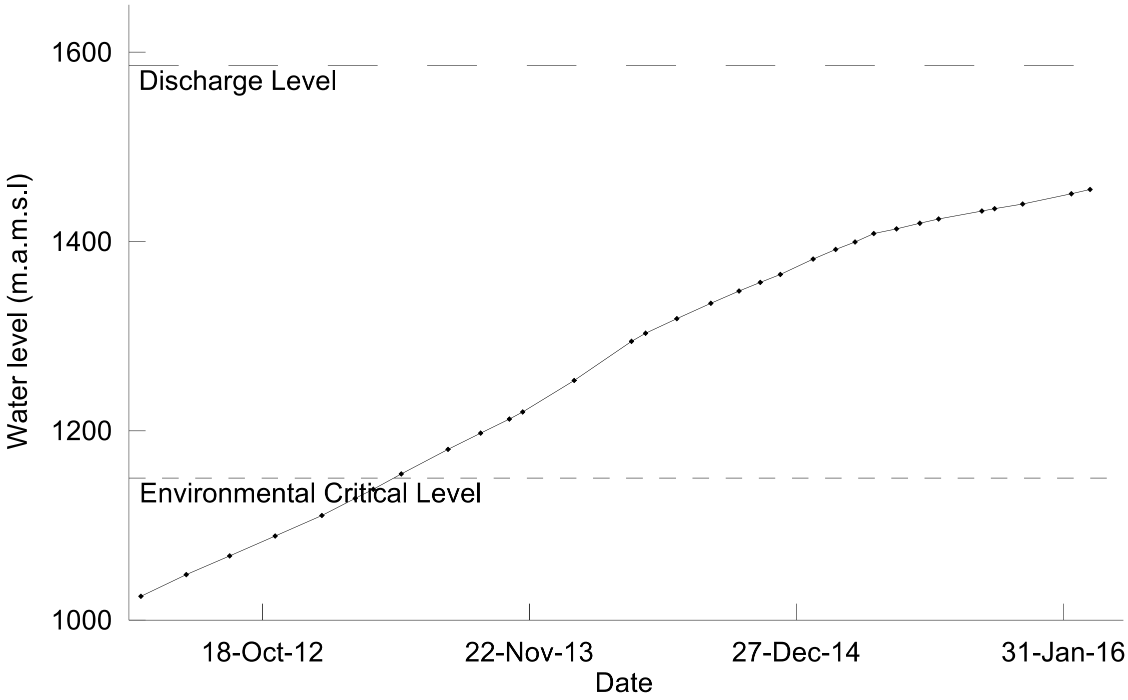

Figure 4. *Flooding of the underground workings of the East Rand Gold Field, 2012-2016*

Mine flooding and protection of the relevant Environmental Critical Levels

Figures **2** to **4** show the historical water levels in the underground workings of the three original Witwatersrand Gold Fields.

In the West Rand, water breached the surface before pumps were installed and has discharged through the lowest lying shaft continuously since then, with the exception of a period in 2013, when sufficient water was extracted from the void to lower the level by a few meters (inset graph on **Figure 2**). The volumes pumped have not been sufficient to control the water level within the underground workings. This may be exacerbated by the discharge of a wet tailings slurry into the void, which will displace water, requiring additional volume to be pumped to compensate for the volume it occupies.

In the Central Rand, the conservative ECL was breached before the pumps were commissioned in 2014. Water levels recorded since then show a small net rise, with a seasonal trend indicating increased recharge during the wet summer season. It is of concern that water levels have risen during the 2015/16 wet season, despite the region experiencing a severe drought. Nevertheless, no groundwater contamination has been reported in low-lying areas.

Similarly, the ECL in the East Rand has been breached. The pumps required to control the water level are scheduled to be commissioned during the course of 2016, after which an assessment of their effectiveness in controlling the water level within the underground mine workings can be assessed.

Potential relaxation of the environmental critical levels

The immediate effect of pumping from a shallower depth will be a substantial reduction in the pumping costs, which are large, given the volume, potentially totaling more than 200 ML/d across the three gold fields. Even a reduction in pumping depth of a few metres can have a substantial effect on costs, especially as the pumping and treatment of water is seen as a long-term measure.

Additional benefits of a shallower ECL may be the opening up of new options for water management in the long term. These include the construction of gravity-fed discharge tunnels (Council for Geoscience 2004), allowing the control of the water level within the underground workings without pumping, using a tunnel intercepting the workings at an appropriate level. Previous work on such a tunnel in the Central Rand identified this possibility but was deemed too costly, given the conservative estimates for the ECL which would require a very long tunnel to drain the underground workings at an appropriate level.

Groundwater quality is still not routinely monitored in all areas likely to be affected by rising water in the underground mine workings. The potential use of groundwater needs to be assessed in the low-lying areas within the gold fields to inform cost-benefit analysis to determine an optimal water level, balancing possible pollution against the cost savings which would result from pumping from shallower depths. An assessment of current groundwater quality in potentially affected areas is also required to determine the pre-existing impacts of surface activities and infrastructure on groundwater, in particular mine residue disposal.

Conclusions

The lack of provision for mine planning as part of the mine closure process in the three original Witwatersrand Gold Fields led to a situation where mines were abandoned and allowed to flood without sufficient information being available for detailed prediction of the rates of flooding and the possible consequences of water levels being allowed to rise in an uncontrolled fashion. This has led to a situation where an adaptive approach to mine water management needs to be adopted, based on limited information and conservative assumptions.

The breaching of the environmental critical levels has led to a situation where impacts need to be assessed and decisions regarding lowering of water levels based on ongoing impact assessment. The cost of lowering the water level in the underground workings is likely to be substantially greater than the cost of maintaining it, as, given the limited ability to maintain the water level in both the West

Rand and Central Rand, additional pumping infrastructure will be required to lower it. An adaptive approach can also be adopted, in which regular monitoring of groundwater levels and quality in the area likely to be impacted by rising water in the underground workings is undertaken and the results used in the determination of an optimal water level.

Water levels in the underground workings, volumes of water pumped and discharged are currently well monitored. This information, along with rainfall data will provide a fuller picture of the hydrodynamics of the Witwatersrand mines, assisting in the search for sustainable solutions to mine flooding.

The lessons learned from the three oldest gold fields in the Witwatersrand provide important insight into the management of the closure of other large interconnected complexes of underground mines. Better understanding of the volumes of water which need to be managed as well as the flow dynamics, seasonal variations etc. are essential to minimise long-term liabilities at closure.

Acknowledgements

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Experience of Mine Water Quality Evolution at Abandoned Uranium Mines in Germany and the Czech Republic

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Extended Abstract

From 1945 to the mid 1990's uranium mining was an important branch both in Germany and the Czech Republic. However, a marked phase-out of the industry in the 1990's led to the closure of all underground uranium mines except of Rozna in the Czech Republic. Recently, uranium mines were decommissioned by natural flooding and mine waters are either kept below their decant point by pumping (and water treatment) or the flooded mines have been abandoned with natural mine water discharges.

Wismut (Germany) and DIAMO (Czech Republic) are in charge of remediation and aftercare activities and regularly monitor the quality of the uranium mine waters.

The study presents analyses and the comparison of the experience from long-term mine water monitoring, being performed by WISMUT and DIAMO, in relation to the time since mine closure has commenced as well as the geological and mining conditions.

Principal component analysis and geochemical modeling represent the tools being used for the analyses performed. Similar study has been recently done by Rapantova et al. [1] only for Czech deposits. The paper will describe the validation of results on the common data set of Czech and German uranium mine water discharges. The mine water quality changes with a focus on uranium mobility will be described from recently dewatered mines to shafts with water level maintained in order to prevent outflows to surface water and finally to stagnating shafts and discharges of mine water from old adits. The results are in good agreement with published experience on mine water stratification, its disturbance by pumping or natural water decant and the "first flush" phenomenon after mine flooding.

Studying the natural processes that take place in mine waters of flooded deep mines is very difficult due to the inaccessibility of remote parts after flooding. However, predictions on the rate of the gradual decrease of pollution depending on the complexity of flow dynamics and natural attenuation processes are valuable for planning of remediation and aftercare measures. Although these processes are very complex and site-specific, comparison and analyses of acquired data from German and Czech uranium mines give a chance to improve the general understanding of the physicochemical processes that occur after mine closure.

Key words: uranium, mine water, abandoned mines, PCA

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Pycnocline Dynamics in an Abandoned and Flooded Mine

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Abstract

Data from our time-lapse sampling and measurement campaign on an abandoned mine in Germany revealed an unstable stratification. Significant but reversible dynamics in pycnocline depths were found to be due to changes in physico-chemical characteristics of the upper water layer above a stagnant water body with high mineralization and density. We observed at times the collapse of the stratification. The dynamics of the layering was caused by an increase in temperature, mineralization, and thickness of the upper layer, hence decreasing the density difference until reestablishing of the upper layer by groundwater recharge of low density.

Key words: Mine water, abandoned mine, pycnocline dynamics

Introduction

This study was performed on one of the many abandoned and flooded mines in the Siegerland-Wied-District of the Rhenish Massif, a Variscan mountain range in the central part of Germany mainly consisting of Devonian schists. Within the area, there are a large number of historical iron and non-iron ore deposits. Mining continued over a period of more than 2000 years but ultimately ceased in 1965. Because of subvertical oriented ore veins, the underground mining reached depths of more than 1000 m. Our aim was to investigate the mine "Grube Georg" for their hydrothermal reservoir and storage potential [1]. The water body in flooded mines is often stratified. However, unlike the case with open waters, data on dynamics of this stratification are scarce.

Geology of the mine "Grube Georg"

The abandoned mine "Grube Georg" is situated in the Wied Ore District in the middle of the Rhenish Massif near the town Willroth directly beside the national highway A3. The dominating Devonian schists are hydrogeologically characterized as joint aquifers with low rock permeability. Interbedding layers of greywacke and sandstone have higher permeability. Fractured quartz and ore veins may also store groundwater. In particular, the mined and backfilled ore veins have high water capacities of ±50%. The ore veins are intensively divided by geological fault zones.

The mine was opened up by two transport shafts, one ventilation shaft, and 23 deep mining tunnels (Fig. 1). The two main shafts were worked down to 967 m and 907 m depth below surface. The mineralization within the steeply inclined veins is dominated by siderite ($FeCO_3$). The ore veins covered an area of up to 860 m^2 on the 100 m floor, 4790 m^2 on the 600 m adit, and 2060 m^2 on the 800 m floor.

During mining activities, the veins were excavated completely and the caverns refilled by excavation material. The volume of mined veins can be estimated at nearly two Mio. m^3. The stagnant water within the drained shafts, adits, and fillings has still a volume of about one Mio. m^3 (Wieber et al., 2011). While the hydraulics can be described simply as a communicating pipe system controlled by the open shafts and adits, there are also high permeability zones of mined veins and other voids with stope fillings. Both laminar and/or turbulent flow is to be expected in such complex hydraulic systems (Wolkersdorfer, 2006).

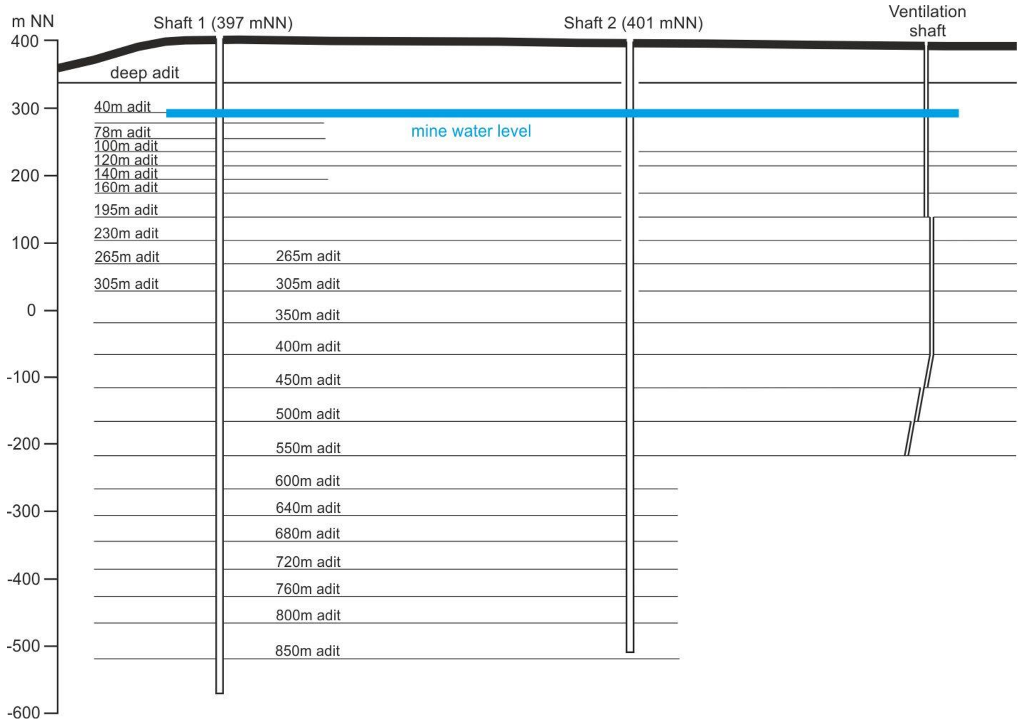

***Figure 1**: Cross profile of the mine "Grube Georg", Rhenish Massif (Germany)*

Hydrochemistry of the mine water

The mine water level was detected at a depth of about 100 m. Groundwater of the saturated zone is actually accessible by shaft #2 only [4] . Water was sampled and analyzed at times over a couple of years (Tab. 1). A debris barrier within shaft #2 hampered measurements below a depth of 65 m.

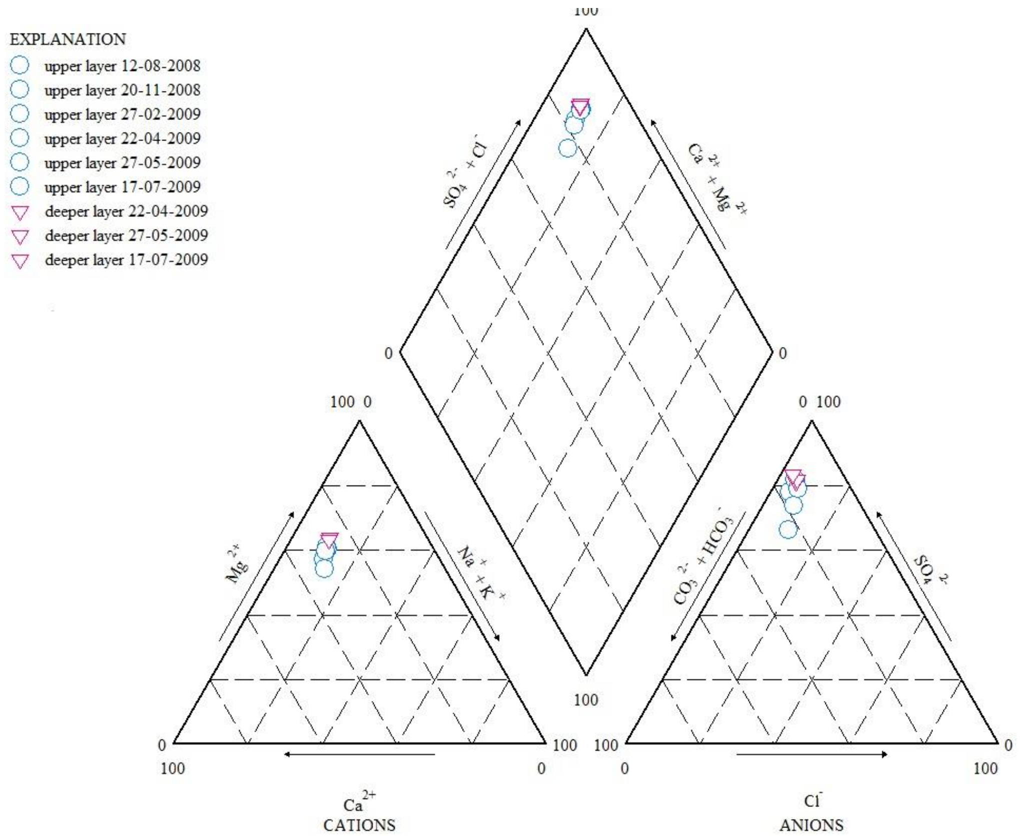

***Figure 2** Piper diagram of mine water*

Table 1 *Composition of mine water samples.*

	Upper layer	Deep layer
Sampling dates	12.08.2008; 20.11.2008; 27.02.2009; 22.04.2009; 27.05.2009;17.07.2009	20.11.2008; 22.04.2009; 27.05.2009; 17.07.2009
Depth below groundwater surface [m]	7 bis 30 m	50 bis 65
Temperature [°C], in situ sensor	15.4 bis 17.8	19.6
pH	7.48 bis7.90	7.39 - 7.45
$eH_{cor.}$ [mV]	278 bis 482	104 - 162
Conductivity [µS/cm]	920 - 2060	2810 - 2840
O_2 [mg/L]	3.1 - 6.3	0.4 - 0.8
Na [mg/L]	36.9 - 78.8	86.5 - 86.8
K [mg/L]	15.5 - 23.6	23.4 - 24.1
Ca [mg/L]	98.0 - 211	229 - 232
Mg [mg/L]	99.0 - 278	328 - 342
Cl [mg/L]	56.4 - 83.8	51.1 - 82.0
SO_4 [mg/L]	480 - 1470	1720 - 1770
HCO_3 [mg/L]	214 - 317	351 - 369
Fe [µg/L]	<25 - 1260	4330 - 4500
Mn [µg/L]	40 - 1930	4160 - 4730
Zn [µg/L	<3 - 120	<3 - 85
Pb [µg/L]	<15 - 60	<43
As [µg/L]	<30	40 - 80

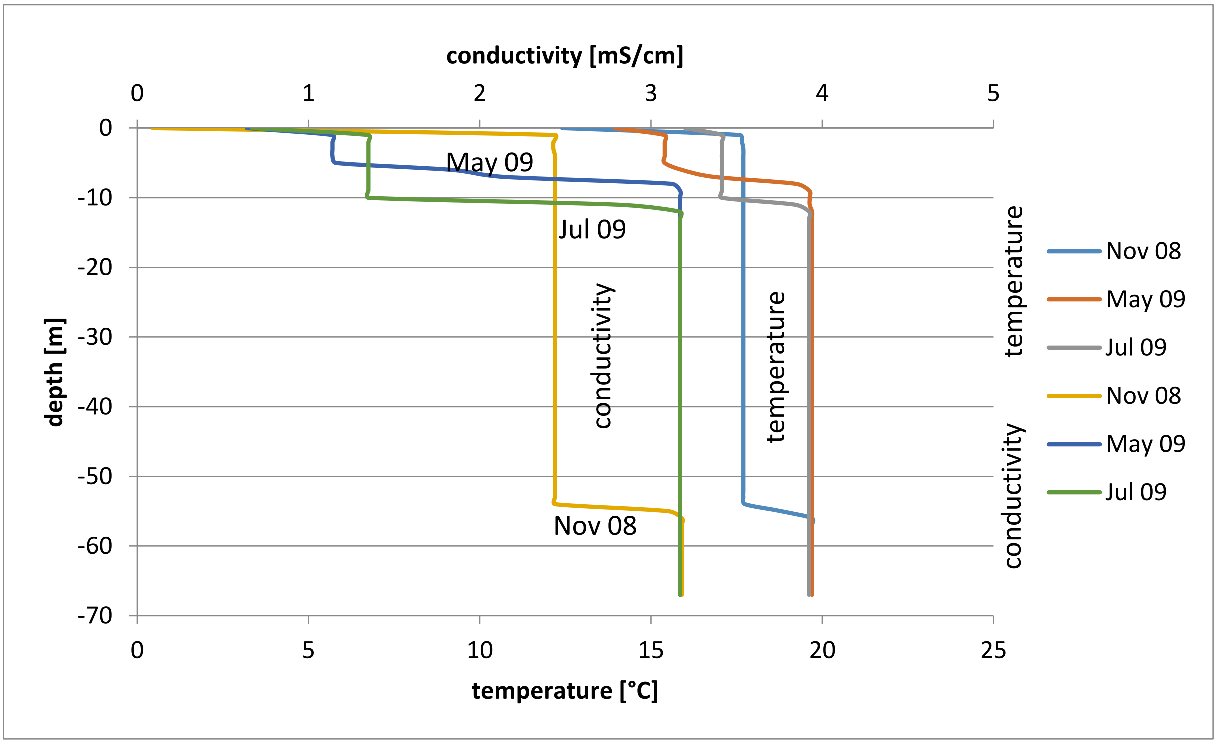

Figure 3*: CTD profiles and depth of the boundary layer measured in 2008 and 2009*

Electric conductivity and temperature (CTD) logs revealed a strong stratification in the years 2008 to 2009, with a quite steep pycnocline at 55 ± 0.4 m depth in November 2008 (Wieber et al., 2011). The upper layer was characterized by temperatures of 15.4 – 17.8 °C (CTD) and electrical conductivities of 0.920 - 2.06 m. The hydrochemical composition of the deep stratum with higher temperature and mineralization did not change during the period of investigations. Sulfate and alkaline earth metals (Fig. 2) dominate the water chemistry. The concentrations of total dissolved (0.45 µm membrane filtered) Fe and Mn were increased, whereas other trace elements (Zn, Pb, As) were detected at low levels only (Tab.1).

Surprisingly, end of May 2009 a change in pycnocline depth has been found (Fig. 3). The upper water stratum was found now at a depth of only 7.2 ± 1.2 m, with a significantly lower temperature of 15.4 °C and conductivity of just 0.92 mS/cm and, hence, a much steeper pycnocline with density difference of 1.3 kg/m^3 (Tab. 2). Already two month later, the density has been found to slowly increase again to 1.14 mS/cm, and the pycnocline was found 4.6 m lower in depth. No any significant change was found in physicochemical characteristics of the lower stratum.

Thermodynamic calculations using the PHREEQC v.3 code with the minteq.v4 database (Parkhurst et al., 2013) indicated that the upper water body was undersaturated while the deep water was at equilibrium (SI = 0 ± 0.5) with gypsum, calcite/aragonite, magnesite, rhodochrosite, siderite, and Na-jarosite. Geochemical equilibration with such minerals typical for the oxidation zone suggests that there was a very minor deep recharge of groundwater, i.e., the groundwater is stagnant.

***Table 2**: Mine water saturation conditions*

	Mineral phases	Saturation index (SI) upper layer	Saturation index (SI) deeper layer
n	number of analyses	6	3
Carbonates	Aragonite $CaCO_3$	-0.10 bis 0.52	0.16 bis 0.25
	Calcite $CaCO_3$	0.10 bis 0.73	0.36 bis 0.44
	Magnesite $MgCO_3$	-0.47 bis 0.26	-0.16 bis -0.08
	Rhodochroisite $MnCO_3$	(-1.38) 0.05 bis 0.37	0.53 bis 0.68
	Siderite $FeCO_3$	-6.10 bis -2.03	0.11 bis 0.22
Sulfates	Anhydrit $CaSO_4$	-1.30 bis -0.79	-0.73 bis -0.71
	Epsomit (Bittersalz) $Mg(SO_4) * 7H_2O$	-3.21 bis -2.53	-2.47 bis – 2.50
	Gypsum $CaSO_4 * 2 H_2O$	-1.02 bis -0.48	-0.44 bis -0.45
	Na-Jarosite $NaFe_3(SO_4)_2(OH)_6$	-0.30 bis 2.58	0.26 bis 0.52
Fe mineral phases	Na-Jarosite $NaFe_3(SO_4)_2(OH)_6$	-0.30 bis 2.58	0.26 bis 0.52
	Siderite $FeCO_3$	-6.10 bis -2.03	0.11 bis 0.22
	Ferrihydrite $Fe(OH)_3$	2.87 bis 3.73	2.84 bis 2.97
Mn mineral phases	Rhodochrosite $MnCO_3$	(-1.38) 0.05 bis 0.37	0.53 bis 0.68

Model of stratification dynamics

The hypothesis of a stagnant water body is corroborated by the fact that there were relatively low water volumes to drain out of the system during active mining, e.g. on the 680 m floor the drainage was only 0.015 m^3/s (Fenchel et al., 1985). Although the mining area is located on a water divide without inflow of upstream groundwater and characterized by a mean surface precipitation of up to 1000 mm/a, because of the low Devonian sedimentary host rock permeability, the drainage regime is dominated by surface runoff.

A key to understand this anomalous pycnocline dynamics lies in the decline of the density difference. In between August 2008 to November 2008, it decreased from 0.47 kg/m^3 to 0.35 kg/m^3. This was due to increasing mineralization of the upper stratum as indicated by a rise in conductivity and decreasing undersaturation with respect to above mentioned minerals. This increasing mineralization has led to a break-up of the stratification in between 11/2008 and 5/2009. For reestablishing of the fresh water stratum, and a rise in depth of the pycnocline by 2 m/month, a groundwater drainage of 40 m^3/month is necessary.

***Table 3**: Mine water densities*

Sampling dates	Density of the upper layer (kg/m^3)	Density of the deep layer (kg/m^3)	Difference (kg/m^3)
12.08.2008	1000.61	1001.08	0.47
20.11.2008	1000.73	1001.08	0.35
17.07.2009	999.77	1001.08	1.31

Main implications of the knowledge about the dynamics in physicochemical water characteristics are for the potential use of the mine water body as a geothermal reservoir and storage system (Wieber et al., 2011). This may become severely hampered by a less stable temperature regime. Therefore, the pycnocline dynamics has to be monitored to understand the extent and key factors driving this dynamics.

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Water management issues in an abandoned coal mine district (Torre del Bierzo, Spain)

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Extended Abstract

The Carboniferous basin of El Bierzo has been intensively exploited by underground mining since the 19th century, and although the extractive activity is currently very low, mine shafts, spoil heaps, coal washeries and other mining installations remain as a legate of the historical mining activities in the district. From this coal mine district, the presented study is focused into the Torre del Bierzo Sector, where abandoned coal mines from nine different mining groups coexist and the underground works are expected to be interconnected.

In a geological context, the Torre del Bierzo Sector is located in the south branch of the Asturoccidental-Leonesa Zone. The most significant characteristics of this Sector are the great thickness of the Lower Paleozoic (Cambrian and Ordovician) and the almost absence of post-Devonian materials, with the exception of some Carboniferous areas (the own coal basin) and tertiary/quaternary materials. The original permeability of the paleozoic rocks is generally very low but it may be locally important in areas affected by fracturing of the suprayacent rocks (secondary permeability); then, in general, the infiltration rate through these materials cannot be considered as very relevant. The tertiary-quaternary materials constitute a permeable detrital aquifer having a low permeability in general, which can be variable according to the lithological composition; with the highest values corresponding to the more abundance of sands and conglomerates.

From an hydrogeological point of view, from a pre-mining stage with aquifers of small importance, the extractive operations induce a post-mining stage with aquifers of triple porosity (intergranular porosity, fractures and mine voids) which can be assimilated to a karstic carbonated aquifer; the fracturation of the coal beds suprayacent materials as a result of the mine operations, increases the original permeability of the rocks and provides the infiltration of the rain water. The pump cessation option gives to the flooding of the mine voids and the creation of an underground mine reservoir, and in consequence to the overflow of the mine waters by the lowest mine portal of the whole system or by permeable levels located at a lower topographic cote, where mine water will present variable flow and quality depending on the characteristics of the geological formations, the drained system and on the exploitation technology.

In order to know if the mine works from the different groups of the mine sector act as an whole hydraulic system drained to the surface waters by one of the shafts, and to have an estimation of the mine water flow, origin and continuity of the water flow over the time and chemical quality, a geological, hydrological, hydrochemical and hydrogeological study has been accomplished. The water contribution received by each one of the mining subsystems (resources) anyway the whole volume of water stored on the mine voids (reserves) have been estimated too. To know if potential interconnections which could to define one or more hydraulic systems that could be considered as underground mine reservoirs (ponds) or to consider only the potential water interconnections through low permeability massifs has been studied.

The water resources for each group have been calculated independently, considering the infiltration of effective rainfall –according to the permeability of outcrops in their drainage basin-, the infiltration from agricultural irrigation and the losses from watercourses into the mining works. This calculation has allowed estimating which groups are currently drained at the point of discharge, the average drainage flow of the system (40-50 $l \cdot s^{-1}$) and the effective volume of the underground mining reservoir (10^6 m^3), which could be employed for mine water storage and water or geothermal use. This drainage is currently discharged into a small creek and high concentrations of Fe, Mn and sulphate are sometimes reached.

The hydrogeological definition of the system implies this discharge will remain permanently, with a flow variable upon the volume and intensity of infiltration. However, given that agricultural activity in the area has decreased significantly, it would be desirable to avoid irrigation and river losses by performing a bypass, waterproofed over the most heavily mined areas. This would reduce the supply of mine water and improve its quality, avoiding fluctuations in the level of filling of the reservoir.

The fact to maintain a centralized pumping on the mine operations in one of the groups and the mine water discharge which is actually at the lowest mine portal of the whole system in the district, point out that the whole of the underground mine works in the district are interconnected and that the receiving water is drained towards this mine portal as corresponding to an unique hydrologic system. An approximate estimation of the water resources for each one of the mine groups for a standard hydrological year has been calculated according to a methodology de-signed for the case having in mind the cartography and the geological sections find in the bibliography.

Key words: mine water, abandoned coal mine, mine water reservoir

Comparing Acid and Metal Loading Before and After Stream Capturing Subsidence Closure

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Abstract

Closing stream-capturing subsidences over abandoned coal mines prevents surface water from entering mine voids and reacting with sulfide materials (pyrite) and oxygen. The common assumption that closures will improve water quality in discharges and receiving streams was tested at multiple sites by comparing acid and metal loadings, pre- and post-closure, using the Stoertz Water Quality Evaluation Method. Proven an effective tool for comparing loading estimations at mean annual flow, even with small sample size, this method still required complete, accurate, and precise data that spanned all flow regimes for statistically significant results. Four test sites in the Wayne National Forest in Ohio were selected for analysis based on data availability in the receiving water bodies.

Where adequate data existed, acid and metal loadings showed reductions after closure, in spite of measured increases in constituent concentrations, due to reduced flows attributable to subsidence closure. The Stoertz Water Quality Evaluation Method was applied to four subsidence closures to analyze the water quality changes due to the project. Two key conclusions can be made from this study. First, monitoring should be planned to collect sufficient time series data to represent chemical conditions across a typical range of flow regimes to facilitate evaluation of water quality changes. Second, this study suggests that subsidence closures do reduce acidity and metal loadings by reducing flow rate, while post-closure acidity and metal concentrations may be higher than pre-closure.

Key words: mine water, subsidence closure, coal mining

Introduction

The vast majority of underground coal mines in Appalachia were opened, “worked out” (meaning as much coal as possible was removed), then simply abandoned at closing (Abramson & Haskel 2006). Mining technique coupled with area geology often left insufficient support for portions of mine roofs, which collapsed, providing pathways for air and surface water to enter the voids left by extracted coal (Hill & Bates, 1979). Water and oxygen react chemically with minerals left exposed in the coal, producing acidic metalliferous drainage (Singer & Stumm 1970). The resulting discharge from mines, known as acid mine drainage (AMD), has degraded thousands of miles of streams in Appalachia (US EPA n.d.), as well as innumerous watersheds worldwide (Bell *et al.* 2000).

Coal mine subsidence occurs when materials overlying a mine void collapse into the empty space left by extraction of coal, causing a depression, hole, or fissure in the land surface over the mine. “Bulk,” or larger, broken up pieces of what comprised the room roof, piles up below the collapse, followed by layers of each subsequent strata material until all layers unable to bear the stress have subsided. In room and pillar mining, it has been shown that overburden up to about 30 times the height of the mined room can subside (Bell *et al.* 2000). Subsidence effects are lessened as the depth of overburden increases. A 4 foot high room at a depth of 130 feet may not show any surface effect at all, for example, compared to a 2 foot high room only 10 feet below the surface. Never, however, does bulk completely fill the mine void (Bell *et al.* 2000; Hill & Bates 1979). Ample space remains for flow of water and/or air, and allows for the possibility of further subsidence. Indeed, even in mine backfilling theory and technology, employed when developing mined areas, further subsidence is expected, and building plans over backfilled areas are designed to withstand a calculated amount of shift (Zhang *et al.* 2015).

Any number of stressors may trigger and influence land subsidence. In fact, mine subsidence is difficult to prevent and anticipate because so many factors may be involved (Marino & Abdel-Maksoud 2006, Lee *et al.* 2013; Bell *et al.* 2000). Lee *et al*. note that "data on subsidences are mostly qualitative and are difficult to convert into quantitative measures" (2013). Influencing factors include the type and depth of mine, type and depth of overburden, groundwater levels, possibility of inundation during high flow events such as torrential rain or flooding, mining method employed in extraction of material, proximity to ground faults, geologic stability, surface activity, airflow, and subsurface erosion (Bell et al. 2001; Bell *et al.* 2000; Hawkins & Smoyer 2011; Hill & Bates 1979; Marino & Abdel-Maksoud 2006; Wei *et al.* 2011; Winters & Capo 2004). Even using the recommended standard room and pillar removal ratio of 1:1, which is generally accepted to be the highest safe ratio (Bell *et al.* 2000; Hill & Bates 1979), subsidence may still occur. In "pillar robbing," subsidence is expected when pillars are mined further on the way out of the spent mine.

Methods for correction of mine subsidences typically utilize one of two approaches, or both: 1) filling and waterproofing an open subsidence so that it no longer captures surface water and sends it into the mine void; or 2) re-contouring and rerouting stream water around the open subsidence. The standard method of closing a stream capturing subsidence used in the Wayne National Forest (WNF) is to clear the area around the subsidence of trees and brush, then back fill the subsidence hole with limestone rock to the level of the mine roof. Borrow material, generally taken from an area close to the site is then used to fill in the remainder of the hole, and compacted. The area is contoured, then lined with an impermeable geo-synthetic clay liner, covered with topsoil and re-vegetated or lined with limestone rock if the subsidence was in a stream channel (Wayne National Forest 1997).

Restricting surface water from entering mine voids is often referred to as a method of preventing AMD from forming, thereby improving water quality (WQ) downstream (e.g. Bell *et al.* 2000; Fields 2003; Kleinmann 1990; Monday Creek Restoration Project 2005; USACE 2005; Wolkersdorfer 2008). Monday Creek Management Plan describes the problem with subsidence, saying "…collapsed overburden captures surface water into the mine voids, allowing contact with sulfide minerals and oxygen, thus generating AMD within the watershed" (Steinmaus & Black 2005). The 2005 final report for the Inventory of Abandoned and Inactive Mines, performed on WNF property by the Army Corps of Engineers (USACE 2005), states "The goal of stream subsidence closures is to…reduce AMD generation by preventing contact between stream water and pyritic minerals located within the underground mines." This is a logical assumption given the known chemical reaction when water, oxygen and sulfide materials (e.g. pyrite) combine (Singer & Stumm 1970). Hill and Bates noted that "water control methods appear intuitively to be good ways to reduce AMD, but their effectiveness has not been well documented" (1979). To this day, few studies have tested this assumption. This study aimed to determine if closing stream capturing abandoned coal mine subsidences affects WQ at their associated discharges.

Methods

Geographic Information Systems (GIS) query of the Abandoned and Inactive Mines (AIM) Inventory database identified 55 closed stream capturing subsidence features in Monday Creek Watershed, southeastern Ohio. Selection by location on a per closure basis, looking for WQ sampling sites within a 10 meter distance of the 55 identified closures did not reveal adequate sites for analysis, so a per mine or drainage area approach was taken instead. The GIS database allowed for a search of existing WQ data at or near discharges and flow paths where captures would have likely discharged prior to closure. Estimating flow paths considered the average 30% southeast slope of the coal seams in the area, and, using georeferenced hand-drawn historical mine maps showing the room and pillar orientation of each mine, identified 5 closed subsidences (Figure 1) which had likely discharge seep or drainage areas where adequate data existed for analysis.

Of these five closures, four were located over one large mine, with two likely discharges with adequate data for analysis. These were separated into two separate sites, with two different drainage points. Long Hollow, the tributary receiving discharge from a seep likely fed by two of the identified stream captures, gave its name to one site. The site with the other two subsidences over the same mine complex was named Cawthorn, for the name of the FS closure project of one subsidence. The other identified closure site was in the drainage area of one large FS treatment project, called Coe Hollow.

In addition to the sites selected with the GIS process, a fourth site, named Majestic Mine was selected for re-analysis of data from two prior thesis projects (Pigati 1997, Graham 2006).

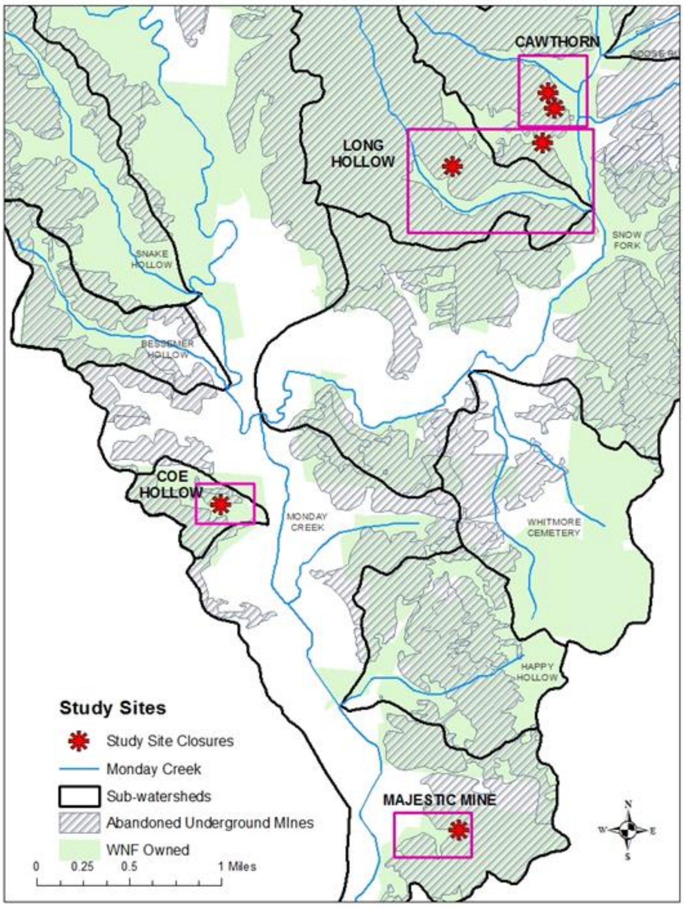

Figure 1 *Proximity of study areas, notated by pink boxes, to area streams, mapped underground mine workings, Wayne National Forest (WNF) ownership, and related subsidence closures, notated by red stars.*

Sample collection records, including field and laboratory data were downloaded from the web database, watersheddata.com. WQ data stored in the database is collected in a manner consistent with Ohio Environmental Protection Agency (OH EPA) WQ collection standards and evaluated at OH EPA certified laboratories, following standards detailed in “Quality Assurance Quality Control (QAQC) Plan for Surface Water Quality Data Collection and Analysis,” developed by Ohio Department of Natural Resources Division of Mineral Resources Management (ODNR-DMRM) (Bowman *et al.*, 2015). Most chemical data in the database is analyzed by the ODNR analytical laboratory, in Cambridge, OH.

Data for the Majestic Mine, which does not appear in the AIM Inventory because the site was remediated prior to the start of that study, and has not been routinely monitored for WQ, came from two Ohio University Masters theses which studied the mine (Pigati 1997, Graham 2006). Five WQ data samples taken between May and December of 1996 for the 1997 Pigati thesis contained the necessary parameters for analysis. Tennessee Valley Authority (TVA) chemical laboratory, utilized by the Forest Service (FS), analyzed the sample collected on 5/6/1996 and 12/9/1996, and ODNR laboratory in Coshocton, OH performed analysis on the other three samples. Pigati recorded flow measurements at the mine seep using a Parshall Flume (1997). In a 2006 thesis Graham completed fourteen sampling events from February to August of 2001. Flows for the study were measured with the same Parshall Flume used in the previous Pigati study. Graham collected all water samples in accordance with water sample collection methods dictated by the TVA laboratory (Graham 2006).

The Stoertz Water Quality Evaluation Method (Stoertz Method) was used to compare pre- and post-closure WQ data at each study site, to estimate loading relationships of acidity and metals before and after subsidence closure. This method is an easy way to assess loading behavior across flow regimes, and pre- and post-intervention, by comparing loadings at a consistent flow regime. The method has been used to assess treatment system performance in southeastern Ohio for more than a decade. The Pine Run Stream Capture project monitoring in Sunday Creek, Ohio, for example, utilized the Stoertz Method to report load reductions following the closing of a stream capturing subsidence (Bowman, 2011). The Stoertz Method is the method employed to determine statistically significant relationships in loading in AMD watersheds, even with small data sets (Kruse *et al.*, 2014). Prior to the development of this method, direct average loadings were compared over a specified period, (e.g. yearly), by multiplying flow times concentrations and then averaging. Direct comparison did not however, provide a means of comparison at a consistent flow regime, nor does it give indication of flushing behavior.

Using the Stoertz Method, loading, flow times concentration, adjusted for units, in this case pounds per day, was log transformed to provide a linear comparison of constituent loading (l) at annual flow (Q_n), pre- and post-remediation activity. Log normalized flow and log loadings with their flushing factors (F), were then plotted to compare in a linear relationship, pre and post-remediation, by means of the following equations:

$$L = l\,(Q/\mathit{Q})^F = l\,Q_n^F \qquad \text{Equation 1}$$

$$\log L = \log l + F \log Q_n, \qquad \text{Equation 2}$$

where F is flushing factor such that $F = 0$ in pure dilution, $F > 0$ for flushing behavior, and $F < 0$ for sparing behavior (Kruse *et al.* 2014). The difference between pre- and post-closure loadings, at the mean annual flow, indicated the estimated change in loading of parameters evaluated.

Mean annual discharge at seep sites (Cawthorn, Coe Hollow, and Majestic) were estimated by averaging measured flows. Mean Annual Discharge for Long Hollow, which considered the entire hollow drainage area for regressions, was estimated by utilizing the US Geological Survey (USGS) Streamstats program (http//streamstats.gov) to arrive at the Long Hollow drainage area, then multiplying draiage area by 1.01, the value of mean annual estimated discharge for basins in the Western Allegheny Plateau (Koltun & Whitehead, 2002).

To arrive at loading estimations Fe, Al, and Mn concentrations were added together to arrive at total metals. Flow measurements normalized by mean annual flow, acid and total metal loads were log transformed, and plotted on a scatter chart. Intercepts are at mean annual flow. Taking the inverse log of the intercepts returned loading estimations at mean annual flow in pounds per day. Post- closure loading estimations were subtracted from pre-closure loading to determine changes in loading from pre- to post-closure.

R^2 values were generated for all regressions to evaluate the fit of the lines, where results closer to 1 indicated best fit, with p values less than 0.05 judged to be statistically significant. All results were evaluated for agreement with the hypothesis that reducing flow into mine voids by closing stream capturing subsidences will improve water quality downstream, with particular weight given to statistically significant results.

Results

Regressions using the Stoertz Method for the Long Hollow site shown in Fig. 2 and 3 show an estimated daily acid load reduction of 3.14 lb/day (1.42 kg/day), and metal load reduction of 3.33 lb/day (1.51 lb/day). Compared to pre-closure loadings of 67.24 pounds per day of acid and 10.98 pounds per day of metals, this is a 4.68% acid load reduction and 20.32% reduction in metal loading. Analysis also revealed that the flushing factor changed from $F > 1$ pre-closure, to < 1 post-closure, indicating that pre-closure behavior purging had changed, post-closure, to sparing. This suggests some structural change influenced the flushing mechanism in the sub-watershed.

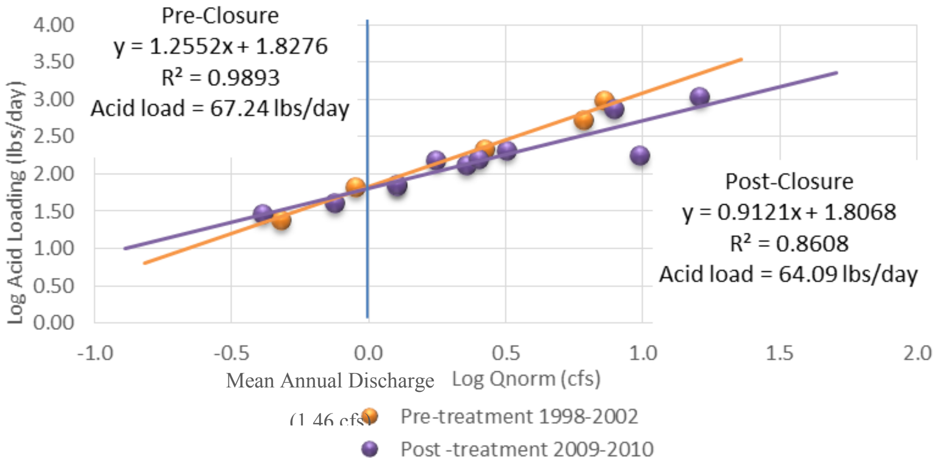

Figure 2 Long Hollow regression graph showing acid loads at mean annual discharge (acid load = 67.42 lbs/day pre-closure and 64.09 lbs/day post-closure), change in flushing behavior (F = 1.26 pre-closure and F = 0.91 post-closure), and trend lines with good fit (R^2 = 0.98 for pre-closure and R^2 = 0.86 for post closure).

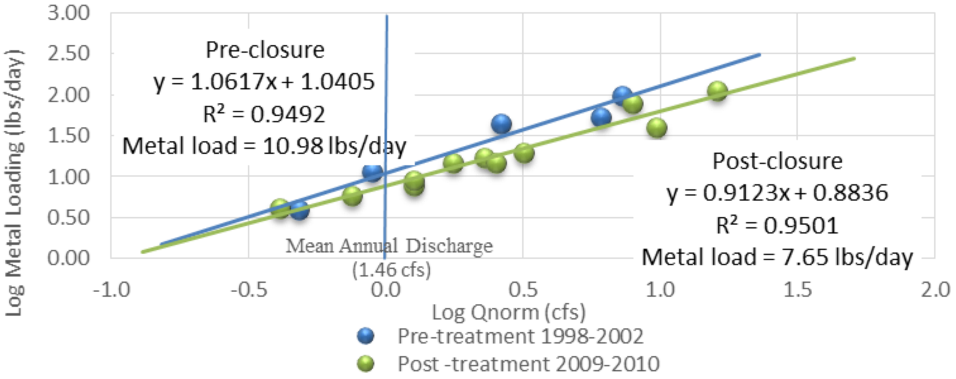

Figure 3 Long Hollow regression graph showing metal loads at mean annual discharge (1.46 cfs/mi^2) (metal load = 10.98 lbs/day pre-closure and 7.65 lbs/day post-closure), change in flushing behavior (F = 1.06 pre-closure and F = 0.95 post-closure), and trend lines with good fit R^2 = 0.95 pre-closure and R^2 = 0.95 post-closure).

Analysis at Cawthorn was stopped upon making the discovery that two historical data points were sampled at the wrong location, but it seemed worthy of note that the two sample events that were taken at the seep for this study, on preliminary analysis, returned lower acid and metal concentrations than pre-closure samples taken during comparable flow regimes. Accurate data could have helped to show if this is a seasonal anomaly or a trend in the mine discharge across flow regimes.

Average acidity concentration at Coe Hollow seep pre-closure was 264.7 mg/l, while post-closure acidity averaged 367.1 mg/l. This average was elevated by what appeared to be a flushing event in June of 2011 which had an acidity concentration of 862 mg/l, more than double other acidity measurements. Metal concentration results were mixed; average Fe decreasing by almost 75%, and Al and Mn both increasing by approximately 62% and 25% respectively.

Stoertz Method regressions of the Coe Hollow data shown in Fig. 4 and 5 showed a decrease in acid loading by 19.7 lb/day (8.9 kg/day), and a metal load reduction of 17.3 lb/day (7.8 kg/day). This is a 5.46% reduction in acid load and a 26.7% reduction in metals from pre- to post-closure data. Regressions on post-closure data were determined to be significant ($p < 0.05$); however, pre-closure p-values were > 0.05 due to the small data set.

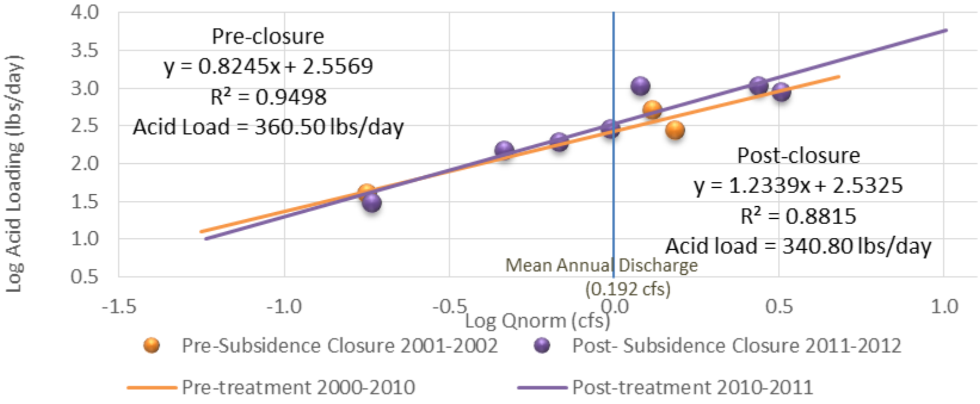

Figure 4 *Coe Hollow regression with treatment flows included, showing acid loads at mean annual discharge (acid load = 360.5 lbs/day pre-closure and 340.8 lbs/day post-closure) and trend lines with good fit (R2 = 0.95) pre-closure and weaker fit (R2 = 0.88) post-closure.*

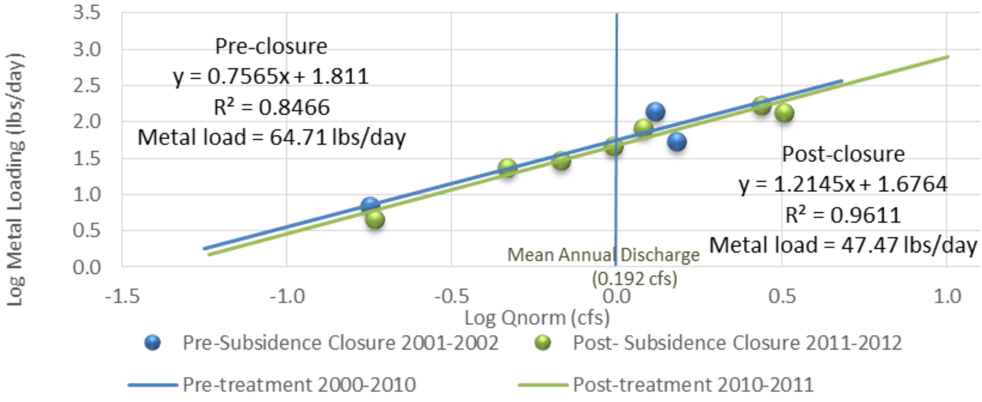

Figure 5 *Coe Hollow regressions, with treatment system flows included, showing metal loads at mean annual discharge (metal load = 64.71 lbs/day pre-closure and 47.47 lbs/day post-closure) and trend lines with good fit (R2 = 0.85 pre-closure and R2 = 0.96 post-closure).*

Using the pre-closure data from Pigati (1997), and post-closure data from Graham (2006), the Stoertz Method was used to compare pre- and post-closing loading conditions at the Majestic Mine. In this case, however, it was necessary to normalize flows using a separate mean annual discharge for each study period. With the drastic reduction in flow in the post-closure data, apparently resulting from the subsidence closure, using the 72% larger normalized pre-closure flow would result in inaccurately high loading estimations after the subsidence closure. Bowman *et al.* made this same adjustment in assessing the Pine Run and Rogers Hollow subsidence closures (2011).

Regressions showed an estimated 60.5% reduction in acid load, shown in Fig. 6 and 7, and a 67.19% total metal load reduction at the seep following closure, data not shown to save space. Iron, manganese, and aluminum are added together for total metals in this regression, however, because Graham compared iron alone, regressions were re-run using only iron loading. Results showed iron reduction of 67.05%, a difference of only 0.14% from total metal reduction.

While concentrations did increase at the seep after remediation, as Pigati (1997) theorized, regression results show that loading decreased. This concurred with Pigati's (1997) expectations and Graham's (2006) findings. Put in different terms, while the WQ of the mine drainage degraded, in terms of constituent concentration, after the closing of the subsidence, the amount of AMD transporting pollution materials out of the mine reduced the total amount of material that could affect Monday Creek.

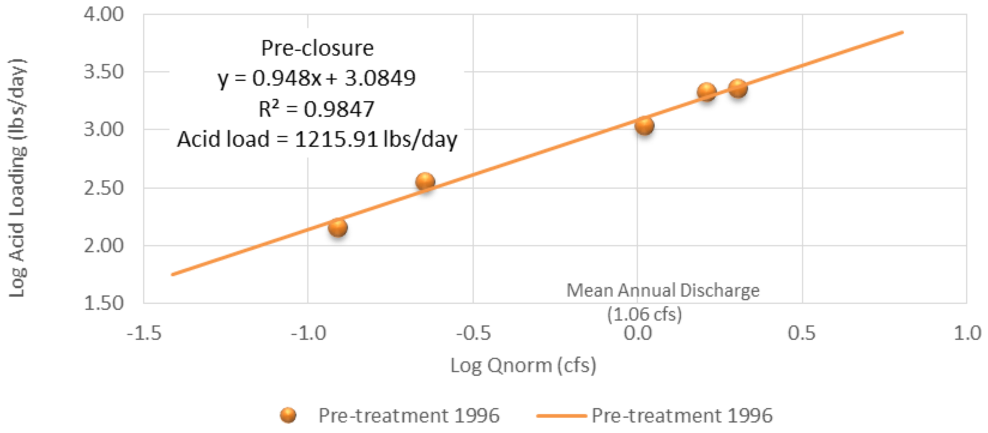

Figure 6 *Majestic regression showing acid loading at mean annual flow (acid = 1215.91 lbs/day pre-closure), pre-closure, with good trend line fit (R^2 = 0.98).*

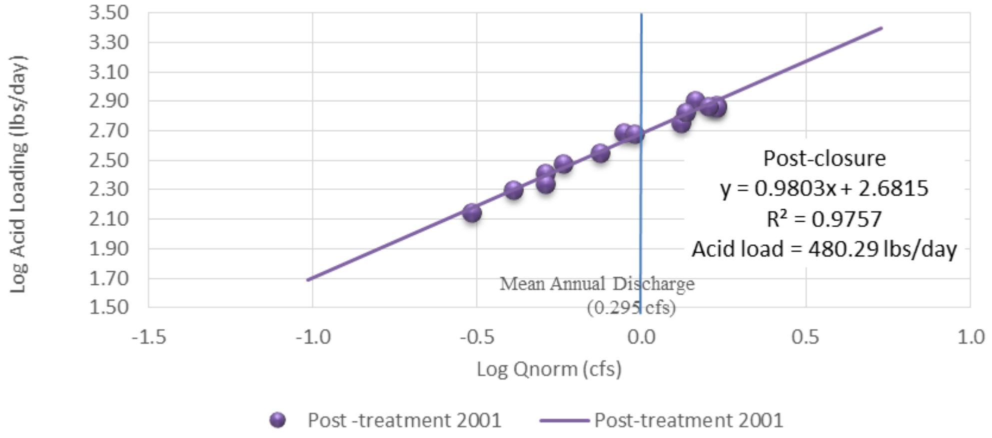

Figure 7 *Majestic regression showing acid loading at mean annual flow (acid = 480.29 lbs/day post-closure) with good trend line fit (R^2 = 0.98).*

Conclusions

Changes in water quality were reflected in comparisons of pre- and post-closure data. Aspects of the study suggest that closing stream capturing subsidences resulted in hydrological and chemical changes at discharges. In the case of the Majestic mine, statistically significant regressions indicate that closing the stream capturing subsidence reduced flows as well as acid and metal loads. Each of the other sites also suggest, albeit not as strongly, that there have been loading reductions after stream capturing subsidence closure.

Data did not conclusively indicate agreement with the common assumption that stream capturing subsidence closures result in WQ improvement at all sites. Technically, at the seeps and discharges where data was adequate for analysis, concentrations were generally shown to increase, a sign of degradation. Where flows were also significantly reduced, however, loadings to receiving streams were also reduced, resulting in an assumed reduction of pollution downstream, agreeing at least cursorily with the common assumption. However, none of these cases proved stream capturing subsidence closure to have prevented AMD from forming.

Acknowledgements

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Column Testing and 1D Reactive Transport Modeling To Evaluate Uranium Plume Persistence Processes

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Abstract

At many U.S. Department of Energy Office of Legacy Management sites, natural flushing was selected as a remedial option for groundwater uranium plumes. However, current data indicate that natural flushing is not occurring as quickly as expected, and solid-phase and aqueous uranium concentrations are persistent.

At the Grand Junction, Colorado, office site, column testing was completed on a core collected below an area where uranium mill tailings have been removed. The total uranium concentration in this core was 13.2 mg/kg, and the column was flushed with laboratory-prepared water with no uranium and chemistry similar to a nearby well. The core was flushed for a total of 74 pore volumes, producing a maximum effluent uranium concentration of 6,110 µg/L at 2.1 pore volumes and a minimum uranium concentration of 36.2 µg/L at the final pore volume. These results indicate complex geochemical reactions at small pore volumes (early time) and a slow uranium release at greater pore volumes (later time). Data indicate the occurrence of nonequilibrium processes that create uranium concentration rebound when column flows are stopped and then restarted. These data confirm the potential for plume persistence, which is occurring at the field scale. One-dimensional reactive transport modeling was completed using PHREEQC (a geochemical model program) and calibrated to the column test data manually and using PEST (inverse modeling calibration routine). Processes of sorption, dual porosity with diffusion, mineral dissolution, dispersion, and cation exchange were evaluated separately and in combination.

The calibration results indicate that sorption and dual porosity are major processes in explaining the column test data. These processes are also supported by fission-track radiography that shows solid-phase uranium residing in less-mobile pore spaces. These procedures provide valuable information on plume persistence and secondary-source processes that may be used to better inform and evaluate remedial strategies, including natural flushing.

Key words: reactive transport modeling, uranium, column testing

Introduction

For several U.S. Department of Energy (DOE) Office of Legacy Management (LM) sites, natural flushing of groundwater uranium plumes to a nearby river was the selected remedy. However, at many of these LM sites, natural flushing has not occurred as quickly as anticipated (Dam et al. 2015) due to persistent uranium in the solid and water phases.

At the Grand Junction, Colorado, office site (fig. 1), the U.S. War Department acquired the property in 1943 for use by the Manhattan Engineer District, which operated a refinery onsite from 1943 to 1946 to concentrate uranium oxide. Beginning in 1953, the U.S. Atomic Energy Commission conducted a research program in a small pilot mill at the site to test experimental uranium-ore-milling techniques, and in 1954, a larger pilot mill was constructed. Approximately 30,000 tons of ore were processed before milling operations ceased in 1958. The milling operations resulted in the contamination of soil and groundwater at the site, and the removal of uranium mill tailings and contaminated soil began in late 1989, with most of the contaminated soil being removed by 1994. Additional small deposits of contaminated soil and material were removed during remedial action conducted from 1998 through 2014.

The compliance strategy for contaminated groundwater and surface water at the Grand Junction office site is natural flushing with institutional controls. Contaminants in the alluvial aquifer were projected to flush to acceptable levels 50–80 years after remediation was completed. However, continued groundwater monitoring has indicated a uranium plume persistence issue (DOE 2015). To better understand this issue, cores were collected below areas where uranium mill tailings were removed. These cores were analyzed for uranium content, and column testing was completed on these cores to better understand the uranium release amounts, rates, and processes.

This paper uses the data from the core with the highest uranium content, which was the only column completed with analyses of full geochemistry data instead of just having uranium data. These data were used to calibrate a one-dimensional (1D) reactive transport model and evaluate the uranium release processes. Processes of sorption, dual porosity with diffusion, mineral dissolution, dispersion, and cation exchange were evaluated separately and in combination.

Figure 1 *Site location and core collection location.*

Methods

Fission-Track Radiography

Fission-track radiography was done in combination with petrography to determine the association of uranium with aquifer sediments. Commonly, uranium resides in mineral grains that are too small to be positively identified, even using electron beam techniques. However, deductions about mineralogy from petrographic methods and fission-track radiography are often possible. Fission-track radiography involves the irradiation of a uranium-bearing sample with a flux of thermal neutrons that causes induced fission of the highly fissionable ^{235}U isotope. Fission fragments recoiling from the sample surface may be detected by covering a polished thin section with a suitable detector material. The detector material used was muscovite mica. Fission fragments entering the detector cause structural disturbances that can be developed for optical inspection by subsequent etching of the detector with concentrated hydrofluoric acid. The developed fission tracks observed under a microscope reveal sources of uranium in the thin section. Uranium concentrations and locations can be estimated by observing the density of fission tracks and comparing the locations to the original thin section.

Column Test

The air-dried core sample was sieved to a particle size of less than 2 mm diameter and used to fill an Omnifit glass chromatographic column that was 21.3 cm long by 2.5 cm wide with a volume of about 30 mL. Care was taken to obtain a representative sample by mixing the sample and minimizing particle size/density bias. Sediment was placed in the column in approximately 1 cm lifts with gentle tapping between lifts.

The column was leached with laboratory-prepared water that matched the composition of groundwater collected from a nearby well. A peristaltic pump with nylon tubing was used to pump the synthetic well water through the column from bottom to top at a flow rate of approximately 0.15 mL/min. The synthetic well water was kept in a collapsible plastic container to minimize exposure to air. The number of flushing pore volumes (PVs) was determined by multiplying the flow rate by the length of time required to fill the column with synthetic well water. A fraction collector was used to collect column effluent in glass test tubes. Outflow water was collected for analysis at approximately every 0.85 pore volumes, and the flow was stopped at every 25 pore volumes (referred to as stop flow). The core was flushed for a total of 74 pore volumes, and the test period was 23 days. Column effluent was analyzed for alkalinity, pH, Ca, Na, Mg, K, Mn, Fe, Cl, NO_3, SO_4, and total organic carbon.

PHREEQC Modeling

The column test data was analyzed using the geochemical modeling program PHREEQC (Parkhurst and Appelo 2013) as a 1D reactive transport model. PHREEQC modeling used a 1D column with 20 cells for a cell length of 0.01065 m and used the inflow water chemistry of the lab-prepared water (tab. 1). Unfortunately, the column was run continuously without any equilibration time, so the simulations with PHREEQC used the first water sample at 0.83 PV (tab. 1) to simulate initial conditions, with equilibration of the water phase onto the solid phase. In PHREEQC, this equilibration is necessary for simulating uranium sorption and for use in cation exchange. This equilibration creates the initial amount of uranium sorbed onto the solid phase based on the sorption parameters and adds the full complement of cations onto the solid phase for subsequent cation exchange. Initial modeling only considered the first 25 pore volumes, and calibration was done manually with an emphasis on matching uranium. A sequential order of processes was simulated to avoid adding too much complexity in one step. Processes of sorption, dual porosity with diffusion, mineral dissolution, dispersion, and cation exchange were evaluated separately and in combination. Sorption was simulated using the generic surface complexation model of Davis et al. (2004) with calibration proceeding through the use of varying sorption equilibrium constants and surface site densities. Dual porosity was simulated using a single diffusion exchange factor between mobile and immobile cells built into the 1D transport code of PHREEQC. The PHREEQC database was updated to use the ternary complexes of uranyl and carbonate with alkaline-earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) from Dong and Brooks (2006) and new uranium thermodynamic data from Guillaumont et al. (2003). Final calibration used the inverse modeling techniques of PEST (Doherty 2005) for every analyzed pore volume and all measured analytes.

Table 1 *Chemistry of a few select analytes for the column inflow water and the first water sample that was used for assumed column equilibration in the reactive transport model.*

Analyte	Inflow Water	Equilibrated Water at 0.83 PV
pH	7.0	7.6
Alkalinity as $CaCO_3$ (mg/L)	313	101
Calcium (mg/L)	192	530
Sulfate (mg/L)	918	4,180
Uranium (µg/L)	0.0	2,000

Results

Fission-track radiography (fig. 2) indicates that uranium is co-located with iron oxide cements between quartz grains. Thus, it is likely that the iron oxide cements represent less-mobile pore spaces with a higher iron content that can likely sorb more uranium onto the solid phase. As such, this is direct evidence before starting any modeling efforts that dual porosity issues should be evaluated (fig. 2).

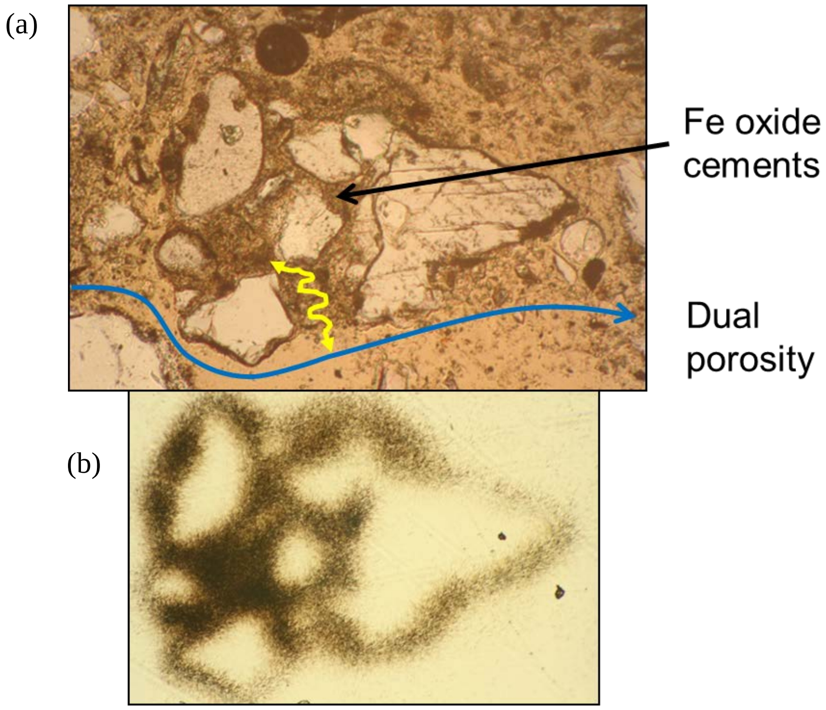

Figure 2 *Fission-track radiography with transmitted light image (a) and fission-track image (b) at the same location in one thin section. A greater density of fission tracks indicates more uranium.*

The total uranium concentration in this core was 13.2 mg/kg compared to background values of less than 1 mg/kg. The maximum effluent uranium concentration of 6,110 µg/L occurred at 2.1 pore volumes (fig. 3), and a minimum uranium concentration of 36.2 µg/L occurred at the final pore volume.

Initial modeling evaluated the uranium concentration from the first 25 pore volumes (fig. 3). Sorption was the first process evaluated (fig. 3a) followed by dual porosity (fig. 3b). Using sorption alone provides a relatively good fit to the measured data (fig. 3a) but could not fit the concentration tailing at PVs 5 through 25. The use of dual porosity seems like a reasonable process, but the use of dual porosity alone does not provide a good fit to the initial uranium concentration spike and subsequent tailing effect (fig. 3b). However, the combination of using sorption and dual porosity in PHREEQC does provide a relative good fit to the measured uranium data (fig. 4) and is logical based on the fission-track radiography results with uranium sorption on iron oxides in less-mobile pore spaces.

Additional processes included the addition of gypsum dissolution and dispersion. The addition of gypsum dissolution provides a better uranium peak (fig. 5a) likely due to added uranium mobility provided by an increasing amount of calcium in solution and, thus, the creation of calcium uranyl complexes (Dong and Brooks 2006). The presence of gypsum in the core material is inferred based on the loss of both calcium and sulfate at 60 PVs along with gypsum being undersaturated in the inflow water but at saturation in the effluent. However, no direct mineralogic data has yet been measured (such as x-ray diffraction). The addition of dispersion provides an additional improvement in the calibration by smoothing out the initial uranium concentration peak (fig. 5b). Saturation indices for uranium minerals were evaluated, but no evidence of possible uranium mineral precipitation was indicated. Thus, mineral dissolution/precipitation for uranium minerals was not included.

Manual calibration could have stopped with the inclusion of sorption, dual porosity, gypsum dissolution, and dispersion, but cation exchange processes were also added (fig. 6), given the presence of clays identified from thin-section petrography. The addition of cation exchange processes provided the best calibration fit that could be achieved using manual calibration techniques (fig. 6).

PEST, a parameter estimation software package, was used for the final simulation over the whole column test period, including the stop flows at 25 PVs. This simulation used sorption, dual porosity, gypsum dissolution, dispersion, and cation exchange processes. PEST varied all the input parameters associated with each process and created a very good fit to the uranium concentration data (fig. 7). The inset in Figure 7 highlights the stop flow data at 25 and 50 PVs, which provides evidence for nonequilibrium processes and the need for the dual porosity factor. Without the use of dual porosity, equilibrium sorption does not simulate the uranium rebound when flow is stopped. The model results did not fit the uranium peak for the second stop flow as well as for the rest of the data (inset in fig. 7), and the reason for this is unclear. Likewise, it is unclear if the column flow rate of 561 m/year compared to actual groundwater flow rates of 0.91 to 1.5 m/year has created nonequilibrium conditions during the stop flow tests that may or may not occur under field conditions.

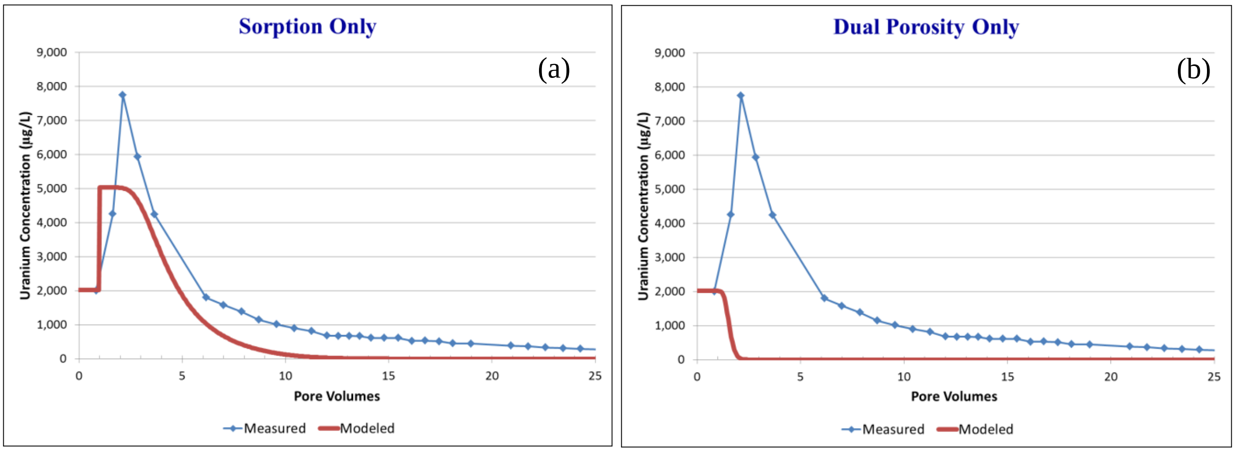

Figure 3 *Measured uranium concentrations compared to modeled results for the addition of sorption only (a) and dual porosity only (b).*

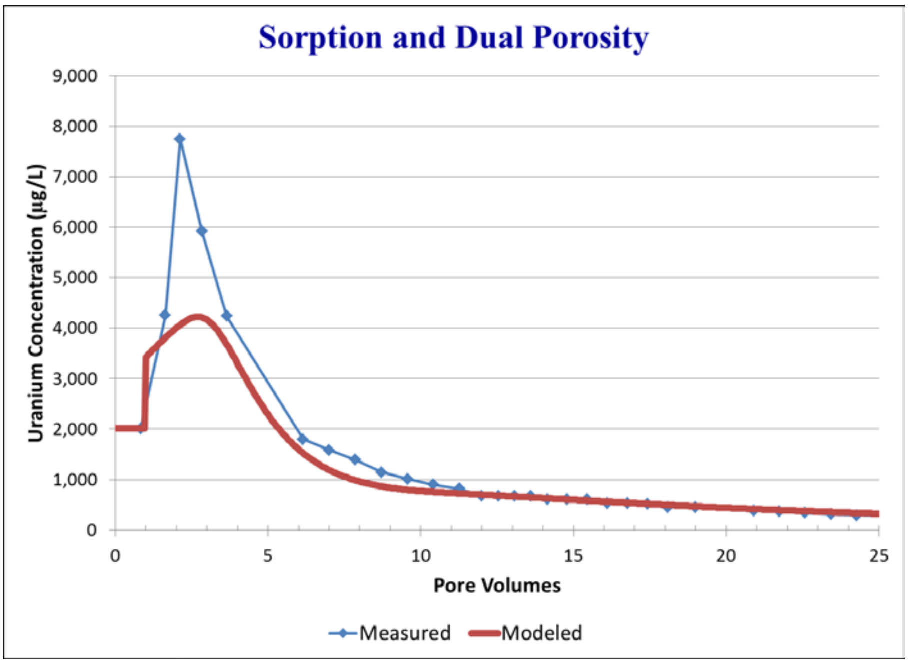

Figure 4 *Measured uranium concentrations compared to modeled results for the use of sorption and dual porosity together.*

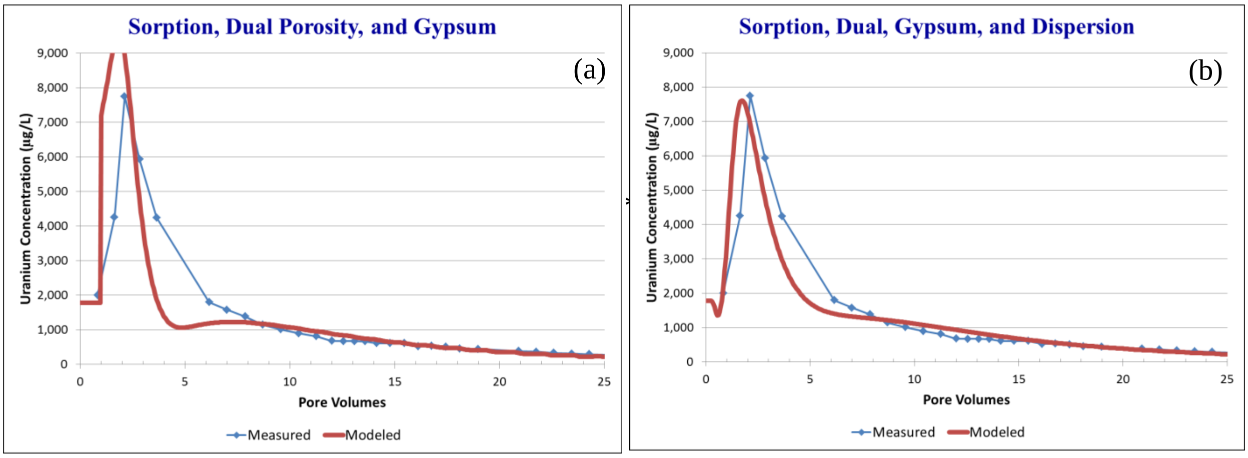

Figure 5 *Measured uranium concentrations compared to modeled results for the use of sorption, dual porosity, and gypsum dissolution (a) and with the addition of dispersion (b).*

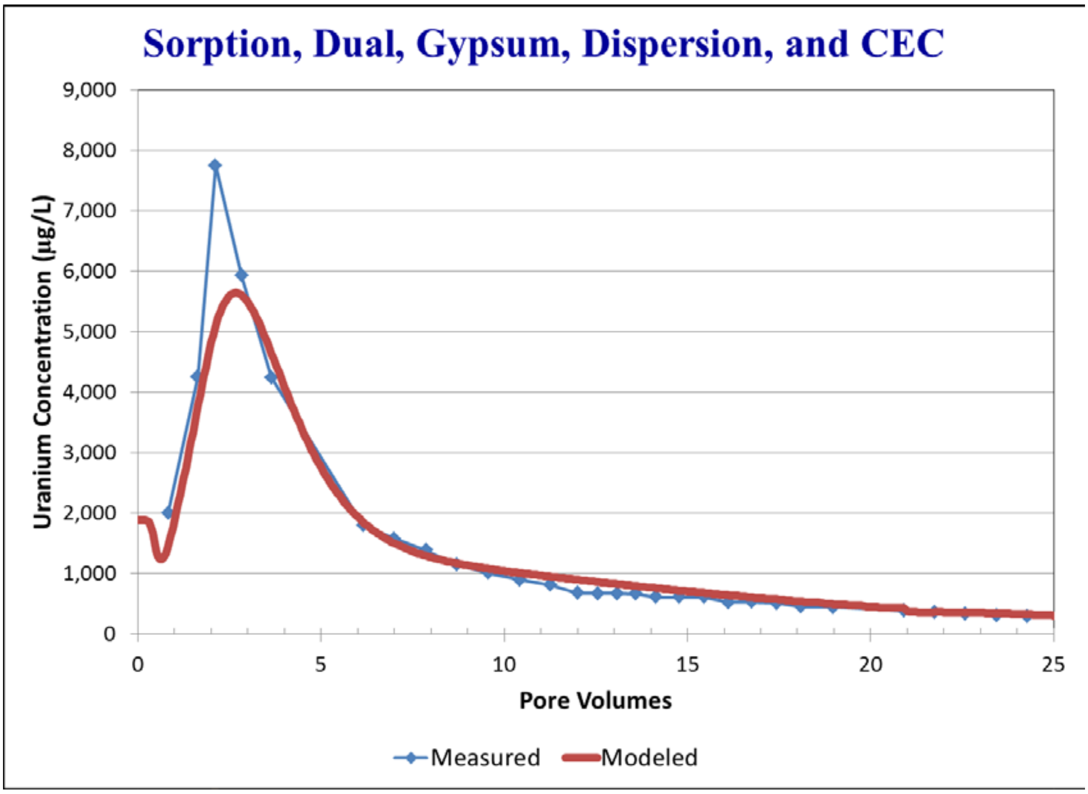

Figure 6 *Measured uranium concentrations compared to modeled results for the use of sorption, dual porosity, dispersion, and cation exchange capacity (CEC). Final best-fit manual calibration.*

Future Work

Future plans include additional use of PEST with each individual process to better quantify the goodness of fit (measured data minus modeled data) for each process. These processes will be evaluated separately and in combination, similar to what was presented for the manual calibration procedures. This will provide a more quantitative evaluation of the importance of each process. In addition, the large amount of calibration data in the concentration tail will be evaluated for weighting and whether or not this large amount of data biases the automated model calibration when using PEST.

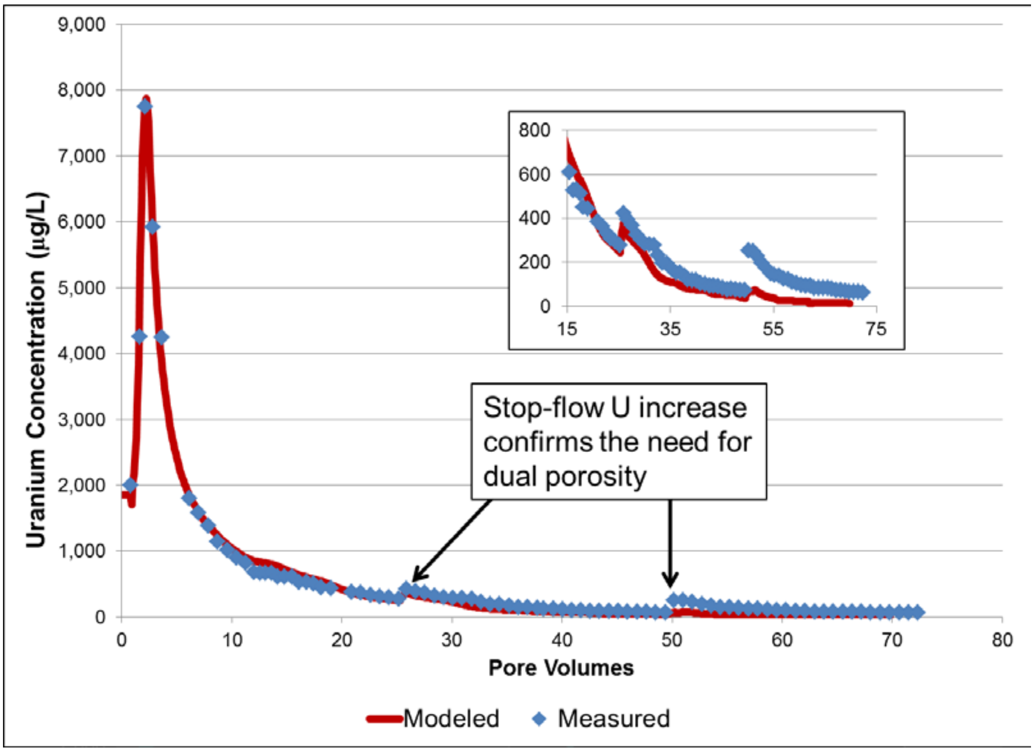

Figure 7 *Measured uranium concentrations compared to modeled results for the use of sorption, dual porosity, gypsum dissolution, dispersion, and cation exchange capacity calibrated using PEST.*

Lessons Learned

Lessons learned that will be considered in future column studies include:

(1) Allowance for column equilibration between the water and solid phase.

(2) Evaluation of slower flow rates with start/stop flows to test nonequilibrium conditions.

(3) More frequent sampling at early pore volumes and less frequent sampling at later pore volumes.

(4) Adding direct confirmation of gypsum occurrence.

Conclusions

Column test data confirm a long tailing process for uranium release from the solid phase, similar to plume persistence issues that are seen at the field scale. Reactive transport modeling provides a useful tool for evaluating the amount, rate, and processes that control uranium release from the solid phase to the column effluent water. Manual calibration results indicate that sorption and dual porosity are major processes in explaining the column test data. These processes are also supported by fission-track radiography that shows solid-phase uranium residing in less-mobile pore spaces created by iron oxide cements. Gypsum dissolution, dispersion, and cation exchange help improve the calibration but visually do not appear to be as important as sorption and dual porosity. Future work will evaluate the importance of each process more quantitatively, along with testing whether or not the weighting of data at greater pore volumes where the long concentration tail that occurs creates bias in the model calibration. All of these procedures provide valuable information on plume persistence and secondary-source processes that may be used to better inform site decision making and evaluate possible remedial strategies, including natural flushing.

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A 3D numerical model to assess the performance of the reclamation measures for an abandoned mine site

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Abstract

Acid mine drainage (AMD) production by mine tailings can be mitigated with a monolayer cover and an elevated water table. This reclamation technique, which aims at using water saturation to limit the diffusion of oxygen, was implemented at the tailings storage facility 2 (TSF 2) of the Manitou abandoned mine site (Québec, Canada). It was observed through physical modeling of this reclamation technique with the Manitou tailings that a key criterion to stop AMD production is the water table level. A hydrogeological numerical model of the site was built to complement laboratory and field data and assess the reclamation performance according to different scenarios. This paper presents the setup and calibration of the 3D model of the Manitou TSF 2 site. Data was gathered from the 38 ha TSF through geophysical, geospatial, and drilling monitoring. A 3D hydrogeological model was built to perform simulations with a numerical variably-saturated groundwater flow model. The steady-state calibration and determination of the main parameters was achieved by comparing the hydraulic heads to average field measurements. A three year transient state analysis is presented here and compared to hydraulic heads measured at 13 field stations. The results are consistent with the field measurements.

Key words: Acid mine drainage, hydrogeological modeling, abandoned mine site, elevated water table, monolayer cover

Introduction

Mine tailings sometimes contain sulphide minerals that can oxidize in the presence of oxygen and water, and produce acid mine drainage (AMD). The AMD production may last hundreds to thousands of years in situ and can be very harmful to the environment.

An effective and economical technique to limit AMD production from tailings, notably under humid climatic conditions, is the implementation of an elevated water table (EWT) with a monolayer cover (SENES, 1996; Aubertin et al., 1999). This method consists of raising or maintaining the water table to an elevated position that will allow the reactive tailings to stay at a high degree of saturation, preventing sulphide oxidation because of the low solubility and low effective diffusion coefficient of oxygen in (nearly) saturated porous media. This reclamation technique has been investigated in the laboratory and numerical models (Dagenais, 2005; Ouangrawa, 2007; Demers et al., 2008; Ouangrawa et al., 2010; Pabst, 2011), but little field work has been conducted to assess the performance of this method.

In the last 25 years, the Manitou site has been studied extensively in order to find a viable and cost-effective reclamation technique that would stop the production of AMD (Aachib, 1997; Aubertin et al., 1999; Molson et al., 2008; Demers et al., 2009; Bussière et al., 2011; Émond et al., 2011; Demers et al., 2013; Pabst et al., 2014). Laboratory column tests were part of a recent experimental program to evaluate different reclamation scenarios. Their interpretation indicated that a water table located close to the surface of the Manitou tailings can progressively improve effluent quality (Pabst, 2011; Demers et al., 2013; Pabst et al., 2014). A field investigation was undertaken at the Manitou tailings storage facility 2 (TSF 2) abandoned mine site to evaluate the performance of the EWT reclamation technique (Ethier et al., 2013); the preliminary results are generally positive (Ethier et al., 2014).

One limitation of field monitoring is that it can only be performed on an implemented design under the prevailing climatic conditions at a site and over a tested period. In order to assess the TSF 2 cover's performance over a broader range of potential conditions, it is important to investigate the influence of factors, such as cover thickness, material properties, and changes in climatic variables, that cannot necessarily be directly evaluated through field monitoring. A numerical model simulating the hydrogeological behavior of the Manitou TSF 2 was developed for this purpose. This paper presents the site description, field monitoring data, numerical model setup and calibrations performed to evaluate the hydrogeological behavior of the Manitou TSF 2 reclamation scenario.

Site description and field monitoring data

Zinc and copper were produced at the Manitou mine between 1942 and 1979. During the operation, nearly 11 million tons of acid-generating tailings were deposited in poorly-confined ponds that cover up to 191 ha. The AMD generated over several decades has had a severe impact on the surrounding environment. TSF 2 is a 38 ha spilling area at the Manitou site. The technique selected to reclaim TSF 2 is an elevated water table with a monolayer cover made of tailings from the nearby Goldex mine. The deposition of Goldex tailings on TSF 2 was carried out in 2009; the fine-grained Goldex tailings are non acid-generating and slightly alkaline, and their thickness varies from 1.2 to 2.1 m.

A map of TSF 2 is shown in Fig. 1. The surface elevation of the cover decreases from 327.5 to 321.7 meters above sea level (masl) in the east-west direction. Thirteen observation stations were installed within the TSF 2. At these stations, from August 2012 to August 2015, groundwater levels were measured at six hour intervals using Mini-Diver pressure sensors (Schlumberger Inc.) in wellpoints. Volumetric water content and suction were also monitored at two different depths in the cover; i.e., at 20 cm from the top and 20 cm from the base of the cover (see Ethier et al., 2014 for details).

Specific information on the site geology and material properties was gathered through trenches, drillings, geospatial data, and results from previous studies (Bussière et al., 2011; Pabst, 2011). Twelve drill holes going 4 to 16 m deep were created throughout the TSF. In addition, 13 trenches were dug to gain more information on the cover's characteristics. The topography was determined from a survey conducted in the summer of 2012. A geophysical study was performed using electrical resistivity imaging (ERI) to gather complementary information on the in situ conditions. The electrical resistivity of soils depends upon effective porosity, degree of saturation, and resistivity of the water (Lesmes and Friedman, 2005). Such measurements give a more global picture (instead of a local view) of the site conditions including water distribution in the different strata, without disturbance. The geophysical data were collected using a Lund Imaging SAS4000 (ABEM Instrument) with dipole–dipole and Wenner protocols, using 5 m as the electrode spacing. Two pseudo-sections (i.e., 2D areas under the apparatus and where resistivity is measured) were analyzed (see Fig. 1) and the results allowed for differentiation between the bedrock, till, and clayey soils. More information on these tests results can be found in Ethier (2016). A 3D geological model was developed with GOCAD using the available information on the non-reactive Goldex tailings, Manitou tailings, and underground soil structure.

Precipitation data were retrieved from the Val D'Or meteorological station (Environment Canada, 2015). The average yearly precipitation amounts to 914 mm; the yearly potential evaporation is 490 mm; the average minimum and maximum daily temperatures are -17°C (in January) and 17°C (in July) respectively.

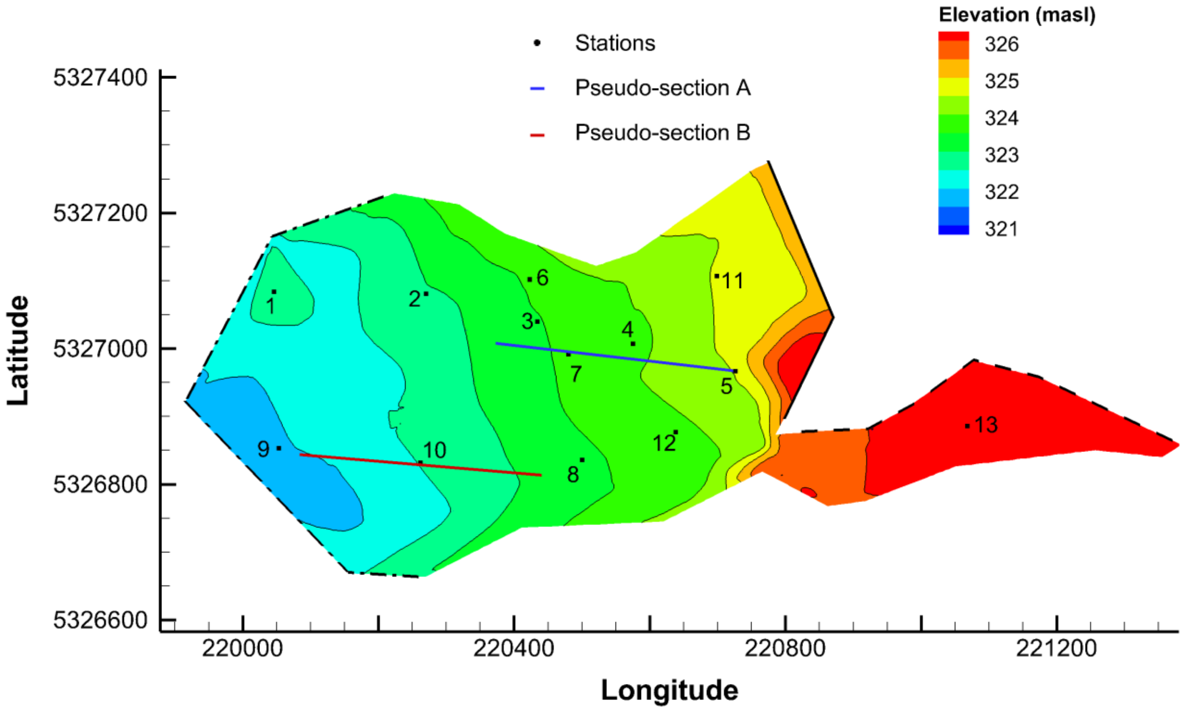


***Figure 1** Model configuration of the Manitou TSF 2 site, with the 13 measurement stations, the pseudo-sections for the geophysical surveys and the boundary conditions at 319 masl (dash-dotted line), 322.5 masl (thick plain line), and 323.5 m (dashed line).*

Model construction

The simulation of the water table position over time was conducted using the HydroGeoSphere code, a fully-integrated 3D finite element subsurface and surface flow and transport model based on Richard's equation to represent variably-saturated groundwater flow (Therrien and Sudicky, 1996; Therrien et al., 2010). This code was also used in previous studies to simulate unsaturated water flow within tailings (e.g. Carrera-Hernández et al., 2012; Broda et al., 2014; Ben Abdelghani et al., 2015). The finite element numerical x- and y- plan of the domain was discretized into 5 m wide elements. The total area is 44 ha. Vertically, the domain was made of 11 layers which gradually increased in thickness from 0.1 m at the soil-atmosphere interface to 3.33 m at the base of the model. The base of the model is at 305 masl, and the maximum elevation at the surface is 327.5 masl. This resulted in a mesh with 30 489 nodes and 60 227 prismatic elements. As illustrated in Fig. 2, the domain contains layers of rock, till, and clay soil below the Manitou tailings and the Goldex tailings cover layers.

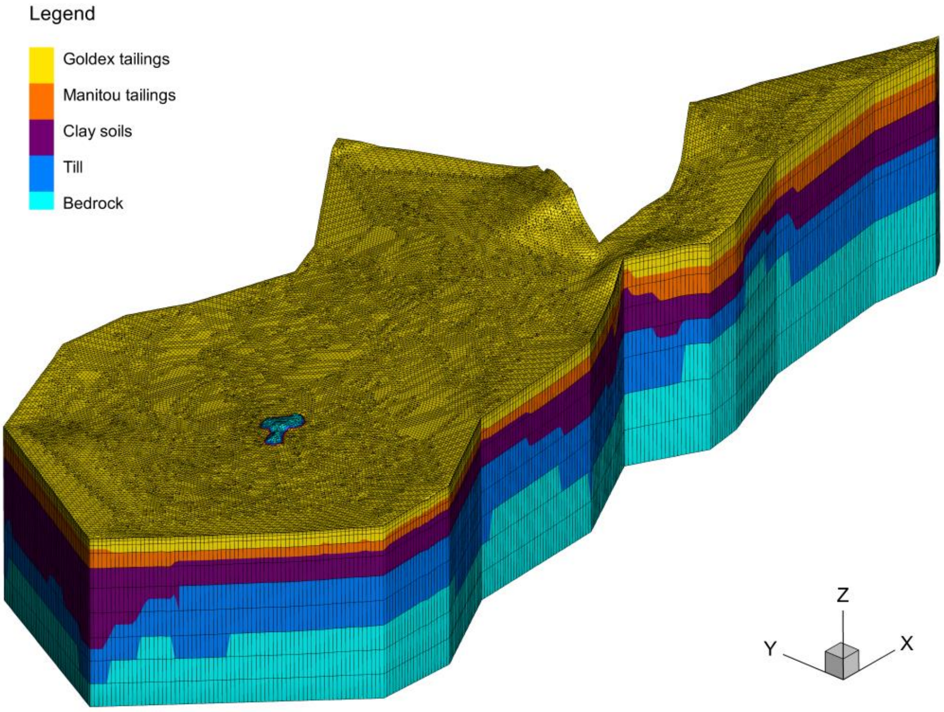


Figure 2 *Model configuration of the Manitou TSF 2 site constructed with HydroGeoSphere.*

Steady-state calibration

A calibration was performed under (pseudo) steady-state conditions, using the correspondence between simulated heads and average measured heads at each station. A recharge of 262 mm/year, which is approximately 30% of the mean annual precipitations, was applied. This ratio for recharge-precipitation is typical for tailings in this region and was used in other studies (Nastev and Aubertin, 2000; Leblanc, 2010; Broda et al., 2014).

As topographic slope is oriented East-West, flow is expected to mainly occur in this direction; domain boundaries in the North and South were defined impervious. Dirichlet type (fixed head) boundary conditions were set to an elevation of 319 masl in the West of the site, 322.5 m in the East of the site and 323.5 m at the North edge of station 13.

The calibrated parameters are listed in Table 1. These include, for each material, the saturated hydraulic conductivities (K) and porosities (n). Parameters α and β, which are related to the AEV and shape of the WRC respectively, were calibrated only for the Manitou and Goldex tailings. The rock, till, clay soils, and Goldex tailings were considered to be homogeneous and isotropic throughout the domain. Manitou tailings were considered anisotropic with a horizontal/vertical hydraulic saturated conductivity ratio (K_h/K_v) of 10, based on typical values for tailings impoundments (Vick, 1990; L'Écuyer et al., 1992). The calibrated values agree with previous studies (Gosselin, 2007; Demers et al., 2013; Pabst et al., 2014) and with typical properties of the corresponding soils (Chapuis and Aubertin, 2003). The unsaturated properties of the two tailings were defined with the van Genuchten (1980) model and the corresponding water retention curves are displayed in Fig. 3a. The air entry values of the Manitou and Goldex tailings are 2.2 m and 1.1 m of water respectively. Since the foundation layers (rock, till, clay soils) remain saturated for most of the domain, their respective water retention characteristics were not explicitly defined, thus the default values of HydroGeoSphere were used.

***Table 1** Calibrated values for the horizontal hydraulic conductivity (K_h) and porosity (n) of each material; α and β van Genuchten WRC fitting parameters and air entry values (AEV) for Goldex and Manitou tailings.*

Material	K_h (m/s)	n [-]	α [m-1]	β [-]	AEV [m]
Rock	2.E-06	0.02	3.5237*	3.1768*	0.16*
Till	8.E-05	0.32	3.5237*	3.1768*	0.16*
Clay soils	8.E-08	0.50	3.5237*	3.1768*	0.16*
Manitou tailings	2.E-06	0.46	0.188	1.89	2.2
Goldex tailings	7.E-07	0.42	0.15	1.87	1.1

*Default values of the code (not calibrated)

The model was calibrated in (pseudo) steady-state using the measured hydraulic head averages of 2012-2014 (see Fig. 3b). The line in Fig. 3b represents equality between modeled and observed results. The dispersion of the data can be attributed in part to the local seasonal variations of the hydraulic heads. The results are acceptable, with a root mean square error (RMSE) of 0.561 m for the head and an R^2 of 0.84.

Transient state predictions

A transient state simulation was performed to demonstrate the ability of the numerical model to predict the hydrogeological behavior of the Manitou TSF 2. Hydraulic heads from September 2012 to July 2015 were reproduced. Boundary conditions and material properties selected from the steady-state calibration were applied to the transient analysis.

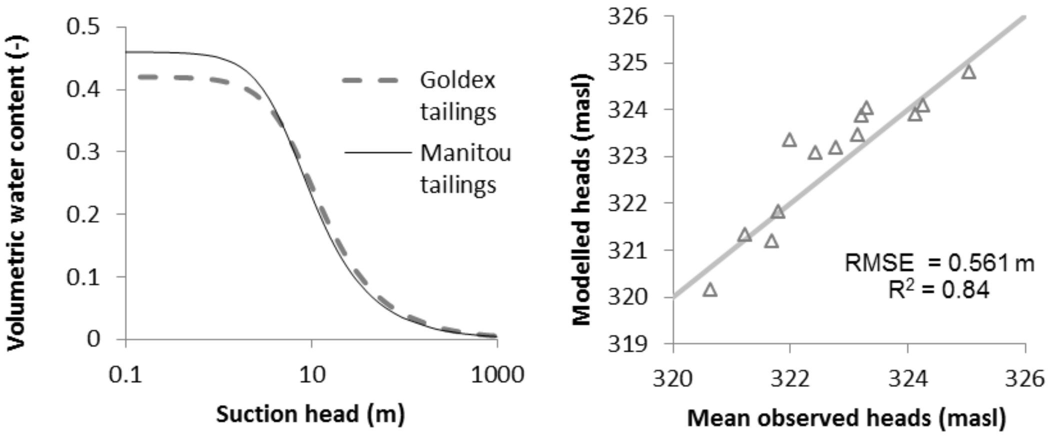
The day-degree snowmelt method was integrated into the simulation to model the dryer winter season during which solid precipitation (i.e., snow) occurs, and the spring snowmelt with a larger water supply. The degree-day method is a temperature index approach that relates the total daily melt to the difference between the mean daily temperature and a reference (freezing) temperature (in this case, 0 °C); the corresponding equation for snowmelt, M, can be expressed as follow:

$$M = C_M (T_a - T_b) \qquad [1]$$

where C_M is the degree-day coefficient (mm/degree-day C), T_a is the mean daily air temperature (°C) and T_b is the base temperature (°C). The coefficient C_M varies seasonally and with the location; for this study, a typical value of 2.74 mm/degree-day Celsius was used (United States Department of Agriculture, 2012).

A recharge equivalent to 15% of the precipitation was applied for the period from June to August, while 30% was applied to the rest of the year. The fit between the model and field data was generally good with these parameters, except for days with heavy rainfall or heavy snowmelt (> 20 mm/d). For these more extreme conditions, which occurred 28 days over the simulated three-year period, the daily recharge was reduced to 15% of precipitation instead of 30%, while recharge due to snowmelt was halved to better represent field results.

Simulation results were compared with hydraulic heads measured four times a day over a three-year period (September 2012 - August 2015). Results are presented in Fig. 4 for four stations. For three stations (i.e., stations 3, 6, and 8 in Fig. 4), the match between the simulated and measured hydraulic heads is quite good. Winter and summer decreases, as well as spring and fall hydraulic head increase, are well captured by the model. The effect of the fixed-head boundary can be observed at station 9, which is close to the limit of the model. The variations of simulated head were dampened at this station and do not well represent observations during the wet period; nonetheless, the seasonal trends are quite well reproduced. The other stations were not affected by this condition so the fit is better and deemed satisfactory for additional numerical analyses with this model.



a b

Figure 3 *a) Water retention curves defined by the van Genuchten (1980) equation for the Goldex tailings (dashed line) and the Manitou tailings (solid line). b) Modeled vs. observed hydraulic heads (triangles), root mean square errors (RMSE) and correlation coefficient R^2.*

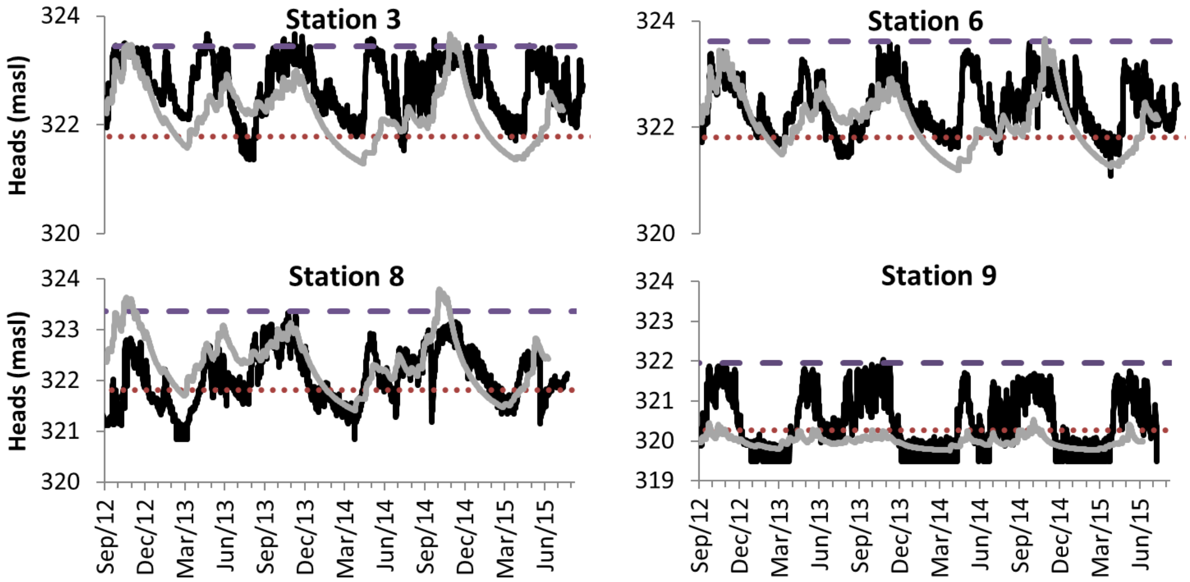


Figure 4 *Observed (black line) vs. simulated (grey line) piezometric heads and locations of Goldex/Manitou (dotted line) and Goldex/atmosphere (dashed line) interfaces at the observation wells 3, 6, 8, and 9 from September 1st, 2012, to August 31st, 2015.*

Ongoing work

This article presents the construction and calibration of a 3D numerical model that is used to evaluate the response of the reclamation technique applied at the Manitou mine site; i.e., an EWT combined with a monolayer cover. As the water budget greatly influences the efficiency of reclamation by controlling contaminant production, this 3D model will subsequently be used to evaluate the influence of several parameters on the performance of the reclaimed TSF 2. For instance, simulation using the normal climatic data shows the natural evolution of the hydraulic heads on site. Additional simulations with recurrent dry spells will assess their potential impact on AMD production at the Manitou site. A sensitivity analysis will also be performed to evaluate the model's response to changes in the main influence parameters.

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Long-Term Remediation of Acid Mine Drainage from Abandoned Coal Mine Using Integrated (Anaerobic and Aerobic) Passive Treatment System, in South Africa: A Pilot Study

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Abstract

Acid mine drainage from abandoned mines is primarily responsible for degradation of scarce water resources in South Africa. Owing to the nature of previous legislations, the South African government has inherited environmental liabilities of most of the abandoned mine sites, and hence there is a need to develop long-term sustainable remediation solutions. To contribute towards development of sustainable mine water management solutions in South Africa, a pilot passive treatment plant consisting of integrated anaerobic and aerobic units has been constructed to treat 1440 liters of acid mine drainage per day from an abandoned underground coal mine. During the first six months of operation, the pilot plant has successfully neutralized the water and substantially removed contaminants, such as Fe, Al, Co, Zn, Ni, As, Pb, V, but with limited SO_4 reduction (only 30% removal rate was achieved). Thereafter, there has been a decrease in treated water quality with time, and this was largely due to clogging and/or depletion in the treatment materials. The study demonstrated that passive treatment can be used as a long-term remediation of polluted mine water from abandoned mine sites in South Africa. The results of this pilot-scale test will be used to design an optimised full-scale plant, and also assist in an optimized design of additional pilot plants in other abandoned mining areas.

Key words: Acid mine drainage, Passive treatment, Anaerobic and Aerobic units

Introduction

Many of the abandoned mines in South Africa generate contaminated mine drainage, and over the years this has led to a deterioration in the water quality in many surface streams and ground water, as reported by a number of researchers (Naicker et al. 2003; McCarthy 2011; Yibas et al. 2013). Owing to the nature of previous legislation, the South African government has inherited environmental liabilities of most of the abandoned mine sites, and hence there is an urgent need to develop long-term sustainable remediation/management strategies (Swart 2003). Passive treatment is a technology of choice for long term remediation of polluted mine water in many parts of the world such as the United States, United Kingdom and Germany, due to the following benefits over active treatment(Hedin et al. 1994; Kleinmann & Hedin 1993; Younger 2000; Wolkersdorfer 2008):

- usually low operational cost; can be very efficient in metals removal;
- can reduce or eliminate the use of hazardous chemicals;
- potential to recover valuable products that can offset the cost of maintenance; and
- acceptance by social communities since the systems employed are more natural and aesthetic in their appearance and may support plants and wildlife

However, the application/adoption of passive treatment in the South African is limited and not well understood. Hence, there is a need to explore the potential application of these systems for a long-term remediation of acid mine drainage. Research in South Africa has been mainly on lab/bench-scale, using artificial mine water and only focusing on the development of passive anaerobic sulphate reduction technology. To contribute towards development of sustainable mine water management solutions in South Africa, a pilot passive treatment plant consisting of integrated anaerobic and aerobic units has been constructed to treat 1440 litres of acid mine drainage per day from an abandoned underground coal mine.

Study area

The pilot plant is situated near Carolina in the Mpumalanga Province on the farm Witkranz 53 IT, portion 11. Geologically, the area forms part of the Ermelo coalfield, situated south of Carolina. All the coal seams occur within the Vryheid Formation of the Ecca Group, Karoo Supergroup. Sandstones with subordinate shales represent the bulk of the Vryheid Formation (Bell & Jermy 2002). There is very little information about the mining history of the area. However, an old mine plan obtained from a local mining company shows mining activities in a portion of land to the east of the main discharge point, using both underground and open-cast methods (Figure 1). In terms of hydrology, the site is situated in the Komati–Crocodile catchment area. The acid mine water discharges into the Boesmanspruit, which flows in a northwest direction into the Boesmanspruit dam. The pilot plant was constructed adjacent to the discharge point (Figure 1).

Figure 1 *Old underground mine plan adjacent to the Witkranz discharge point.*

Methods

Field observation and sampling were conducted to characterise the acidic mine water discharge. The hydrogeochemical parameters are summarised in Table 1. On-site measurements/analyses in respect of parameters such flow rate, pH, electrical conductivity (EC), and elemental concentrations were conducted. Water samples were also analysed by means of ICP-MS and IC and the element concentrations were compared with the South African domestic water quality standards. Both discharges are generally characterised by a low pH, with concentrations elevated by as much as two and even three orders of magnitude than the acceptable limit of Fe, Al, Mn and sulfate and slightly elevated arsenic (As).

The selection of a suitable passive treatment system was done with the aid of the periodic table for passive treatment developed by Gusek (Gusek 2009; Gusek 2013) and the flow chart, as adopted from Hedin et al. (1994). Based on the chemistry of the seepage and the site characteristics, the selected passive treatment system consists of two cells of vertical flow ponds or a Reducing Alkalinity Producing System (RAPS), which combines the mechanisms of anaerobic treatment wetlands and anoxic limestone drains, as developed by Kepler and McCleary (1994), a settling pond and an open/ cascading limestone bed for Fe removal. Figures 2 and 3 show a layout of pilot passive treatment system in Carolina.

The RAPS and oxidation units were constructed in a 1 000 L (height = 1 160 mm, length = 1 200 mm and width = 1 000 mm) plastic containers (Figure 2). About 1.5 t of limestone (with at least 85% $CaCO_3$) was placed at the bottom of the tank, forming a layer 0.5 m deep. Directly above the limestone layer, about 0.3 t of organic substrate (consisting of manure, cow manure, chicken manure and powdered limestone) was placed to form a layer about 0.2 m deep. A layer about 0.3 m deep of water was maintained above the organic substrate layer, to encourage vertical flow. The RAPS units were followed by a settling/oxidation pond to collect treated or partially treated waters. This pond allows iron and other precipitates to settle and is useful in providing a more constant flow rate into a down-gradient treatment system. The settling pond was sized to allow a primary retention time of 8 hours. The last unit in the system was a cascading limestone trench for the oxidation and removal of Fe under oxidising conditions (Figure 3). Since dissolved oxygen decreases with depth, this shallow cascading trench helped to increase rate of oxidation.

Acid mine water was piped directly from the source and the flow rate was controlled by means of gate valve to the initial RAPS unit. A flow rate of 1L/min was used as the primary flow rate, which provided the optimal residence time of 8 hours for each RAPS unit. The influence of residence time on the neutralisation rate and removal of metals was examined by varying the inflow rate, which is inversely proportional to residence time. The construction of the pilot plant started on 27 October 2014, and it has been operational from 1 November 2014. On-site analyses of water quality parameters including, pH, redox, electrical conductivity, dissolved oxygen and temperature were done using a WTW multi 3430 meter. Alkalinity was also analysed in the field by means Hach DR 900 spectrophotometer. In addition, flow rate was measured by means of the bucket and stopwatch method. Water samples were collected using 100ml plastic bottles. The samples were filtered using 0.45 µm filters. For trace and major metals and metalloids, samples were preserved by acidification using 3M nitric acid (HNO_3). Analyses were done by means of ICP-MS and IC analytical techniques. Precipitates that had formed in the treatment units (RAPS1, RAPS2 and oxidation pond) were collected after 12 months of operation from the tops and bottoms of the units, and analysed for mineralogical compositions using XRD and SEM.

Table 1 *Analytical data for acid mine drainage sources in the study area.*

	Carolina/ discharge	DWAF guideline
Flow (L/min)	34	
pH	3.06	6-9*
EC (mS/m)	254	
Dissolved oxygen (mg/L)	5.20	
Redox (mV)	350	
Calculated acidity	967.77	
Na (mg/L)	8.16	
Mg (mg/L)	61.25	
Al (mg/L)	40.62	0 - 0.15*
K (mg/L)	7.54	
Ca (mg/L)	170.16	
V (mg/L)	0.01	
Cr (mg/L)	0.01	
Fe (mg/L)	331.56	0 - 0.1*
Mn (mg/L)	20.3	0 - 0.05*
Co (mg/L)	1.65	
Ni (mg/L)	1.67	
Cu (mg/L)	<0.02	
Zn (mg/L)	2.26	0 - 3.0*
As (mg/L)	0.06	0 - 0.01*
Cd (mg/L)	0.01	
U (mg/L)	0.01	
SO_4^{2-}(mg/L)	2524.77	0 - 200*

*Department of Water Affairs limit for Human consumption

Figure 2 *Carolina pilot passive treatment RAPS and oxidation units*

Figure 3 *Carolina pilot passive treatment cascading trench*

Results and Discussions

Alkalinity generation

The system added substantial alkalinity during the first six months of operation (Figure 4). Consequently, there was an increase in the pH of the water from the source throughout the treatment plant. The pH from the inlet ranged from 2.5 to 3 and it increased to an average 6.5 (from RAPS 1 to 2, respectively). This conforms to what is expected for alkalinity generation, which averages at 120 mg/L and 230 mg/L (as $CaCO_3$) for both RAPS 1 and RAPS 2, respectively. The alkalinity generation of the two RAPS units is attributed to bicarbonates released from microbial SO_4 reduction and the dissolution of limestone. However, after six months there was a decrease in alkalinity addition over time, which was attributed to clogging and depletion of the treatment materials. Clogging is associated with precipitate build-up when the pH increases and the formation of algae on top of the treatment units. After 15 months of operation the average pH in the RAPS units was 4.5 and 6, for RAPS1 and RAPS2 respectively. This also conforms to alkalinity, with average values of 40 and 80 mg/L (as $CaCO_3$), for RAPS 1 and RAPS2 respectively.

The pH in the oxidation pond remained above 6.5 during the initial 60 days. After this period, up to the present date, the pH has dropped to below 5 in the oxidation ponds. This is likely to have been caused by the hydrolysis of iron and manganese. The reactions of Fe and Mn under oxidation conditions are known to add to the proton acidity, and hence this led to a decrease in the pH of the oxidation pond over time. Another possible cause for the decrease in the pH and alkalinity may be ascribed to the oxidation of metal sulfides that have precipitated in the pond. The likely reactions in this regard are similar to the reactions responsible for the generation of AMD.

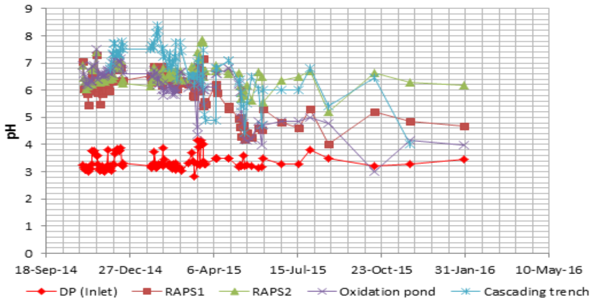

Figure 4 *pH of inflow and outflow water in the passive treatment system*

Metals removal

Figure 5 shows the concentration of iron in the inflow and outflow water of different units in the pilot passive treatment system. There was a gradual decrease in the concentration of iron throughout the passive treatment units. The average Fe in the inlet (source) is 250 mg/L, and the concentration decreased to an average of 150 mg/L and 100 mg/L in the RAPS 1 and RAPS 2, respectively. The decrease of Fe in these anaerobic units is attributed to microbial sulfate reduction process, which releases hydrogen sulfide. The hydrogen sulfide then reacts with Fe and precipitates as iron sulfide. Iron removal rates in the RAPS units increase with time during the initial stages of operation, and this could be attributed to an increase in the community of sulfate reducing bacteria. Iron was further decreased in the oxidation pond and cascading trench, resulting in a concentration as low as 10 mg/L and to below detection limit, respectively. The decrease of iron in these units is associated with oxidation, where iron precipitates as hydroxides. Cascading trenches show the highest rate of iron removal, which is attributed to a high rate of oxidation in the trench. The average Fe removal in the passive treatment system was at least 95% during the first six months. After six months there was a decrease in the removal rate of Fe, mainly due to clogging/armouring and depletion in the treatment materials. Armouring and clogging in the RAPS units relates to the precipitates built up in the organic substrate and the limestone bed.

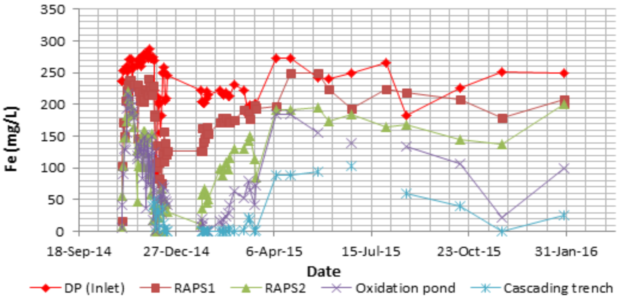

Figure 5 *Fe concentrations of inflow and outflow water in the system*

Figure 6 and 7 show the concentration of Al, Zn, Ni, and Co in the inflow and outflow water of different units in the pilot passive treatment system. Al concentration of the inlet (the source) averages 30 mg/L, which is way above the required limit, as per the domestic water use standard. Figure 6 shows that Al decreased to below zero in the system from the RAPS 1. This is attributed to the increase in the pH to above 6 and, hence, Al is likely to precipitate at this pH. White precipitates were observed on top of RAPS 2, and this could be associated with a hydroxide of aluminium, such as gibbsite. Metals such as Zn, Ni and Co are removed in a similar manner in anaerobic and aerobic units. These metals are initially removed as sulfides in the RAPS units owing to microbial sulfate reducing and the residual or remaining dissolved metals co-precipitating with hydroxides of iron. The hydroxides of Fe are known to be excellent sorbents of trace metals, such as Co, Ni, and Zn and, subsequently, can control their mobility, fate and transport in the environment.

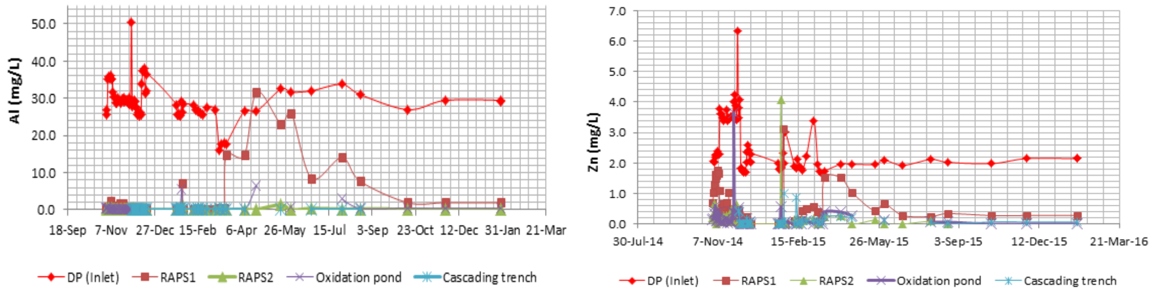

Figure 6 *Al and Zn concentrations of inflow and outflow water in the system*

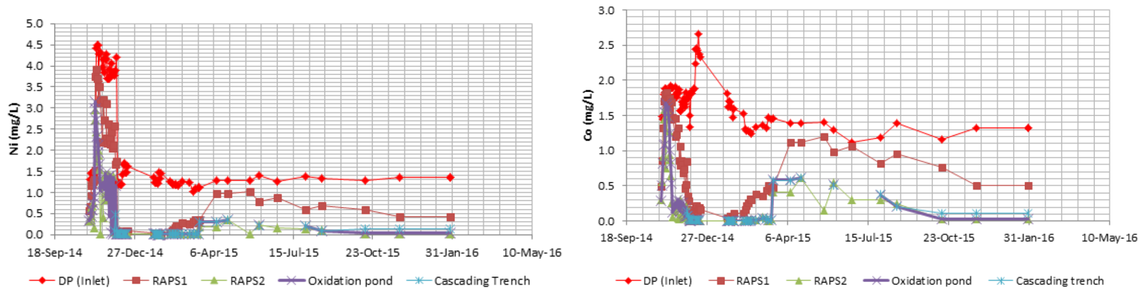

Figure 7 *Ni, and Co concentrations of inflow and outflow water in the system*

Sulfate reduction

Figure 8 shows sulfate reduction with time in the treatment plant. The SO_4 level in the inlet averages 1 500 mg/L which slightly decreases in the RAPS units to an average of 1 000 mg/L. There has been substantial SO_4 reduction in the anaerobic units, especially RAPS2 during the first six months of system operation, and this has been attributed to microbial processes. The average removal of sulfate in the system was only 22%. After six months, SO_4 reduction has been decreasing with time and this is attributed to clogging and depletion of the treatment materials. Sulfate reduction is important in the system for more effective secondary alkalinity addition and the removal of metals.

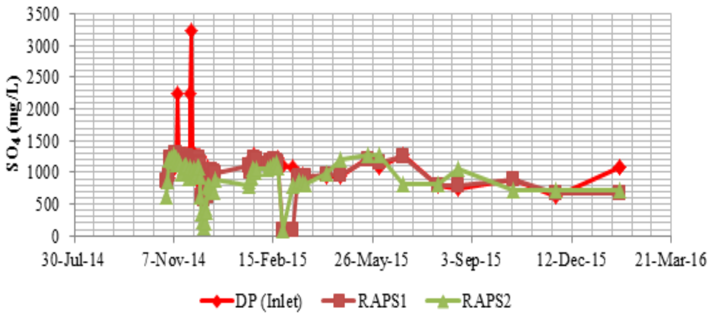

Figure 8 *SO_4 concentrations of inflow and outflow water in the system*

Mineralogical composition of precipitates

Mineralogical compositions of the precipitates were analysed by means of XRD and SEM, (figures 9, 10, and 11). The top layer of RAPS 1 principally consists of goethite (FeOOH) (84.8%), followed by jarosite [$KFe_3(SO_4)_2(OH)_6$] (8.3 wt%) and hematite (3.32 wt%), whereas the bottom layer consists of palygorskite $(Mg,Al)_2Si_4O_{10}(OH).4(H_2O)$ (47.7 wt%), gypsum ($CaSO_4.2H_2O$) (23.15 wt %), jarosite (10.96 wt %), sulfur (7.91 wt%), calcite (6.37 wt %), dolomite (2 wt %) and quartz (3.6 wt %) (Figure 9). It should be noted that palygorskite, calcite, dolomite and quartz are not secondary minerals, since there are weathered from the limestone used in the system. The presence of high concentrations of iron hydroxide minerals on the top layer of RAPS1 is indicative of a high rate of oxidation. The presence of jarosite is indicative of a low pH on top of RAPS1, which is an inlet of the system. However, since this is vertical flow system, the pH increases downwards — hence the formation of gypsum at the bottom of the unit.

The top layer of RAPS2 principally consists of amorphous contents (100 wt %) or poorly crystalline materials that do not contribute to diffraction peaks (figure 10). Based on field observations, the top layer of RAPS2 consisted of white to orange slurry-like precipitates. The white could be attributed to Al oxy-hydroxides and orange could be indicative of Fe oxy-hydroxides. Gypsum (68.9 wt %) is predominant at the bottom of the RAPS2 unit, where the pH is higher. Figure 11 shows a well-developed gypsum crystal at the bottom of RAPS2. Goethite is the dominant mineral species in the oxidation pond, especially in the top layer, and this is again attributed to high rate of oxidation in the pond (figure 10).

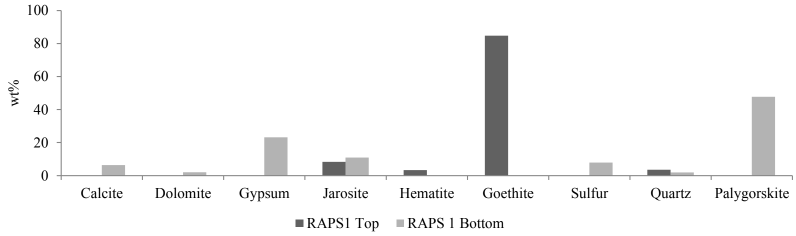

***Figure 9** Mineral composition of precipitates formed in the RAPS 1 top and bottom layers*

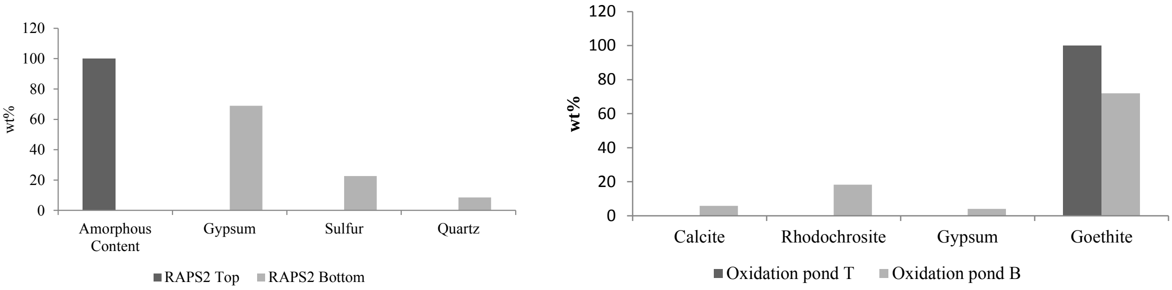

***Figure 10** Mineral composition of precipitates formed in the RAPS 1 top and bottom layers*

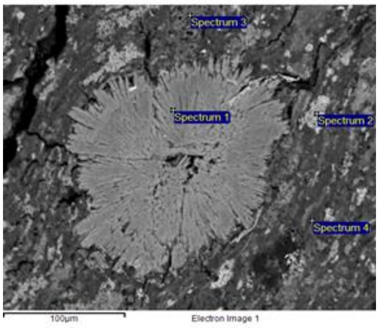

***Figure 11** SEM image for the RAPS2 unit bottom layer, showing a well-developed gypsum crystal*

Conclusions

The pilot passive treatment system at Carolina demonstrated that passive treatment is a potential long-term suistainable remediation measure for polluted mine water from abandoned mine sites in South Africa. The geochemical mechanism of passive treatment of polluted mine water is a complex process, comprising of a number of reactions that occur under different redox conditions. Hence, to achieve optimum long-term remediation of polluted mine water in South African abandoned mine sites; an integrated passive treatment approach is envisaged. Some of the lessons learnt and recommendations for future design of appropriate passive treatment systems are as follows:

- During the first six months of operation, the Carolina pilot plant successfully neutralised the water and substantially removed contaminants such as Fe, Al, Co, Zn, Ni, As, Pb, V, but achieved limited SO_4 reduction (only a 30% removal rate was achieved). Thereafter, there was a deterioration in treated water quality over time, largely due to clogging and/or depletion of the treatment materials. Periodic flushing of the system is envisaged. In addition, the system should be optimised for SO_4 removal. SO_4 reduction is mainly attributed to microbial activities, and hence conditions necessary for optimum reduction should be considered. Such conditions include, use of appropriate organic substrate, pH, redox, flow rate/contact time.
- There was minimal or no removal of Mn in the system and this may be attributed to the presence of Fe in the oxidation pond and cascading trench, which tend to compete for oxygen consumption. A Mn removal bed is envisaged in this regard.
- Mineralogy and bulk geochemical analyses undertaken showed a clear variation in the geochemistry of the precipitates formed in the passive treatment units. This conforms to the quality of the inflow and outflow water in the system. Metals such a Fe, Zn, Cu precipites as sulphides in the anaerobic units and as oxides or hydroxides in the aerobic units. Accumulation of these mineral/metal species in the passive treatment units present an opportunity to recover valuable products that can offset remediation costs.

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Impact of Fertilizer Effluent Disposed in Dolerite Quarries on the Groundwater Quality

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Abstract

Coal-based fertilizer effluent with high concentrations of nitrate (>12 500 mg/L), ammonium (>11 900 mg/L) and sulphate (>2 500 mg/L) from a coal-based fertilizer plant was stored in two unlined dolerite quarries. This resulted in the degradation of the groundwater quality in a nearby borehole to a state that is not suitable for human or animal consumption. Elevated nitrate concentrations in groundwater are a concern because, when ingested by infants, it could potentially interfere with the blood-oxygen levels and cause methemoglobinemia (blue baby syndrome). A Geohydrological investigation was therefore initiated to quantify the impact of the fertilizer effluent on the groundwater regime.

A hydrocencus was conducted to determine if other boreholes in the vicinity of the quarries had elevated nitrate, ammonium or sulphate concentrations. A geophysical survey was also conducted to understand the geological regime by identifying geological structures that may influence the movement and act as preferential pathways for groundwater. The geophysical survey included a detailed magnetic survey that consisted of 30 profiles at line spacing of 200 m, and with average lengths of approximately three kilometres. Where areas of interest were identified from the interpretation of the magnetic data, two-dimensional (2D) electrical resistivity tomography (ERT) surveys was conducted to obtain a model of the subsurface resistivity distribution.

The magnetic survey revealed a well-defined linear magnetic anomaly corresponding to the position of a mapped dolerite dyke less than 200 m from the Fertilizer Quarry. A broad linear zone of increased magnetic field strength with a south-east/north-west strike was also identified. The hydrocencus identified boreholes situated along these structures that are highly contaminated with nitrate. It is therefore plausible that these lineaments acts as preferential pathways for groundwater flow and contaminant transport from the quarries.

The quarries have been rehabilitated since the investigation was initiated. Thus, if there is no natural attenuation of nitrate in the groundwater regime over time, the results of the geophysical investigations will then be used to identify five sites for the drilling of boreholes to investigate the geological and geohydrological conditions in the vicinities of the quarries. All the geological and geohydrological information gathered will be used during the feasibility phase of the study to determine the most feasible option to remediate or manage the contamination of the groundwater regime.

Key words: Fertilizer effluent, preferential pathways, hydrocencus, geophysical surveys, natural attenuation

Introduction

Coal-based fertilizer effluent with high concentrations of nitrate (>12 500 mg/L), ammonium (>11 900 mg/L) and sulphate (>2 500 mg/L) from a coal-based fertilizer plant (production of fertilizer based on coal gasification) was stored in two unlined dolerite quarries (labelled Fertilizer Quarry & Farmhouse Quarry). This resulted in the degradation of the groundwater quality of the underlying aquifer to a state that is not suitable for human or animal consumption. Elevated nitrate concentrations in groundwater are a concern because, when ingested by infants, it could potentially interfere with the blood-oxygen levels and cause methemoglobinemia (blue baby syndrome). A Geohydrological investigation was therefore initiated to quantify the impact of the fertilizer effluent on the groundwater regime.

Objectives

The objective of the investigation is to (1) understand the geological regime by identifying geological structures that may influence the movement/flow of groundwater, (2) understand the geohydrological regime (aquifer parameters), (3) determine the extent by which the underlying aquifer have been effected by contaminants and (4) determine the most feasible option for remediation if there is no natural attenuation.

Materials and Methods

A hydrocencus was conducted to determine the extent by which the underlying aquifer have been affected. This involved the identification, sampling and chemical analyses of boreholes in a ten kilometres radius from the two dolerite quarries that was filled with fertilizer effluent.

Two geophysical techniques were employed during the investigation, namely the ground magnetic method electrical resistivity tomography (ERT). The ground magnetic survey consisted of 30 profiles at line spacing of 200 m, and with average lengths of approximately three kilometres (fig. 1). The ERT survey consisted of three profiles across the mapped dolerite dyke situated near the dolerite quarry labeled as Fertilizer Quarry. The ERT survey made use of the Lund Imaging System developed by ABEM Instruments. Four cables with 21 take-outs each and a standard electrode spacing of 5 m were employed to allow a maximum depth of investigation of approximately 70 m.

A quarterly groundwater monitoring programme was also initiated to monitor the quality of the boreholes that have been affected by the dolerite quarries filled with fertilizer effluent over time. This is to monitor if there is any natural attenuation of the contaminants in the underlying aquifer.

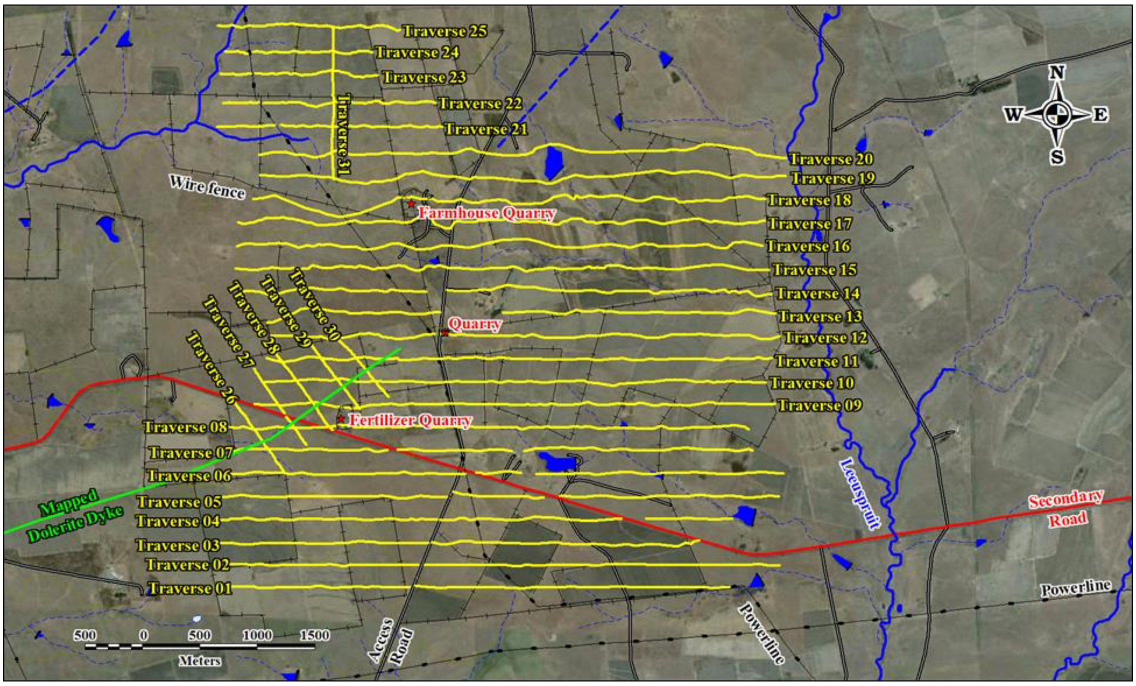

***Figure 1** Position and orientations of the traverses on which ground magnetic data were recorded.*

Nitrogen in the Environment

Nitrogen is present in the environment in a wide variety of chemical forms including organic nitrogen, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), nitric oxide (NO) or inorganic nitrogen gas (N_2). Organic nitrogen may be in the form of a living organism, humus or in the intermediate products of organic matter decomposition. The processes of the nitrogen cycle transform nitrogen from one form to another.

This transformation can be carried out through both biological and physical processes. Important processes in the nitrogen cycle include fixation, ammonification, nitrification, and denitrification. The majority of Earth's atmosphere (78%) is nitrogen, making it the largest pool of nitrogen (Carrol & Salt 2004). However, atmospheric nitrogen has limited availability for biological use, leading to a scarcity of usable nitrogen in many types of ecosystems. The nitrogen cycle is of particular interest to ecologists because nitrogen availability can affect the rate of key ecosystem processes, including primary production and decomposition. Human activities such as fossil fuel combustion, use of artificial nitrogen fertilizers, and release of nitrogen in wastewater have dramatically altered the global nitrogen cycle (Galloway *et al.* 2004). The diagram below (fig. 2) shows processes of the nitrogen fit together to form the nitrogen cycle.

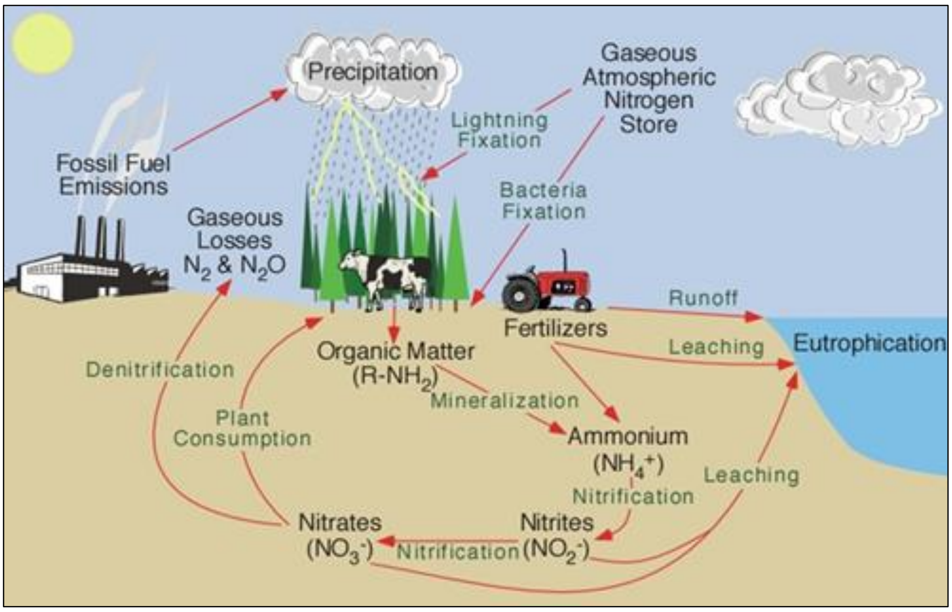

Figure 2 *The nitrogen cycle. (Source: PhysicalGeography.net)*

Geological Setting

The 1:250,000 geological map presented (fig. 3) is the intellectual property of the Council for Geoscience and is used by permission. Copyright and all rights are reserved by the said Council.

The study area is mostly underlain by a massive dolerite sill intrusion. Sedimentary rocks belonging to the Vryheid Formation of the Ecca Group (Karoo Supergroup) are exposed in the central and eastern parts of the study area. These exposures occur at positions where the dolerite sill has been eroded away to reveal the underlying Karoo formations. The sedimentary rocks predominantly consist of sandstones and shales. Coal beds occur within the Vryheid Formation, but no coal exposures at surface are observed within the study area.

A dolerite dyke with an approximate south-west/north-east strike has been mapped in the south-western parts of the study area. In addition, a number of prominent magnetic lineaments with south-west/north-east strikes have been mapped in the vicinity of the study area. These lineaments are thought to be due to large dolerite dykes that do not appear as outcrops.

Regional Magnetic Setting

The airborne magnetics map presented in this section is the intellectual property of the Council for Geoscience and is used by permission. Copyright and all rights are reserved by the said Council. From the airborne magnetics map (fig. 4) it is seen that prominent linear magnetic anomalies with south-west/north-east strikes occur to the west, north-west and north of the study area. These anomalies correspond to the magnetic lineaments shown in the geology map covering the study area (refer to fig. 3).

The mapped dyke does not yield a strong magnetic response in the airborne data. This observation suggests that the dyke is a much smaller feature than the dykes responsible for the large linear magnetic anomalies. A possible magnetic lineament with a south-east/north-west strike may be identified within the study area (black dashed line in fig. 4).

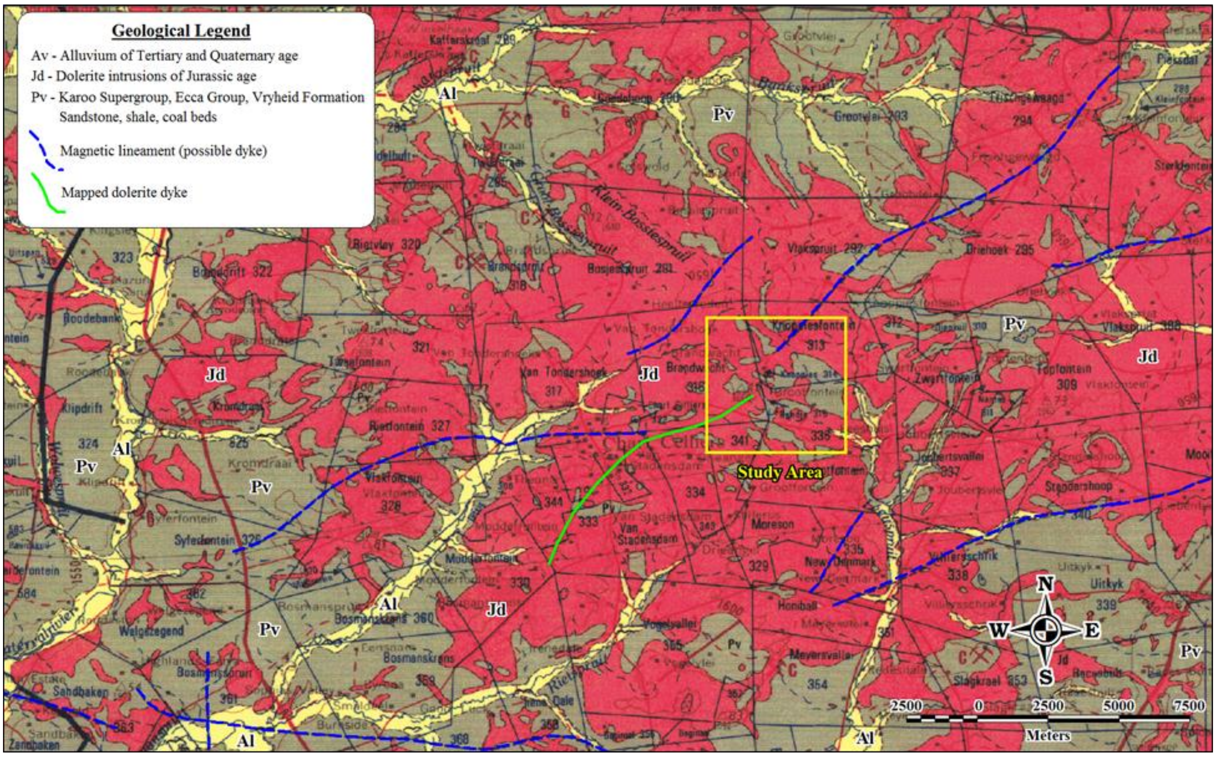

Figure 3 *Geological setting of the study area*

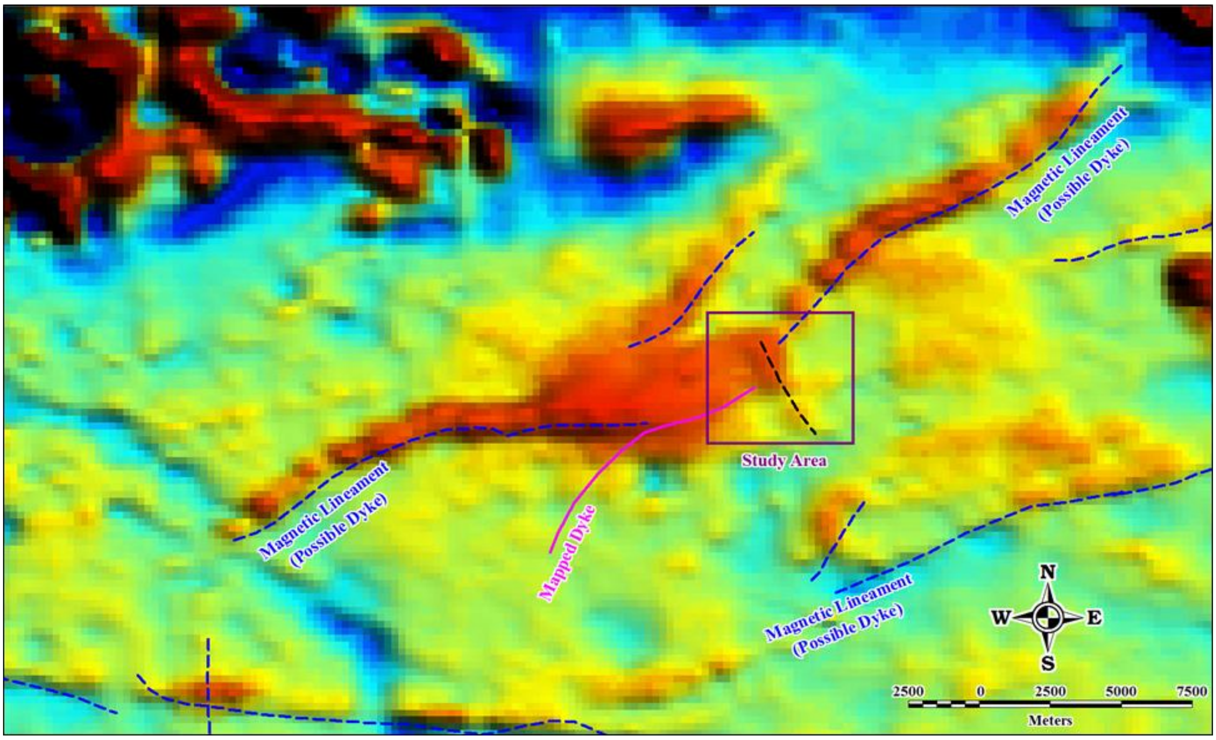

Figure 4 *Airborne magnetics map covering the study area.*

Results and Discussion

A contour map of the total magnetic field is presented in (fig. 5). From the contour map, a number of observations may be made:

- A well-defined linear magnetic anomaly corresponds to the position of the mapped dolerite dyke. This dyke occurs at a distance of less than 200 m from the Fertilizer Quarry.

- A change in the magnetic field intensity is observed along a linear boundary with a south-east/north-west strike running between the Fertilizer Quarry and the Quarry. This apparent contact runs parallel to the linear magnetic anomaly identified from the airborne magnetics map (refer to fig. 4, indicated by the right-hand dashed white line in fig. 8). The broad linear zone of increased magnetic field strength demarcated by these lines may be a large linear dolerite intrusive, but may also be due to a local upwelling of the underlying dolerite sill. The Farmhouse Quarry occurs within this broad zone.
- A zone of low magnetic field intensity occurs to the east of the eastern contact of the broad zone of high magnetic field intensity (see fig. 5). This zone is in all probability due to the fact that the shallow sill has been eroded away at this position (refer to fig. 4), exposing the underlying, non-magnetic Karoo sedimentary rocks. This zone also corresponds to a change in the colour of the vegetation; within the zone, the vegetation appears to be greener.

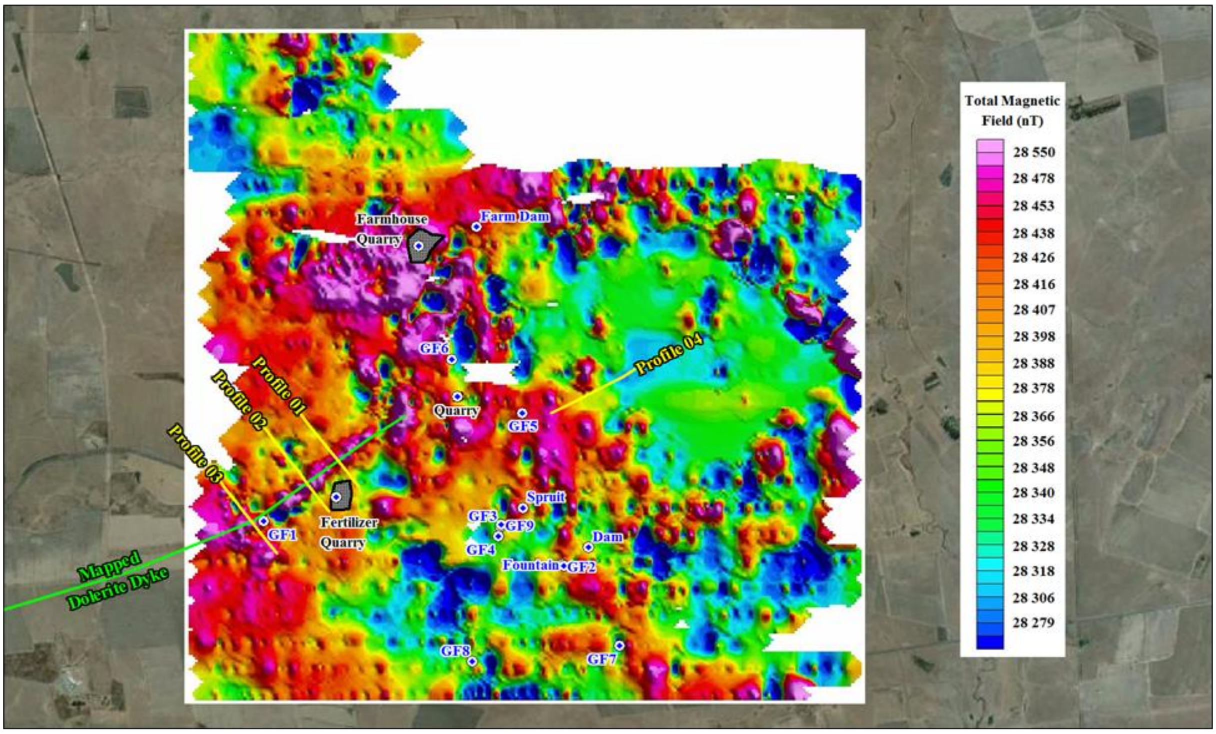

Figure 5 *Contour map of the total magnetic field recorded during the ground magnetic survey and positions and orientations of the four ERT profiles.*

The results of the ERT surveys along Profiles 01, 02 and 03 are shown in fig. 6. The positions where the mapped dyke was traversed are indicated in these profiles. A number of observations may be made:

- On Profile 01, the position of the mapped dyke corresponds to a local zone of high resistivity at shallow depths. Immediately to the east of this zone, a zone of low resistivity is observed. This zone may indicate the presence of earth materials with a higher degree of water saturation. It is possible that this zone acts as a preferential pathway for groundwater migration.
- Profile 02 displays a similar resistivity distribution as Profile 01. A pronounced change in the resistivities of the near-surface materials is observed to the east of the mapped dyke, possibly indicating higher degrees of water saturation.
- The character of Profile 03 is somewhat different to Profiles 01 and 02. The position of the mapped dyke does not correspond to a local zone of high resistivity. In addition, the materials to the west of the mapped dyke now have lower resistivities as compared to the material to the east. The reason for the different response on Profile 03 is probably related to the fact that it is located in an area with higher magnetic field intensities as compared to Profiles 01 and 02 (refer to fig. 5). Local magnetic anomalies observed on the eastern part of Profile 03 correspond with the zones of high resistivity and are likely due to the presence of shallow dolerite.

Resistivity data were recorded on Profile 04 to detect and map the boundary between the dolerite sill and the Karoo rocks exposed by erosion of the sill (refer to fig. 5). The inverse resistivity model along Profile 04 is presented in fig. 7. The most prominent feature of the resistivity model is the dramatic change in the resistivities of the deeper earth materials near position 515 m. The model suggests an abrupt ending of the dolerite sill at this position. The low resistivity material to the east of this position probably consists of Karoo sedimentary rocks, possibly with a high degree of water saturation.

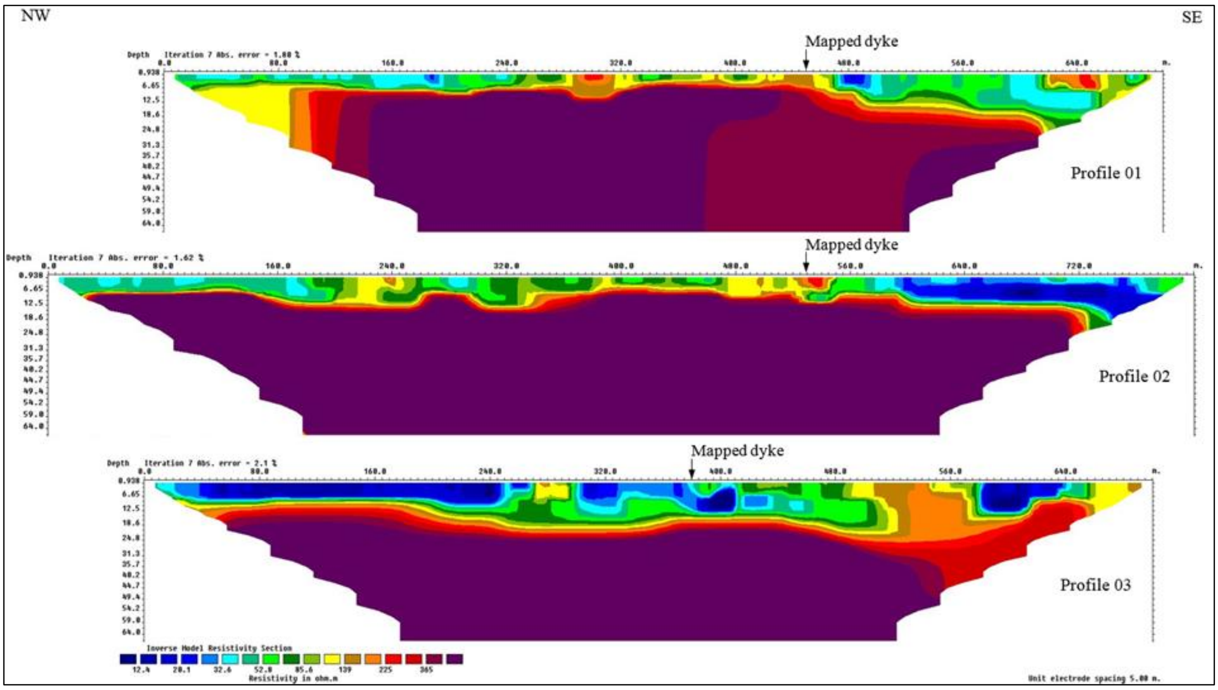

Figure 6 *Inverted resistivity models along Profiles 01, 02 and 03 (north-west to south-east)*

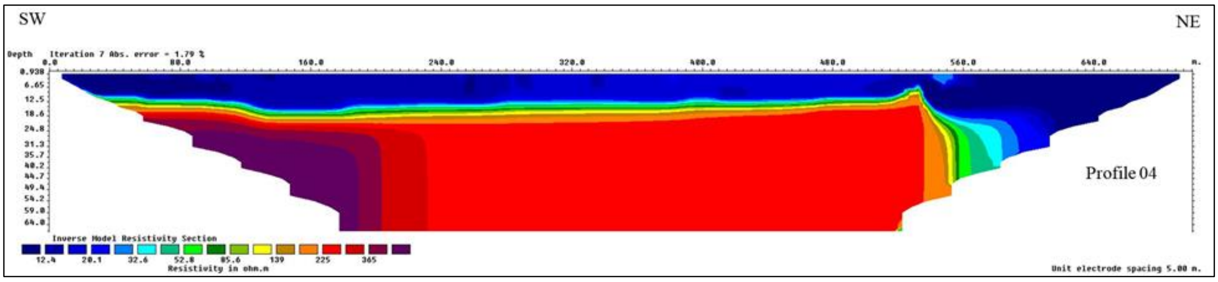

***Figure** 7 Inverted resistivity model along Profile 04 (south-west to north-east)*

Analyses of samples collected from the Fertilizer Quarry and the Farmhouse Quarry showed that the quarries contained water that was heavily contaminated with nitrate, ammonium and sulphate. The chemical composition of the water samples had a typical fertilizer effluent signature.

In fig. 8, the nitrate concentrations of the groundwater and surface water at the various sites sampled are shown using a colour-coding scheme. Five groundwater sites showed nitrate concentrations above the allowable limits. Borehole GF1 is located adjacent to the mapped dyke that runs past the Fertilizer Quarry. The high nitrate concentration (1725 mg/L) recorded at this groundwater site suggests that the fertilizer effluent may have migrated along preferential pathways associated with the dyke.

Boreholes GF3 and GF9 are heavily contaminated with nitrate, exhibiting concentrations of 581 and 447 mg/L, respectively. These two groundwater sites occur within the broad magnetic lineament that extends beyond the Farmhouse Quarry in the north. It is plausible that this lineament is due to a dolerite structure that may also be associated with preferential pathways for groundwater flow and contaminant transport. The elevated nitrate concentration (16 mg/L) at borehole GF6 may also be due to the mobilisation of contaminants from the Farmhouse Quarry along the broad magnetic structure.

High nitrate concentrations were also recorded at borehole GF2 (102 mg/L) and at the spring (316 mg/L; labelled Fountain). Although these elevated concentrations may be due to the mobilisation of fertilizer effluent from the Farmhouse Quarry.

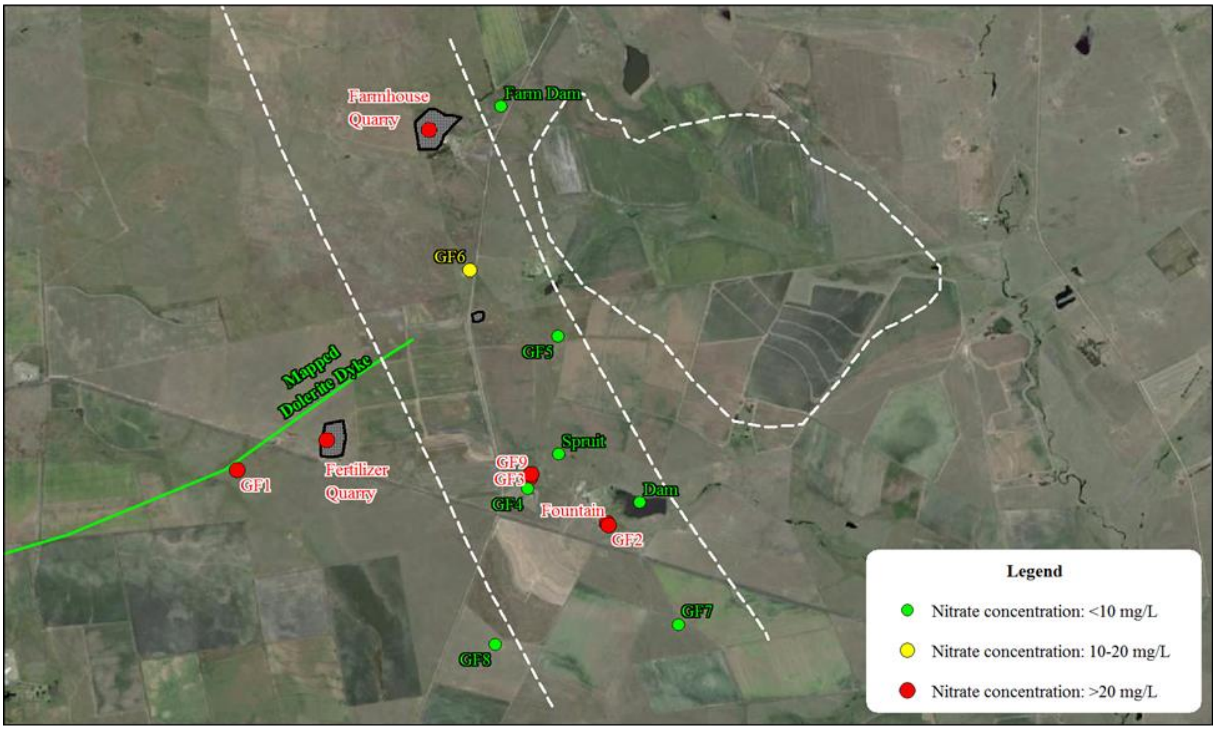

Figure 8 *Nitrate concentrations observed at groundwater and surface water sites.*

The quarries have been rehabilitated since the investigation was initiated, thus the pollution source have been removed. The time graphs of the electrical conductivity and nitrate concentrations of boreholes sampled is displayed in fig. 9. From this it is clear that most contaminated boreholes (GF1, GF3 & GF9) have improved significantly since November 2015, indicating that the rainfall received since then might have a dilution effect on the groundwater quality, as the sources of pollution is now removed.

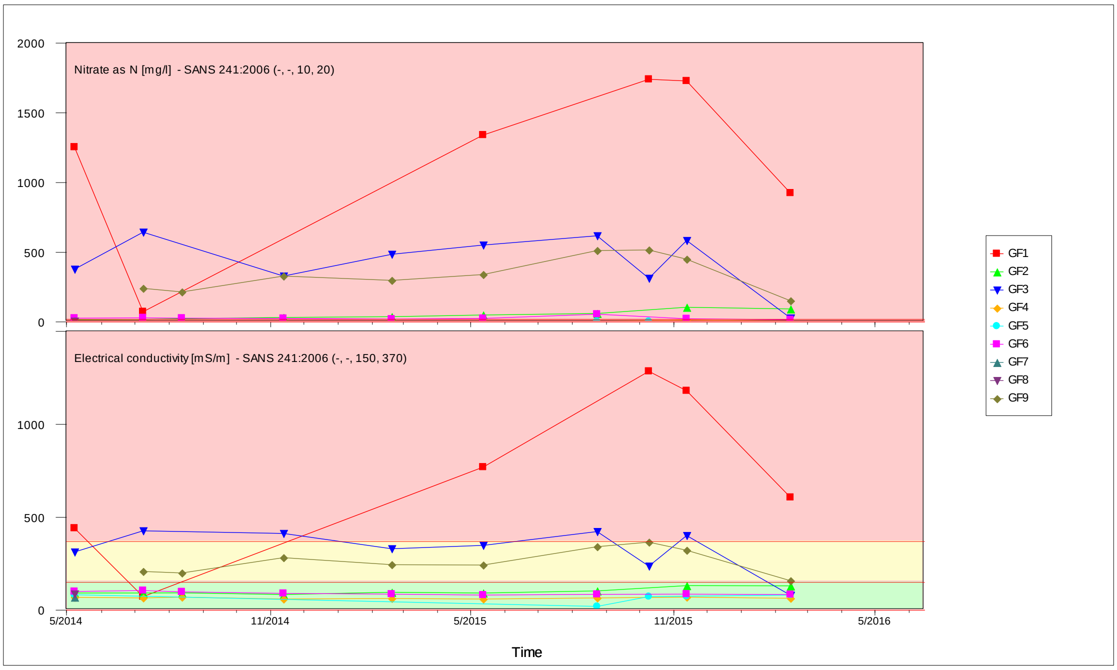

Figure 9 *Time graphs of the electrical conductivity and nitrate concentrations of the boreholes since 2014.*

Conclusions and Recommendations

The magnetic survey revealed a well-defined linear magnetic anomaly corresponding to the position of a mapped dolerite dyke less than 200 m from the Fertilizer Quarry. A broad linear zone of increased magnetic field strength with a south-east/north-west strike was also identified. The hydrocencus identified boreholes situated along these structures that are highly contaminated with nitrate. It is therefore plausible that these lineaments acts as preferential pathways for groundwater flow and contaminant transport from the quarries.

The water quality in the most contaminated boreholes (GF1, GF3 & GF9) have improved significantly over the last three months, thus indicating that the rainfall in this three month period might have flushed the underlying aquifer (and the source of contamination has been removed). These trend will be monitored during the course of 2016.

The quarries have been rehabilitated since the investigation was initiated. Thus, if there is no natural attenuation of nitrate in the groundwater regime over time, the results of the geophysical investigations will then be used to identify five sites for the drilling of boreholes to investicate the geological and geohydrological conditions in the vicinities of the quarries. All the geological and geohydrological information gathered will be used during the feasibility phase of the study to determine the most feasable option to remediate or manage the contamination of the groundwater regime.

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Investigation of the effects of groundwater resurgence and subsequent exfiltration of ferrous groundwater from the dump site of the Witznitz former lignite mine into the Pleisse and Wyhra rivers

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Abstract

Decades of open-cast lignite mining and groundwater lowering have substantially affected the landscape and hydrogeology of the South Leipzig Region. The overburdens of the opencast mining industry in Saxony mostly contained pyrite, which had to be excavated and dumped. After the closure of the mining industry, groundwater resurgence started and pyrite weathering was initiated, leading to acidification and accompanying mobilization of acidity, iron and sulfate through direct and indirect diffuse groundwater inflows into the water courses. The study presents a remediation measure for the reduction of acid, iron- and sulfate loaded groundwater leachates from the Witznitz lignite dump site into the Pleiße River. Embedded in a monitoring and modelling investigation program, different remediation approaches were examined to minimize negative impacts on the aquatic ecosystems. According to groundwater modelling results, an influx of around 935 kilogram of iron load per day have entered the Pleiße River through diffuse groundwater exfiltration from the balance areas of the dump site of Witznitz in 2009. In order to reduce the exfiltration volume of ferrous groundwater from the Witznitz dump site an optimized and adapted land cultivation scheme for post-mining landscapes has been tested since 2009. The aim was to minimize the amount of percolation water and thus to reduce groundwater recharge quantities. Thereby a comparison between cocksfoot *(dactylis glomerata)*, lucerne (*medicago sativa)* and reference crops indicated that lucerne performed promisingly in regard of reducing percolation quantity as well as having high yields. Based on these positive results, a large-scale experiment was developed and implemented starting in 2014, in which 225 hectares were planted with lucerne. In addition, the plausible impact of the large-scale experiment was estimated through the application of a reactive groundwater flow and transportation model, which showed that in the long term a groundwater discharge reduction of 33, 40 and 34 percent could be attained through the tested counter-measure in 2027, 2040 and 2100 respectively. This in turn should lead to an iron load reduction of approximately 342, 433 and 324 kg/d respectively, accounting for around 1/3 of total iron influx from the Witznitz dump site. Further evidence of the effectiveness of the measure has to be evaluated during the forthcoming years.

Key words: post mining landscapes, lignite, iron, groundwater exfiltration, remediation measure, land use conversion

Introduction

For many decades the landscape of the South Leipzig Region has been shaped by intensive lignite mining. During the mining activities an enormous artificial lowering of the groundwater table by pumps was made and large amounts of overburden and spoil were generated. Through the movement and disintegration of unconsolidated rocks (from depths of up to 60 meters) pyrite oxidation processes were initiated and large quantities of iron oxides and sulfate have been, and are still being, generated. Consequently, a massive intervention involving the surface and subsurface water catchment areas has been put into place. Whereas most of the site remediation measures above ground are completed, there are still major efforts required to remedy appropriately the long term impacts from mining-impaired areas - which are increasingly affecting the water quality of the catchment areas that have rising groundwater levels and groundwater inflows. Therefore, the diffused sources of groundwater inflow into the rivers and post-mining lakes as well as the long-term nature of the problem) require a high level of reliable data to help devise appropriate and effective countermeasures.

In 2003, an ochre coloring of the Pleiße River was observed. Ochre colored water streams and the accumulation of iron hydroxide sludge indicate the effects of groundwater exfiltration with high loads of soluble ferrous iron and insoluble ferric iron into a water course. The unpleasant coloring of the water leads to negative impacts on the recreational and touristic use of the watercourses as well as to impairments of the aquatic communities of fish, macrozoobenthos and macrophytes. In absence of appropriate additional countermeasures the continuous discharge of acid iron- and sulfate compounds would last even beyond the 24th century (IBGW 2010). In accordance to the German Federal Mining Act the Lausitzer und Mitteldeutsche Bergbauverwaltung GmbH (LMBV) has the obligation to remediate the former opencast mining sites in East Germany. For the clarification of the complex issue an investigation framework was developed and a pilot project entitled "Investigation of the effects of groundwater resurgence and subsequent exfiltration of ferrous groundwater from the dump sites of the former Witznitz lignite mine into the Pleisse and Wyhra rivers" was set up by the LMBV in 2007. The project area and an image of the ochre colored Pleiße River is shown in *Figure 1*.

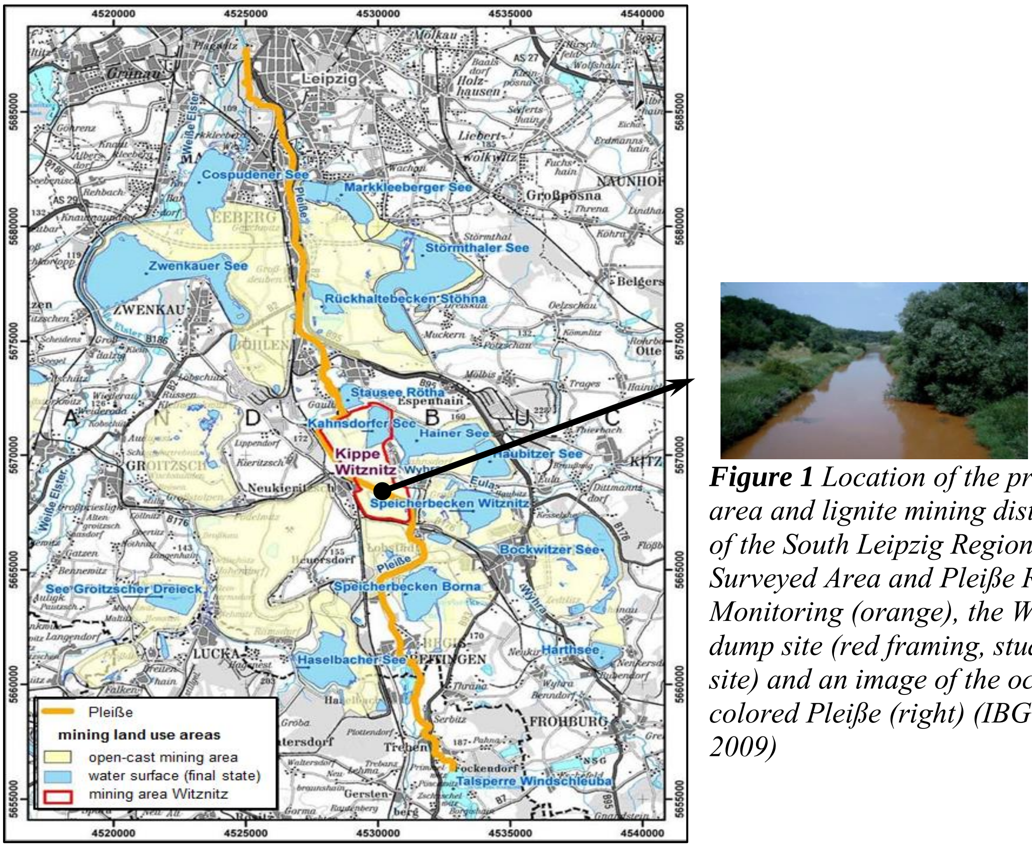
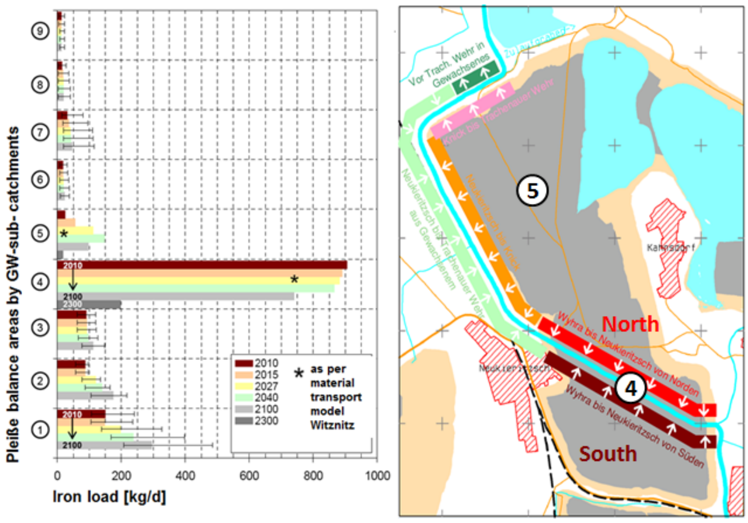


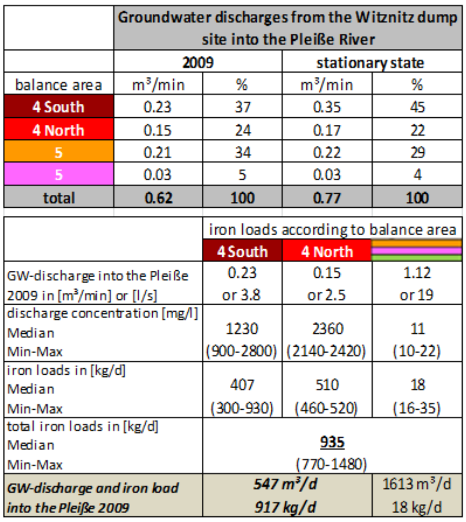
***Figure 1** Location of the project area and lignite mining districts of the South Leipzig Region, Surveyed Area and Pleiße River Monitoring (orange), the Witznitz dump site (red framing, study site) and an image of the ochre colored Pleiße (right) (IBGW 2009)*

Pilot project - Approach and baseline conditions

The overall aim of the project was the detection, evaluation and prediction of the diffuse sources of acid iron and sulfate substance flows and quantities in order to determine appropriate and economically feasible measures for immediate and medium-term hazard prevention and improvement of the water quality in the catchment area of the Pleiße River. Furthermore, a transfer of the applied conceptual framework and of the key project outcomes to other locations of the region with similar problems was desired. The investigation, monitoring, evaluation and implementation steps of the project were organized within three phases, and from the outset of the pilot project, the involvement of a range of institutions and authorities was enabled through the establishment of a working group under the leadership of LMBV, as the agency executing the project. Thus, since 2008 a monitoring program has been in operation to observe and document constantly the water quality and sedimentation quantities along the Pleiße River. Additionally, the groundwater level and quality was measured. Parallel to this, a groundwater flow and substance transport model was set up for the Witznitz mining area through the utilization of the available geological data, mine plans, groundwater monitoring results and water quality monitoring results from the Pleiße (IBGW 2009, 2009a, 2010). Consequently, the water course was subdivided into respectively nine groundwater balance areas, whose groundwater exfiltrates from the eastern and western sides into the Pleiße. Based on these data sets the localization and quantification of the hot spots of the diffuse iron-loaded groundwater inflow was determined and it was confirmed that the highest loads of iron enter the Pleiße River directly from the groundwater inflow of the former Witznitz mining area. The iron concentrations at this section of the Pleiße River are ranging between average values of 3 to 6.5 mg/l, whereas higher concentrations were detected during low and medium runoffs (IBGW 2009, SLG 2014).

In *Figure 2* the results of the model calculations of groundwater discharge volumes and iron loads are presented. In 2009 an average iron load of 935 kilogram has been exfiltrated from the Witznitz dump site into the Pleiße River per day. This corresponds to 55 percent of the total iron load of the investigated catchment areas. According to the simulation model, the iron loads of the balance area 4 (South and North) are by far the most significant (917 kg/d). In regard to the groundwater discharge volumes, the stationary state of the balance area 4 North was almost achieved in 2009, whereas for the balance area 4 South an increase from 0.23 m³/min to 0.35 m³/min until 2100 is predicted. The total iron load from the Witznitz dump site (balance area 4 and 5) was estimated with around 1000 kg/d until 2100 and it was projected that it will decline to around 250 kg/d until 2400 (IBGW 2009b, *IBGW 2010)*.





	Groundwater discharges from the Witznitz dump site into the Pleiße River			
	2009		stationary state	
balance area	m³/min	%	m³/min	%
4 South	0.23	37	0.35	45
4 North	0.15	24	0.17	22
5	0.21	34	0.22	29
5	0.03	5	0.03	4
total	**0.62**	**100**	**0.77**	**100**

	iron loads according to balance area		
	4 South	**4 North**	🟧 🟪 🟩
GW-discharge into the Pleiße 2009 in [m³/min] or [l/s]	0.23 or 3.8	0.15 or 2.5	1.12 or 19
discharge concentration [mg/l] Median Min-Max	1230 (900-2800)	2360 (2140-2420)	11 (10-22)
iron loads in [kg/d] Median Min-Max	407 (300-930)	510 (460-520)	18 (16-35)
total iron loads in [kg/d] Median Min-Max	**935** (770-1480)		
GW-discharge and iron load into the Pleiße 2009	***547 m³/d*** ***917 kg/d***		1613 m³/d 18 kg/d

Figure 2 *Projection results of iron loads entering the Pleiße from the balance areas 1 to 9 in 2010, 2015, 2027, 2040, 2100, 2300 (*as per material transport model Witznitz) (left) (IBGW and Ecosystem Saxonia 2011); Baseline balances of groundwater flow and iron loads entering the Pleiße from the Witznitz dump site between the mouth of the Wyhra and the Trachenauer Weir (right) (IBGW 2009b)*

Description of the Witznitz former lignite mining area

The Witznitz former lignite mining area is located around 15 kilometers south of Leipzig between the villages of Neukieritzsch, Kahnsdorf and Rötha. It was operated in a series of successive stages from 1900 to 1990. The Kahnsdorf Lake belongs to the area and it is an acid mining lake with a depth of around 40 to 60 meters. The area has a size of around 450 hectares and the overall volume of the dump site is around 360 million cubic meters (IBGW 2010). It is situated in a tributary of the Pleiße in the section between river kilometer 23.8 where the Wyhra enters the Pleiße and the Trachenauer Weir at river kilometer 17.5. Because of mining activities, the course of the Pleiße and Wyhra rivers was relocated in a westerly direction so that since the 1960s the Pleiße River flows through the Witznitz dump site. The mean annual runoff at this part of the Pleiße is around 6.5 m³ per second. Preliminary studies indicated that the top soil of the Witznitz post-mining area consists of loamy-silty sands to sandy loam with indications of waterlogging conditions and acidity in the subsoil (FIB 2012, Haferkorn 2011). The land use is dominated by agricultural use (65 %). Furthermore, around 19% of the area is forested, 5 % grassland and 10% ruderal sites (IBGW 2009).

Materials and methods

Aim and Scope

From a set of evaluated remediation measures of the pilot project this study presents the results of a coordinated and scientifically accompanied land use conversion from crop land to quasi permanent pasture on the former dump site of the Witznitz mining area. The general approach of the measures was to establish optimum growth conditions for plants so that an increased evapotranspiration is enabled which leads to a reduction of percolation. Thus, the overall goal was to prove that an optimized land use conversion and adaptive water balance management can lead to a reduction of groundwater recharge considering moderate hydrological conditions. Especially for the study site, it is expected that improved water balance management - i.e. through permanent soil covering - will minimize the groundwater recharge and subsequently induce a decrease of the exfiltration of ferrous groundwater from the Witznitz dump site into the Pleiße River. In Figure 3 a scheme of the theoretical approach of the measure and the system behavior is given.

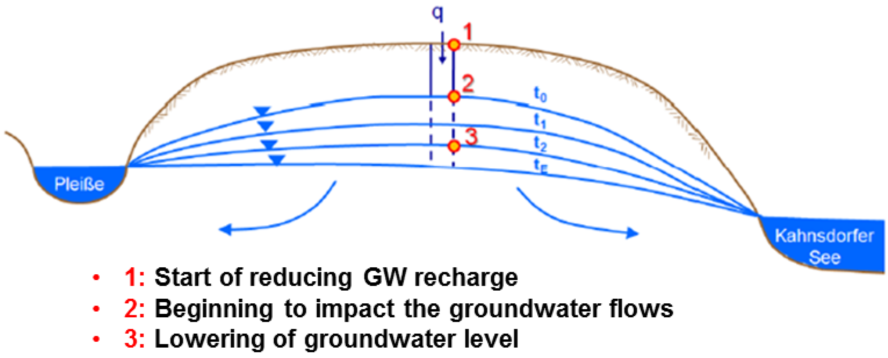


Figure 3 *Theoretical Approach of the measure (GFI 2012)*

Basically, the land use conversion was restricted by the preferences of the landowner. For example a conversion towards forest with high evapotranspiration rates was not welcomed; however, an agreement on the cultivation of perennial energy and fodder crops was reached. From a selection of the testing cultivars, cocksfoot *(dactylis glomerata)* and lucerne (*medicago sativa)* as alternatives to conventional crop rotations (with high share of grains and rape) were chosen. The selection was based on the following criteria: 1. good adaptation to local conditions, 2. reduction of groundwater recharge through strong above- and underground growth, 3. high exhaustion of the soil moisture storage, 4. shortening of the fallow period, 5. positive effects on soil development and fertilization of the post-mining soils, 6. short-term effects on the water balance as well as 7. being suitable for cultivation and harvesting using conventional agricultural technology and 8. the opportunity to integrate the productivity of the land into profitable business processes (FIB 2012).

Experimental set up

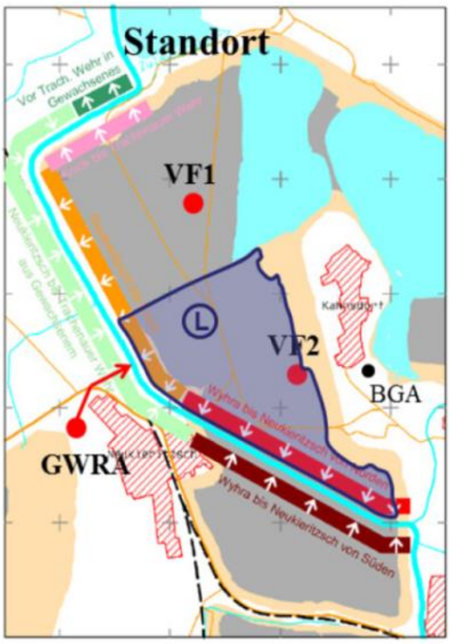


Figure 4 *Sampling sites (VF1, VF2), large-scale experiment area (blue shaded area L) at the former mining area of Witznitz (IBGW)*

From 2009 until the present, field tests were conducted to estimate an order of magnitude for the effectiveness of the proposed measure. During the assessment, optimized cultivation preconditions in regard to fertilization, soil improvement and preparation and their impact on yields and water percolation were tested and evaluated. Overall, six test areas with a size of 20 meters by 50 meters (VF1), four test areas at the side of the mining area (VF2) and six control plots on the agricultural land were installed and tested before a large-scale experiment was carried out in 2014 (L). A detailed overview of the study sites is given in *Figure 4*. In addition to the field tests, two lysimeters on the Witznitz mining area and four prepared lysimeters at the lysimeter station in Brandis and another reference lysimeter were included in the experimental program. In this way, an array of multiple test configurations at the field trials and lysimeter plots could be arranged concurrently. The plot cultivation was organized in a synchronized manner with lucerne, cocksfoot, a mixture of cocksfoot and lucerne and different reference crops like silage maize, winter wheat and winter barley being planted. At the test sites and for the preparation of the monoliths of the lysimeters the following soil enhancement methods were applied: 1. up to 80 centimeters of soil loosening, 2. liming and 3. application of an admixture of 125 or 500 tonnes dry matter from sewage sludge compost per hectare. Depending on the growth height, three to four harvests were made. From the outset, the test field was accompanied through a comprehensive soil-water-plant monitoring program as well as water balance modelling. The monitoring was complemented through laboratory tests and test-related modelling of the percolation quantity considering all site-related water balance components. Thus, the interactions between soil improvement and preparation and its impact on growth and the overall water balance could be investigated (GFI 2012, 2013, 2014, 2015).

Based on promising results of the field test, a concept for a large-scale experiment was proposed, an area of 225 hectares was selected (cf. *Figure 4*) and a cultivation management contract with the land tenant was signed in 2014. The soil preparation was derived from the key findings of the field tests and a soil survey of the agricultural land. The large-scale experiment with a determined crop rotation scheduling will be continued in the long-term (GFI 2015). Soil preparation, maintenance and harvesting will be organized in cooperation with the land tenant.

Results

Comparison of the soil enhancement methods and the annual yields of lucerne, cocksfoot and cocksfoot/lucerne

At the test fields VF1 und VF2 as well as at the lysimeter plots, soil loosening and liming had a positive effect on the biomass production of the cocksfoot and a marginal impact on the yield of lucerne. Also the application of varied admixture of sewage sludge compost influenced positively the biomass production of cocksfoot and had less impact on the growth of lucerne. As cocksfoot had lower yields than lucerne and due to intermediate outcomes that soil improvement through sewage sludge compost application was not feasible because of environmental restrictions a modification of the experimental set-up was applied in 2012. Accordingly, the testing area VF2 was dismantled, the lysimeter monoliths containing sewage sludge compost were set up without sludge and the cocksfoot testing plots were replanted with a mixture of cocksfoot and lucerne. Overall, the lucerne yield remained relatively stable, with an average yield of 12 to 13 tonnes dry matter per year during the test period from 2010 to 2015. For cocksfoot the yield was generally lower and more variable. Depending on the preconditions it ranged between 8 to 10 tonnes dry matter per year. The yield increased to an average of around 10 tonnes dry matter per year when a mixture of cocksfoot and lucerne was cultivated. Generally, the yields at the lysimeter plots were lower than the yields of the test plots and control plots because of drought damage and an island effects. The basic findings of the phenology parameters confirmed that lucerne performed best in regard to biomass production. From an economic perspective, a lucrative utilization of it as an energy crop and fodder crop by the land tenant is possible and thus this remediation measure can be classified as financially self-sustaining (Grontmij 2015, Luckner 2015).

Lysimeter results - Soil-water balance and effectiveness of the measure

In *Diagram 1* and *Diagram 2* an overview of the lysimeter and water balance results for the period from 2009 to 2015 is presented.

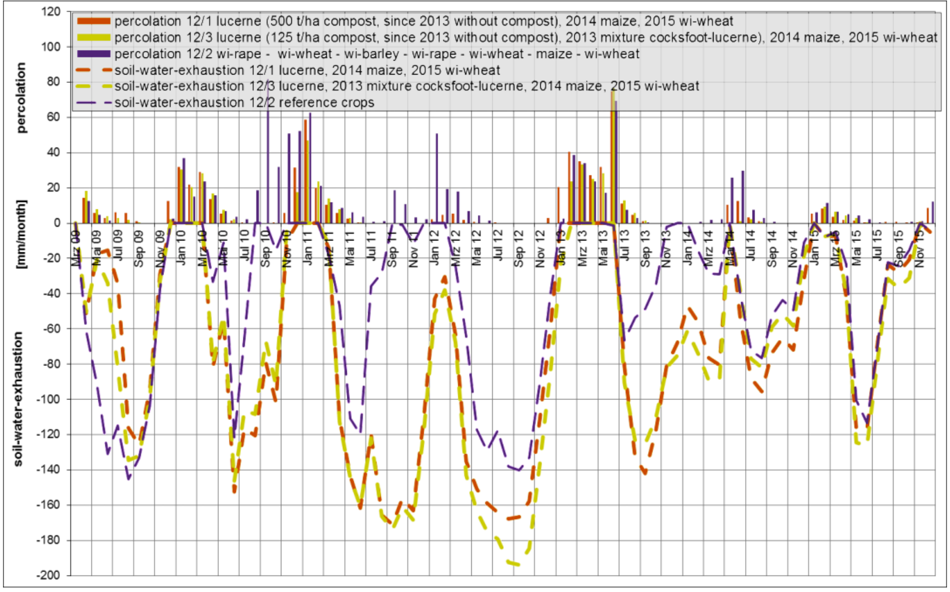


***Diagram 1** Lysimeter results of soil-water exhaustion and quantity of percolation per month 2009 - 2015, Comparison of lucerne, cocksfoot/lucerne and reference crops (GFI 2015)*

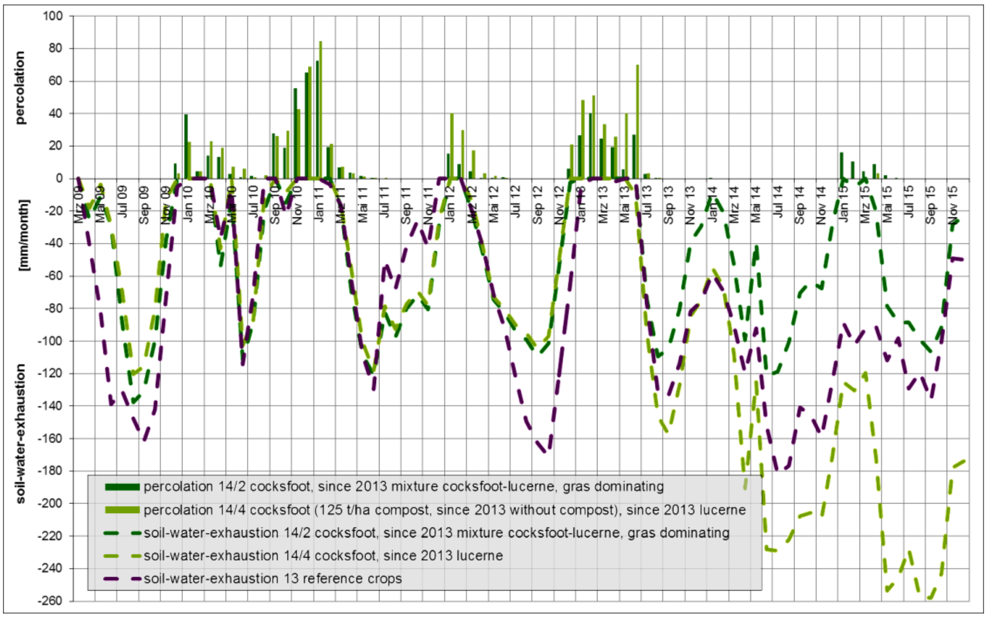


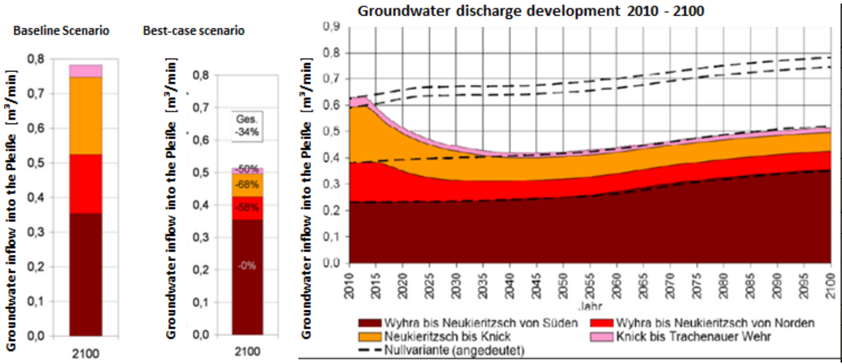
***Diagram 2** Lysimeter results of soil-water exhaustion and quantity of percolation per month 2009 - 2015, Comparison of lucerne, cocksfoot, cocksfoot/lucerne and reference crops (GFI 2015)*

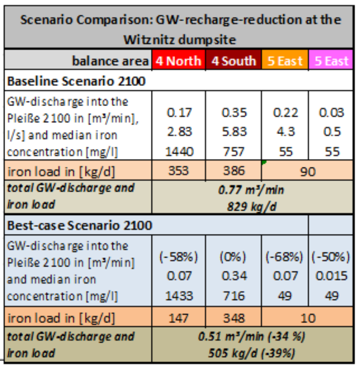
Lucerne was cultivated at the lysimeter plot 12/1 and 12/3 (orange and yellow line) from 2009 to 2012, in 2013 at the lysimeter plot 12/1 (orange line) and since 2013 at the lysimeter plot 14/4 (light green line, cf. *Diagram 2*). In general, it could be observed that lucerne required an establishment phase of around one year and it performed better in summer than in winter months. The highest impact on the soil-water balance and, thus, the highest effectiveness of the measure were especially obvious for the years 2010, 2012, 2014 and 2015 (cf. *Diagram 1* and *Diagram 2)*. In these years, the measured soil-water exhaustion was highest and, thus, induced a reduction of the percolation quantity at the lysimeter plots of lucerne, whereas the percolation volume could be reduced by more than 60 percent in comparison to the reference lysimeter plots (12/2 and 13). Due to high precipitation and the modification of the experimental set-up in 2013 (removal of the sewage sludge compost), another initial phase was required and all lysimeter plots monitored showed almost similar high percolation quantities in this year. However, the monitoring results of the soil-water balance at the lysimeters indicated that a quasi-permanent cultivation with lucerne was most useful in increasing the soil-water exhaustion quantity and, thus, in enabling a reduction in the quantity of percolation compared to cocksfoot, cocksfoot/lucerne and conventional crop rotations.

Based on these results, lucerne became the preferred plant to be cultivated for the large-scale experiment (GFI 2012, 2013, 2014, 2015; FIB 2011).

<u>Projections 2100: Comparison between the baseline scenario and plausible effects of the lucerne large-scale experiment</u>

Assuming that a land use conversion of 225 hectares lucerne cultivation will allow a reduction of 75 percent in the groundwater recharge, a “best-case scenario” was developed and compared with the baseline scenario. In *Figure 5* an overview of the results of a reactive groundwater recharge model for the year 2100 is presented. Based on the stated best-case conditions, the currently implemented large-scale experiment would have an impact on the balance area 4 North and, due to impacts on the groundwater flow, also in part on the balance area 5 (orange and pink). Here, the median iron load at stationary state in 2100 was estimated with 829 kg/d. From this balance area the groundwater discharge volume and iron loads could be reduced by 58, 68 and 50 percent respectively. This in turn would lead to an iron load reduction of around 324 kg/d in comparison to the baseline scenario (IBGW 2010, IBGW and Ecosystem Saxonia 2011). Assuming a 75 percent reduction of the groundwater recharge, the groundwater table in the central part of the Witznitz dump site will decrease by around 6 meters. Thus, the currently implemented large-scale experiment would account for a groundwater discharge reduction of 34 % and an iron load reduction of about 39 percent of the overall load that is entering the Pleiße from the Witznitz dump site.





Scenario Comparison: GW-recharge-reduction at the Witznitz dumpsite				
balance area	4 North	4 South	5 East	5 East
Baseline Scenario 2100				
GW-discharge into the Pleiße 2100 in [m³/min], l/s] and median iron concentration [mg/l]	0.17 2.83 1440	0.35 5.83 757	0.22 4.3 55	0.03 0.5 55
iron load in [kg/d]	353	386	90	
total GW-discharge and iron load	***0.77 m³/min 829 kg/d***			
Best-case Scenario 2100				
GW-discharge into the Pleiße 2100 in [m³/min] and median iron concentration [mg/l]	(-58%) 0.07 1433	(0%) 0.34 716	(-68%) 0.07 49	(-50%) 0.015 49
iron load in [kg/d]	147	348	10	
total GW-discharge and iron load	***0.51 m³/min (-34 %) 505 kg/d (-39%)***			

Figure 5 *Comparison of groundwater discharge development from 2010 to 2100 between the best-case scenario (assuming 75 percent of groundwater reduction through lucerne cultivation on the 225 hectares of the large-scale study area) and the baseline scenario (Grontmij 2015, GFI 2012, IBGW 2010)*

The estimated groundwater recharge reduction for the years 2010, 2015, 2027, 2040 and 2100 is summarized in *Table 1*. Based on the modelling results, the highest groundwater recharge reduction and iron load reduction will be attained in the year 2040. However, a measureable impact can be expected already in the next years.

Table 1: *Groundwater discharge and iron load development for the years 2010, 2015, 2027, 2040 and 2100 and scenario comparison of the plausible impact of a groundwater recharge reduction through lucerne cultivation (adjusted from Appendix 6, IBGW and Ecosystem Saxonia 2011)*

		2010	2015	2027	2040	2100
Baseline-Scenario	[m³/min]	0.62	0.64	0.66	0.68	0.77
	[kg/d]	924	939	993	1009	829
Best-case scenario	[m³/min]	0.62	0.59	0.44	0.41	0.51
	[kg/d]	924	910	651	576	505
GW-recharge-reduction	[%]	0	-8	-33	-40	-34
iron load reduction	[%]	0	-3	-34	-43	-39
	[kg/d]	0	- 29	- 342	- 433	- 324

Discussion and Conclusion

During the last seven years of field studies at the Witznitz post-mining landscape it could be generally confirmed that a land use conversion towards a quasi-permeant pasture cultivated with lucerne allowed a considerable reduction in groundwater recharge in comparison to conventional crop rotation, taking into account moderate hydrological conditions (GFI 2015, Beims et al. 2015). Initial soil loosening, liming and fertilization provided optimized soil conditions for plant growth and the stated culture criteria (strong above- and underground growth, high exhaustion of the soil moisture storage, shortening of the fallow period, positive effects on soil development and fertilization of the post-mining soils, short-term effects on the water balance, self-sustaining) could be confirmed for lucerne. Based on the results of the conducted investigation, a reduction of the ferrous groundwater inflows into the Pleiße River should occur gradually through the applied counter-measure. Thereby, the results of the scenario comparison indicated, that in addition to the very slow natural decline of iron concentrations in the groundwater, a plausible reduction of about 34 to 43 percent (-342 kg/d to -433 kg/d) of iron load could be attained during the years 2027 to 2100 through large-scale lucerne cultivation. The results highlight that the overall effectiveness of the counter-measure can be regarded as highly efficient.

Further studies in regard to impacts of crop rotation and heavy precipitation are proposed. Here, also additional investigation in regard to the plausibility of peak loads, rebound effects and effects of climate variability and change need to be conducted and evaluated. Furthermore the delayed exfiltration and time dimensions of the problem need to be discussed in greater detail. Finally, the long-term impact of the presented remediation measure has to be proven during the forthcoming years of the large-scale experiment implementation and its actual effectiveness has to become evident through the monitoring results, which will need to indicate a decreasing groundwater table and declining iron concentration in the Pleiße River. The 225 hectares of the large-scale experiment area have been safeguarded for the next few years, and after further adjustments and a denser data set, the knowledge base will increase, enabling a more precise final evaluation of the effectiveness of the proposed and discussed remediation measures to be made. In general, the transfer of the process know-how, implemented methods and tools for the projection of iron loads from groundwater inflows to comparable mining sites is possible after an adaptation to the site specific conditions and clarification of the hydrogeological preconditions. The transfer of the measure depends, amongst other things, on the land use preferences of the landowners.

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Geochemical and microbial conditions of a lignite coal spoil and overburden area in Middle Germany and environmental impact decades after remediation

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Abstract

During the 20th century, Germany represented one of the world's largest producers of lignite coal. Coal spoil seepage waters from these mine sites can impact billions of cubic meters of ground water for an extended period of time (eternity impacts). Approaches to remediate lignite spoil and over-burden material have been ongoing for more than the past 50 years. The relative effectiveness of remediation methods at different lignite coal mining sites can be evaluated based on changes in geochemistry and microbial communities. The results of these long-term measures and the possible improvement of the environmental situation or an ongoing environmental impact give lessons for the advancement of modern remediation methods at current and future coal spoil locations.

In this study, a coal spoil site in Middle Germany with cohesive soil substrates and layers of drift clays was investigated and characterized with geochemical and microbial parameters. The evaluated site partially had a remediated topsoil layer for 40 years, and since this time agricultural cultivation of different plants (grains, legumes, *Pocaceae*) on top was performed. The geochemical background data and results of investigation of different microbial populations in the coal spoil substrate are evaluated, and the remaining impact of spoil substrate to the environment is demonstrated. Finally, the results of long-term remediation of such sites, the influence onto microbial life and impact to the environments is compared and discussed.

The investigations resulted in new knowledge and insights into the long-term biogeochemical processes decades after the remediation of coal spoil sites. Measures for the improvement of the actual and future remediation are concluded.

Key words: Lignite coal spoil area, acid mine drainage formation, biodegradation of coal humic matter, ammo-nia accumulation in groundwater, impact on ground and surface water

1. Introduction

In the 20th century, Germany was one of the world's largest producers of lignite coal. Lignite coal represented an important resource for energy and chemical production during a period of important economical growth. Spacious coal spoil areas and the occurrence of large and numerous pit lakes today demonstrate the legacy of the extended open pit lignite coal mining.

Coal spoil seepage waters from these mine sites can impact billions of cubic meters of ground water for an extended period of time (in some cases, perpetuity). Approaches to remediate lignite spoil and overburden material have been ongoing for more than the past 50 years. The relative effectiveness of remediation methods at different lignite sites can be evaluated based on changes in geochemistry and microbial communities (Willscher et al. 2013, 2012a, 2012b). Therefore, lignite coal spoil areas that had been remediated decades ago are investigated today for their changes in geochemical and microbial characteristics. The results of these long-term measures and the possible improvement of the environmental situation or an ongoing environmental impact, respectively, give lessons for the advancement of modern remediation methods at current and future coal spoil locations.

2. Investigated site and objectives of the study

In the last years, lignite coal spoil sites in the Lusatia (East Germany) with sandy substrates and fast vertical mass transport processes were characterized by geochemical and microbial investigations (WILLSCHER 2013). In this study, another coal spoil site in Middle Germany (the area of Witznitz in the south of Leipzig) with more cohesive soil substrates and layers of calcareous drift clays was investigated (WILLSCHER et al. 2015). The evaluated site partially had a remediated topsoil layer for 40 years, and since this time agricultural cultivation of different plants (grains, legumes, *Pocaceae*) on top was performed.

Objectives of the current investigations were

- to figure out the effects of long-term agricultural utilization and amelioration (since 40 years after recultivation of the spoil area)
- to investigate the influence of cohesive soil substrates and of drift clay (calcareous material) onto the biogeochemical acidification process
- to characterize the effects of groundwater rerise onto biogeochemical transformation processes in the coal spoil underground (the final flooding level was accomplished 13 years ago)
- to investigate the effects of different covering layers more than 40 years after remediation, and characterization of the effects of plantation and fertilization on top,
- and to elucidate the fundamental principles of the biogeochemical processes proceeding in the coal spoil substrate

Finally, conclusions should be deduced for the results of the former remediation measures, and recommendations should be given for the further improvement of the environmental situation especially of the ground- and surface waters. As a hypothesis it was assumed, that

- more cohesive soil substrates and drift clays would delay mass transport in the spoil substrate and therefore a retardation of biogeochemical acidification takes place
- agricultural cultivation on the surface for decades could reduce the acidification of the upper spoil layers underneath
- a groundwater rerise will shortly establish anaerobic conditions in the saturated zone and therefore maintain the immobilization and elimination of water pollutants like dissolved iron, high sulfate concentrations and acidity

Fundamentals of biogeochemical processes figured out in the Lusatian coal spoil substrates should be confirmed or differences should be figured out.

3. Methods for geochemical and microbial characterization

Main analytical methods for characterization of the chemical- physical and geochemical parameters were the measurement of total content of organic carbon (TOC), total content of inorganic carbon (TIC), total content of sulfur (S_{total}), content of mineral disulfides, content of mineral nitrogen (N_{min}), pH, redox potential E_h, electrolytic conductivity, dissolved sulfate, dissolved Fe (total), Fe(II) and Fe(III), dissolved ammonia, nitrate and nitrite (Ihling et al. 2013).

Microbiological investigation methods of important metabolic groups in the spoil substrate and ground water were the quantification of colony forming units (CFU) of general bacteria and additionally of fungi (aerobic cultivation), microbial sulfate reducers (MPN, anaerobic, for heterotrophic and autotrophic organisms), iron reducers (MPN, anaerobic), heterotrophic nitrate reducers (MPN, anaerobic), autotrophic nitrate reducers (MPN, anaerobic), measurement of the rates of anaerobic ammonification, nitrification and denitrification in flask experiments, and measurement of enzyme activities (urease, amidase and esterase) for an evaluation of the N cyle activity as well as for general microbial activity (Willscher 2012).

A total of 101 samples was taken, including coal spoil samples from different locations and depths, as well as ground- and seepage water samples

4. Main results

4.1 Results of geochemical investigations of the coal spoil substrate and environmental impact

The acidification of the coal spoil substrate essentially depends on the contents of total organic carbon (TOC), total sulfur (S_{total}) and the oxidation grade of the sulfur (ratio of mineral sulfides to oxidized products). The analysis of these parameters in different depths of the coal spoil deposit allows a good investigation of the depth profiles of the coal spoil substrate and its oxidation state (investigations here were accomplished at several sampling points down to a depth of 18 m). All other geochemical parameters basically depend on these main parameters of the coal spoil substrate. The biogeochemical weathering of the tertiary coal spoil substrate finally generates the acidification of the deposit, and dissolved Fe, sulfate, NH_4^+, dissolved heavy metals and As can be mobilized.

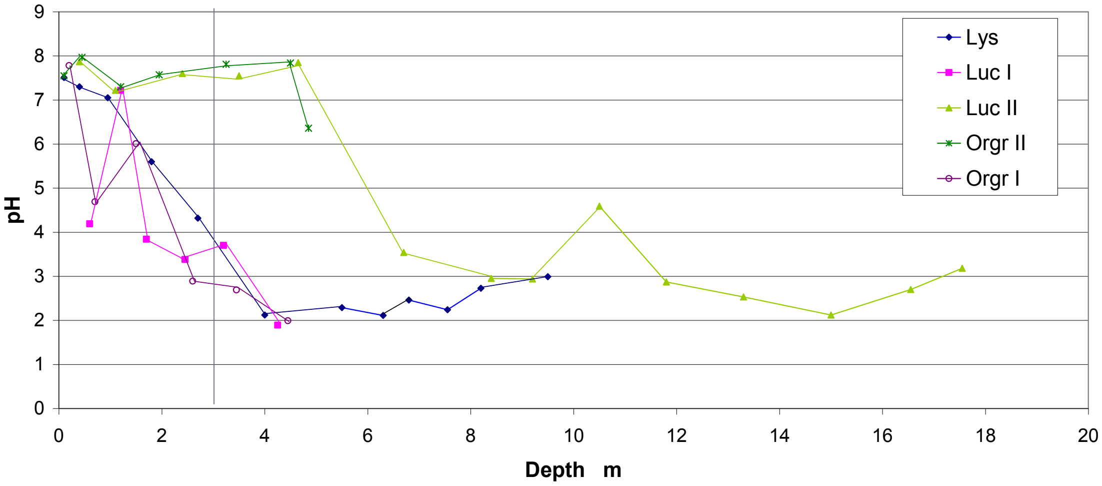

Fig. 1. *pH values of the eluates of the samples from several sampling points and different depths (Lys – lysimeter; Luc – Lucerne; Orgr – orchard grass; I – test field I; II – test field II)*

In the spoil substrate near the surface (0.6 – 1.0m) partially low pH values were detected (pH 4 – 5), see Fig. 1 (Lucerne I, Orchard Grass I). Due to the technical stacking arrangement, the spoil substrate can be located already that close to the upper top soil layer. Despite the existence of cohesive covering layers at some sampling points, weathering and acidification processes could be detected even in deeper layers down to 18 m (see Fig. 1, Lucerne II). Also in deeper layers down to 18m weathering and acidification processes could be detected. An explanation for the weathering in deeper layers is the former air contact of coal spoil substrate during coal production and during the subsequent stacking process.

At sampling locations with covering layers (clay, cohesive substrates) neutral pH values were detected (see Fig 1 0 – 5m, Lucerne II and Orchard Grass II); at the end of these layers and at the transition to the coal spoil substrate the pH is decreasing within the following 2 – 3m in the depth (see Fig 1).

The biogeochemical weathering process of the coal spoil substrate results in highly increased concentrations of dissolved Fe (up to 1.7 g/l), dissolved sulfate (up to 6.6 g/l), dissolved NH_4^+ (up to > 20mg/l), and of electrolytic conductivities of up to 7.5 mS/ cm. The pH partially is decreasing below a value of 3 (see Fig. 1). The measured data correlated well with previous long-term monitoring data of the coal spoil groundwater in the investigated area. They demonstrated well the weathering state and high environmental impact of this site onto the ground and surface water in the vicinity.

4.2 Results of the microbial investigations of sulphate reducers

The acidification in the tertiary coal spoil substrate also inhibits the microbial sulfate reduction (see Fig. 2). At sampling points with only flat topsoil layer and spoil substrate near the surface, a fast decrease of microbial counts of sulfate reducers could be observed (see Fig. 2, Lucerne I and Orchard Grass I).

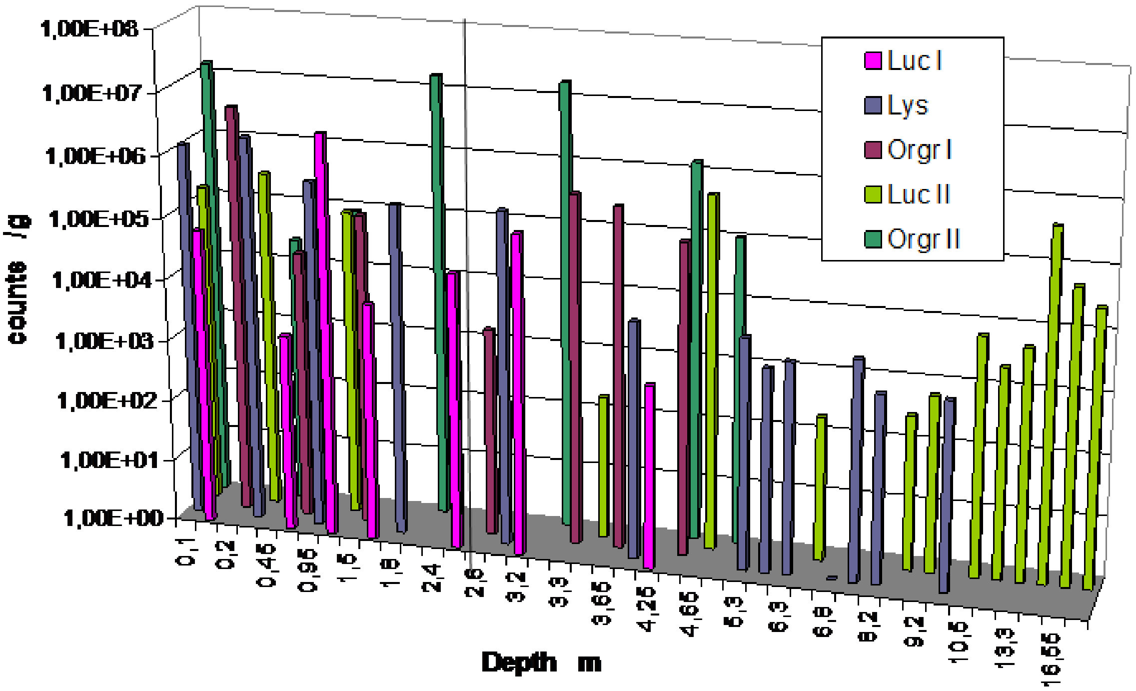

Fig.2. *Counts of sulfate reducers at several sampling points and in different depths (Lys –area besides lysimeter; Luc – Lucerne; Orgr – orchard grass; I – test field I; II – test field II). (Every stack column is a result of 96 single measurements)*

In the covering layers, the counts of sulfate reducers were constant at nearly neutral pH conditions (see Fig. 2, Orchard Grass II, 0 – 4m) and decreased dramatically to 10^2 – 10^3 counts /g after transition to the coal spoil substrate with a falling pH (see Fig 2, Orchard Grass II below 5m, and see Fig 1). Underneath a depth of 15m, growth of sulphate reducers is rising again to 10^4 - 10^5/ g (see Fig. 2), but these counts are still too low for a substantial activity of sustainable sulfate reduction in the coal spoil layers and the ground water zone, respectively.

4.3 Results of the microbial investigations of nitrification and denitrification and environmental impact

As a result of the investigations of the contained N species (NH_4^+, NO_3^-, NO_2^-, N_{total}, $N_{mineral}$) and the the microorganisms participating in the N cycle (nitrificants, autotrophic and heterotrophic denitrificants), an increased fertilization (e.g. a depot fertilization) results in raised concentrations of NH_4^+ in the underground. The biogeochemical degradation of lignite coal substrate (humic matter) in combination with the weathering of the mineral sulfides also contributes to the increased NH_4^+ concentrations in the ground water (Willscher et al. 2012b; Ihling et al. 2013).

Furthermore, the cultivation of lucerne as remediation plant (legume) results in increased N-accumulation in the underground. Therefore an adapted plantation concept of remediation plants, e.g. of legumes with grass (“clover grass”) is recommended.

4.4 Influence of the dumping technology and presence of cohesive substrates

Investigations were carried out at several sampling points with covers of different thickness (0.6m top soil cover; 1m top soil cover; 2.5 – 5.0m of clay partially with calcareous drifted clays).

As a result of these investigations, a top soil layer of only 0.6 – 1.0m thickness is not sufficient to prevent effectively the weathering and acidification of the coal spoil substrate in the underground. Due to the technical dumping, tertiary coal spoil substrates can be located near the surface; hence they can be exposed to an intensified weathering and acidification finally resulting in a contamination of the ground and surface water with the dissolved weathering products (acidity, salinity, dissolved Fe and sulfate, NH_4^+, heavy metals and As). A reinforcement of the covering layers by cohesive substrates (clay, calcareous drift clays of 2.5 – 5.0m thickness) result in a stabilization of the geochemical conditions of the coal spoil substrate which shows lower weathering and acidification and its weathering parameters. The neutralization by covering layers acts stabilizing over the following 2 – 3m; underneath after the transition into the coal spoil substrate the biogeochemical weathering again is acting due to the former oxygen contact of the fine grained spoil material (see Fig 1 and subsection 4.1)

4.5 Influence of the rerise of the ground water level after the ending of the mining water management

The rerise of the ground water level currently results in no substantial reduction of the oxic conditions in the coal spoil substrate (even not in the saturated, but oxidized zone). This result is in accordance with previous experimental results in lysimeters at the site of Witznitz as well as at the experimental lysimeter station at Brandis (Haferkorn 2011). This result implies that even 13 years after completion of the final ground water level near the surface (2 – 4m below top ground surface) no substantial reduction of oxic conditions in the coal spoil substrate could be detected.

As an impact of the high acidification process in the coal spoil substrate, the microbial sulphate reduction as a sustainable process for the immobilization of the weathering products is widely inhibited. In the meantime a gradually biogeochemical Fe reduction can be detected generating the high dissolved iron mass transport in the coal spoil aquifer and subsequently into the surface waters in the vicinity. This Fe mobilization process is currently arising and it will presumably continue for the next centuries.

5. Conclusions

Following main conclusions were deduced from the substantial results of the investigations:

- Despite recultivation, amelioration and agricultural utilization over decades on top, there occurs no substantial neutralization of the coal spoil substrates underneath.
- The influence of the cohesive substrates and of calcareous drift clays is detectable, the action range is only limited (up to 2m).
- The final ground water level after the flooding is accomplished since 13 years, but reducing conditions in the upper saturated zone were not achieved within this time.
- An Influence of the covering layers on top onto the coal spoil substrate is detectable (redox potentials and –processes), but there occurs no complete prevention of the weathering processes of the mineral disulfides in the spoil material.
- In the coal spoil material occur biogeochemical degradation processes in the underground, which were characterized. In analogy to the spoil substrate in the Lusatia, also here a degradation of lignite humic substance and a generation of ammonia were observed.

The investigations resulted in new knowledge and insights into the complex long-term biogeochemical processes decades after the remediation of coal spoil sites. Measures for the improvement of the actual and future remediation are concluded.

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Municipal sludge ash for abatement of ARD

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Abstract

Abatement of ARD with passive treatment systems can quite often rely only on pH-control if the iron content is high enough and to allow for the formation of ferric hydrous oxides, which act as efficient adsorbents. The stability of ferric hydrous oxides is sensitive to lowering of pH as well as Eh why they must be controlled. Hence, it would be favourable to use a well ordered adsorbent that is stable over time and under the chemical conditions of ARD. Municipal waste water sludge is a growing problem in many countries and incineration under oxidative conditions can be used to oxidize anthropogenic organic molecules which pose a threat to the environment. Sludge ashes rendering from wastewater treatment in which iron is used as a flocculation agent have high concentrations of calcium/magnesium and ferric oxides, and should therefore, in theory be a suitable candidate for treatment of ARD. This study has therefore focused on the ability for these ashes to act as a sorbent for the removal of metals from ARD. The stability and potential release of metals from the material were quantified in batch experiments by extraction at pH 2-10, resulting in equilibrium concentrations (at pH 8) of 11.9, 0.08 and 24.1 mg L-1 for Al, Fe and Mn respectively. However, after washing with water the corresponding values were 0.01, 0.03 and 0.09 mgL-1. In fact, after washing the sludge ash is stable from pH 4 to 10, with only slightly higher concentrations found at pH 2. Batch experiments on metal adsorption from ARD showed more than 99% sorption of Cr, Cu, Pb and V, corresponding values for Co, Ni and Zn were 56, 86 and 34% respectively. The overall results from this study show that sludge ashes are a promising solution for treatment of ARD.

Key words: metals, sorption, equilibrium, sludge, ashes

Introduction

Acidic rock drainage (ARD) typically contains high concentrations of metals, which have a detrimental effect on the life of aquatic systems. Release of ARD constitutes widespread environmental problems and treatment is therefore in many cases demanded. As a consequence, substantial research has been focusing on different treatment options for ARD (Gazea *et al.*, 1996; Akcil and Koldas, 2006; Wei *et al.*, 2014). One of the more intensely studied solutions rely on adsorption of metal ions onto different kinds of adsorbents, including various types of ferric materials (Gitari *et al.*, 2006; Ardau *et al.*, 2014; Florence *et al.*, 2016).

Sludge from municipal wastewater treatment plants (MWWTPs) constitutes a growing problem in many countries, in terms of usage and disposal. The sludge contains high concentrations of phosphorus, which is highly valuable as a fertilizer. However, direct application in agriculture is limited due to the presence of heavy metals, pathogens and a multitude of organic pollutants, as well as the uncertainties regarding the fate of these if applied on arable land (SEPA, 2001). An alternative to direct usage of sludge within agriculture is incineration, where organic material is effectively combusted, leaving an ash residue with high concentration of metal oxides which have high potential for metal adsorption (Hua *et al.*, 2012). Previous studies have shown promising results for the use of sewage sludge ash as sorbents for phosphorus and metals from different kinds of solutions (Pan *et al.*, 2003; Iakovleva and Sillanpää, 2013; Abdulai and Lee, 2016).

When using waste materials for treatment of aqueous solutions, it is of great importance to investigate their chemical stability and potential release of their constituents, in order to ensure their suitability as sorbents (Ardau *et al.*, 2014). The aim of this study was therefore to i) investigate the stability and potential release of metals from sludge ashes at different pH, and to ii) evaluate their capacities to adsorb metals from ARD.

Methods

Municipal sewage sludge from three wastewater treatment plants in mid-Sweden was used in this study and the general properties for the facilities and relevant data for the sludge are presented in table 1. Sludge samples were taken after the dewatering step and stored at 8ºC until further processing. After drying at 105ºC and they were incinerated at 1000ºC using a chamber furnace, the resulting ashes were thereafter crushed to less than 0.1 mm. Equal amounts of ashes from all three facilities were mixed and used throughout this study.

Release of metals

Stability and potential release of metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, V and Zn) from the ashes, as well as the impact of washing the ashes with water before extraction, was studied in batch experiments. Washing was done by shaking the ashes with 18.2 MΩ deionized water, which was removed by centrifugation before further treatment. Samples of original and washed ash mixtures were equilibrated with distilled water at five different pH values (ranging from 2 to 10) for 24 hours at room temperature, using a rotary shaker and a liquid tosolid ratio (L/S) of 5.

Adsorption of metals

Adsorption of Co, Cr, Cu, Pb, V and Zn to original ashes were quantified at pH 3, 5 and 8 using artificial acid rock drainage (ARD). The elements were chosen according to their chemical properties such as the preference for the formation of cationic and anionic species as well as being common in historic sulphidic mine waste. The ARD was prepared from mine waste from the Ljusnarsberg's deposit, Sweden, by equilibrating 750 g with 1 L of 18.2 MΩ water for three years. This is a rather weathered material that gives an ARD with pH 2.9, Al 320 mg L^{-1}, Ca 450 mg L^{-1}, Fe 3 mg L^{-1}, K 11 mg L^{-1}, Mg 440 mg L^{-1}, Mn 33 mg L^{-1} and Na 5 mg L^{-1} while the anions are dominated by some 5 g L^{-1} SO_4^{2-}. Trace metal concentrations are typically Cd 2 mg L^{-1}, Cu mg L^{-1}, Pb 2 mg L^{-1} and Zn 600 mg L^{-1}. Due to the relatively low concentrations of trace metals in the ARD, it was spiked with nitrate salts of the metals above, to a final concentration of 0.5 mgL^{-1}. For the subsequent sorption studies, the ARD was mixed with ashes (L/S 10) and shaken at room temperature using a rotary shaker for 24 hours.

Analyses

Metals were quantified with microwave plasma - atomic emission spectroscopy (Agilent 4200 MP AES) after phase separations through centrifugation (4000 rpm, 15 minutes) followed by filtration (0.20 µm). The impact of pH on the metal distribution was statistically evaluated by ANOVA analysis and subsequent Tukey post hoc tests, using the statistical software SPSS Statistics 19. The resulting equilibration concentrations at pH 8 were used for geochemical modeling of saturation conditions using Visual Minteq.

Table 1. *Characteristics of the three municipal wastewater treatment plants included in the study*

	Örebro	**Västerås**	**Eskilstuna**
Connected population (p.e.)	121 000	102 000	85 000
Dimensioned flow (m^3h^{-1})	3 750	4 800	3 090
Precipitation agent	Iron sulfate	Iron sulfate	Iron sulfate
Industries connected (p.e.)	5 700	8 000	7 310
Sludge production (tons $year^{-1}$)	11 700	11 900	8 700
Sludge dry weight (%)	27.4	24.3	20.9
Ash content (%)	9.7	10.1	6.3

p.e. = person equivalents

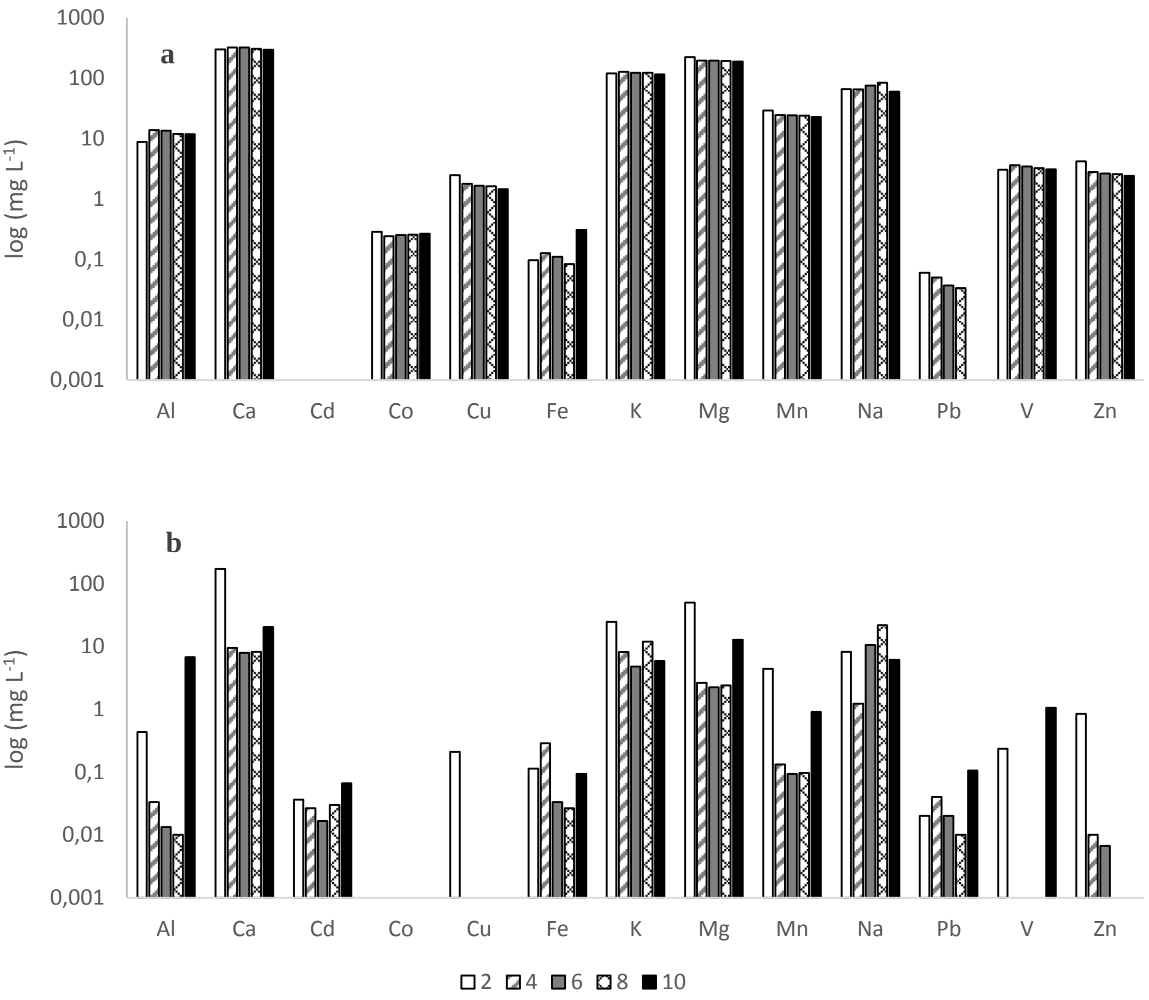

***Figure 1** Equilibrium concentrations of selected metals as a function of pH for original (a) and washed (b) municipal sludge ash*

Results and discussion

Release of metals

Equilibrium concentrations of metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, V and Zn) after 24 hours can be seen in figures 1 a and b for original and washed ashes, respectively. It is obvious that the leaching of metals is decreased by washing of the ashes. Furthermore, the effect of pH on the leaching process is evidently lower for the original ashes, compared to the washed ones. However, the statistical evaluation suggests that pH is significantly ($p<0.05$) affecting the release of metals from ashes in both of the set-ups (table 2). As seen in the tables 2a and b, the most prominent differences are found between leaching at pH 2. These results are consistent with a similar study on the use of fly-ashes as adsorbents (Abdulai and Lee, 2016). In that study they concluded that pH had a significant impact on the uptake of metals as it affects the surface of the adsorbent as well as the speciation of the metal ions, and hence their solid/solution distribution. Furthermore, they ascribed the decrease in sorption at low pH, to the increase of hydrogen ions, which act as competitors for the sorption sites. The results in this study also indicate an increase in the release of metals at high pH (figure 1). Similar results have been reported by Gitari *et al.* (2006) who attributed the increase in concentration at high pH to the formation of hydroxyl species. At high pH the formation of negatively charged coordination compounds with ligands such as hydroxide, bicarbonate and carbonate ions, as well as mixed complexes, lowers the affinity for cation-exchangeable sites.

Table 2 a. *Comparison of leaching of original sludge ashes at different pH, indicated by bold text.. Significant (p<0.05) differences between equilibrium concentrations at different pH are noted in the matrix.*

	4	**6**	**8**	**10**
2	Al, Cu, Mg, Mn, Zn	Al, Cu, Mg, Mn, Zn	Al, Cu, Mg, Mn, Na, Zn	Al, Cu, Mg, Mn, Zn
4		Na	Na	
6				Ca, Na
8				Na

Table 2 b. *Comparison of leaching of washed sludge ashes at different pH, indicated by bold text.. Significant (p<0.05) differences between equilibrium concentrations at different pH are noted in the matrix.*

	4	6	8	10
2	Al, Ca, Mg, Mn, Na, V, Zn	Al, Ca, K, Mg, Mn, V, Zn	Al, Ca, Mg, Mn, Na, V, Zn	Al, Ca, Mg, Mn, Na, Zn
4		Na	Na	
6			Na	Na
8				Ca, Na

Differences in equilibrium concentrations as a function of pH in the two set-ups, given as the percentage amounts of metals in leachates from the washed ashes compared to the original ones, are given in table 3. From the table it can be concluded that the metal concentrations are considerably lower in the leachates from washed ashes, compared to original, with iron at pH 2 and 4 being the only exception. This trend is related to the removal of metals present as soluble salts or surface complexes at the solid ashes interface, following the washing. By removing these from the matrix, the amount of metals available for extraction is drastically decreased, thus resulting in lower equilibrium concentrations. The deviation for iron may be explained by a lower proportion of adsorption sites for the hydrogen ions, due to the pre-washing, thereby leading to lower pH and subsequently a more pronounced dissolution of iron-carbonates (Golubev *et al.*, 2009). The presence of siderite (iron carbonate) in the sludge ashes has been confirmed by XRD (data not shown). For the remaining metals, the concentrations in the leachates from washed ashes, compared to the original, are considerably higher for (one or both of) the extremes (pH 2 and 10), as compared to the intermediate pH-interval. This is expected since the majority of soluble metals have been removed in the washing procedure, thereby leading to a limited amount available for leaching at neutral pH. However, the leachability is higher at the pH end-points.

Table 3. *Differences between metal concentrations in leachate from original and washed sludge ashes at different pH, given as the percentage share found in washed compared to original ashes.*

pH	**Al**	**Ca**	**Cd**	**Co**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Pb**	**V**	**Zn**
2	4.9	56.8		0	8.5	117.2	20.5	22.2	15.1	12.4	33.3	7.7	20.2
4	0.2	2.9		0	0	226.3	6.3	1.4	0.5	1.9	80.0	0	0.4
6	0.1	2.5		0	0	30.3	3.9	1.2	0.4	12.9	54.5	0	0.3
8	0.1	2.7		0	0	32.0	9.7	1.2	0.4	25.6	30.0	0	0
10	57.4	6.8		0	19.9	30.4	5.1	6.9	4.0	10.2		34.4	0

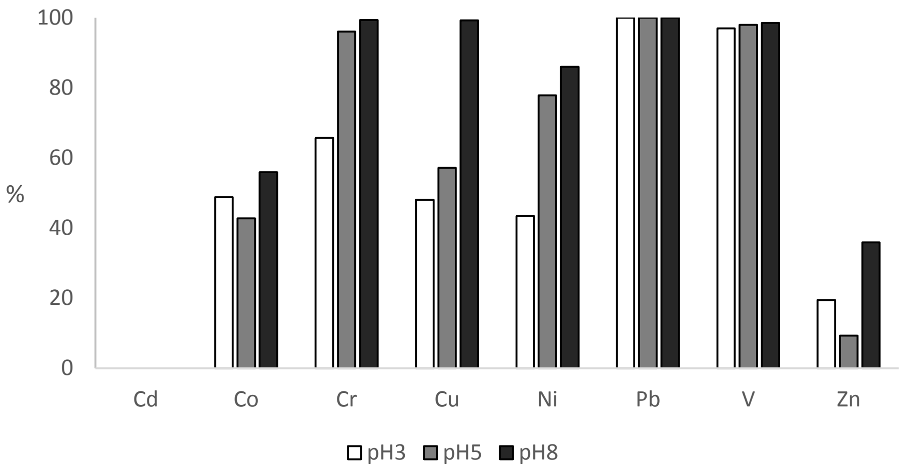

***Figure 2**. Adsorption (% of total) of metals to sludge ashes as a function of pH.*

Removal of metals from ARD

Sorption of metals from the spiked ARD to sludge ashes, as a function of pH, is shown in figure 2. It is evident that the sorption of several of the metals (Cr, Cu, Ni, Zn) increases with increasing pH as expected and consistent with results reported by Jafaripour *et al.*, 2015. In their study on the use of waste gas sludge to remove metals from ARD they reported increasing removal rates following an increase in pH, which they ascribed to the combined action of adsorption and co-precipitation with other metals. In line with their conclusion, geochemical modeling, based on the results in this study (at pH 8), strongly indicate precipitation of $Pb_3(VO_4)_2(s)$. Hence, in this system the concentrations of vanadium and lead in the solution is depend on each other. As expected for ferric oxides the sorption of zinc is low compared to the other metals. This is mainly attributed to its initially high concentration in relation to available specific adsorption sites (Stumm, 1992). This conclusion is further supported by results from an additional study on the sorption capacity of sludge ashes (table 4), where the initial concentration was only a tenth of the one used in this study, showing an almost quantitative removal of zinc. These experiments were conducted at pH 8 and the over-all results are in agreement with the present study. Based on the amounts of metals bound to the ashes from spiked ARD, estimated sorption capacities for the different metals were calculated as a function of pH (figure 3). As seen in figure 3, the sludge ashes have high capacity to sorb all of the metals in this study. This is especially noticeable for zinc but the significantly higher concentration of this element in the spiked ARD must be taken into account. Considering the high removal efficiencies in figure 2 there are reasons to assume that the process is element, or species, dependent why competition would be minor. This invokes the necessity for more refined studies on the specific sorption mechanisms. Capacities and pH dependence for the individual elements must be determined as well as the impact of ligands in the solution phase since they might compete with the adsorption sites. For a full scale application of sludge ashes it is also important to evaluate its hydrodynamic properties to ensure enough contact time between a running ARD and the sorbent to allow for adsorption to work. Finally, the specificity of the adsorption also encourages for further studies on the possibility for specific metal recovery when the sorbent reaches saturation.

***Table 4**. Percentage removal of metals from fly-ash leachate using sludge ash as sorbent material.*

Cd	**Cr**	**Cu**	**Fe**	**Li**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
58,4	100,0	98,8	90,9	9,8	39,4	96,4	94,3	99,9	100,0

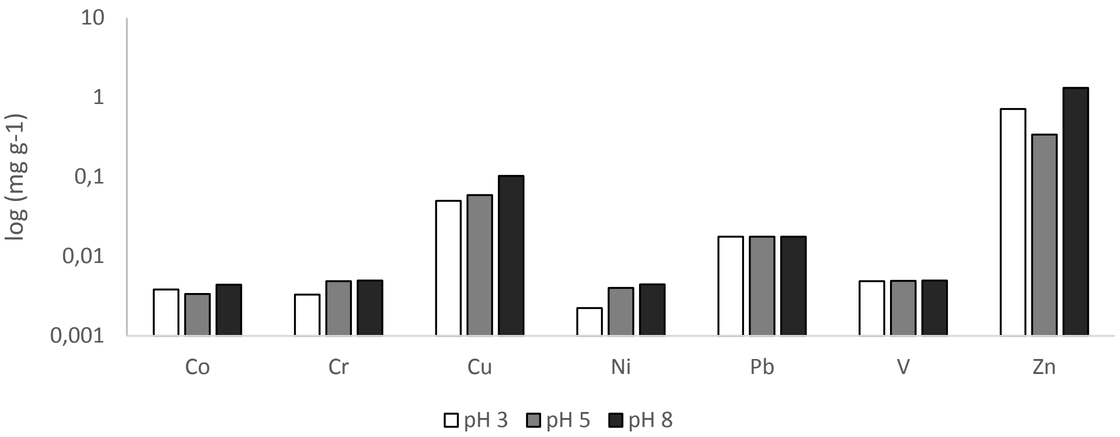

Figure 3. *Estimated sorption capacity of sludge ashes as a function of pH*

Conclusions

This study provides an initial evaluation of the usage of sewage-sludge-ashes for the removal of metals from acid rock drainage (ARD). Batch studies conducted at different pH has shown that the ashes can remove up to 100% of the ions present in solution, especially at pH 8. Furthermore, it has been shown that by washing the ashes with water prior to usage, the release of metals is significantly reduced. Although further research is needed in order to evaluate its potential as a sorbent, the results from this study show that ashes rendering from incineration of sewage sludge constitutes a promising alternative for treatment of ARD.

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Green liquor dregs in mine waste remediation, from laboratory investigations to field application

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Abstract

The oxidation of sulphides in mine wastes is a possible threat to the environment as it has potential to generate acid rock drainage (ARD). A way to reduce ARD formation is to apply a soil cover to reduce oxygen fluxes and water infiltration to the underlying reactive wastes. A typical mine waste cover in Sweden consists of a compacted sealing layer of a fine grained till overlaid by a non-compacted protection layer. However, a fine grained till with low enough hydraulic conductivity (HC) can be difficult to find in the vicinity of the mine and it might be necessary to mix it with a fine grained material. In this study a mixture of till and a residue from pulp and paper production, Green Liquor Dregs (GLD) was studied in laboratory and in a pilot cell study. The objective of the laboratory study was to investigate if an addition of GLD will improve the HC of tills with different clay contents. The results show that HC of the different tills studied decreases with addition of 5-10 w. % of GLD, except from the clayey till that already had a low HC without addition of GLD. In the pilot scale study a cell was constructed to investigate the feasibility to compact a sealing layer of a fine grained till and 10 w. % of GLD. The pilot scale study shows that it can be difficult to reach a high compaction degree in the field. However, it does not necessarily mean that the HC of the sealing layer will increase. In fact the laboratory study shows the opposite trend, a decrease in HC with a decrease in dry density for tills with low clay content. The main conclusion of the study is that addition of GLD can be an alternative option to improve the properties of a local till that alone does not meet the requirements for HC.

Key words: Mine closure, green liquor dregs, sealing layer, mine waste, acid rock drainage

Introduction

The oxidation of sulphides in mine wastes and the production of acid rock drainage (ARD) is a major long-term threat to the environment as sulphides may become mobile with access to oxygen with metal leaching as a result (Nordström et al. 2015; Saria et al. 2006). One method to reduce sulphide oxidation is to apply a dry cover on top of the mine waste deposit (Höglund et al. 2004). A dry cover in Sweden usually consists of a sealing layer placed on top of the mine waste and above this, a protective layer. The sealing layer is typically made of a fine-grained local till and its purpose is to mitigate oxidation of sulphides by reducing infiltrating water and oxygen to reach the mine waste (Höglund et al. 2004). The presence of a fine grained material is known to decrease the hydraulic conductivity (HC; Benson et al. 1994; Benson and Trast 1995; Leroueil et al. 2002). To further lower HC the sealing layer should be compacted to a high density (Leroueil et al. 2002; Watabe et al. 2000). Connected with compaction is the molding water content which is also known to affect the HC. The lowest HC can be reached 1-2 % wet of the line of optimum water content (Benson and Trast 1995). The optimum water content is the water content where the highest dry density can be reached in the material.

When a fine-grained till with a low enough HC is not present nearby the mine, other materials that can replace the till needs to be used. Previous studies have shown that a residue from pulp and paper production, Green Liquor Dregs (GLD), has potential to be used as a sealing layer (Mäkitalo et al. 2014; Mäkitalo et al. 2015a; Mäkitalo et al. 2015b; Mäkitalo et al. 2016; Ragnvaldsson et al. 2014) i.e. it is fine grained ($d100 < 63 \mu m$), commonly has a HC in the range of 1E-08 and 1E-09 m/s and a high WRC capacity. Other characteristics of GLD are high pH (10-11), relatively high porosity (73 - 82 %), a bulk density of 0.44-0.67 g/m^3, a compact density of 2.47 to 2.60 g/cm^3 (Mäkitalo et al. 2014). GLD consist of up to 75 % of $CaCO_3$, which generates from the retrieving process where a pre-coat lime mud filter (mixture of $CaCO_3$, CaO and $Ca(OH)_2$) is used leading to various amounts of lime mud mixed with the green liquor (Mäkitalo et al. 2014). However, to solely use GLD in the sealing layer is not reasonable neither from economical or a geotechnical point of view. In a geotechnical perspective GLD is not suitable due to its stickiness, low shear strength and high water content (Mäkitalo et al. 2014). Recent field studies have shown that a mixtures between till and GLD exhibit potential to be used in a sealing layer on top of mine waste (Mácsik and Maurice 2015; Mäkitalo et al. 2015b). However, the properties of the till and its effect on the HC of the mixture have not yet been studied.

In this study 5 to 20 w. % of GLD were mixed with three sieved (<20 mm) tills with different contents of fines and clays to investigate how the fine grained material in the tills affect the HC and compaction properties of the mixtures. The tills consisted of two fine grained (~35 % <63 µm) tills with different clay content (2.6 and 4.3 % <2 µm respectively) and one sandy till (~14 % <63 µm). The compaction properties and hydraulic conductivity of the different mixtures were investigated.

To asses feasibility, a pilot scale study consisting of a dry coverage with a sealing layer made of a mixture between a fine grained till (~30 % < 63 µm) and 10 w. % GLD from four different paper mills was conducted.

The objective of the laboratory study was to (i) investigate if an addition of GLD will decrease the hydraulic conductivity of tills with different fines- and clay contents. The objective of the pilot scale study was to investigate (ii) which dry densities could be reached in a sealing layer of till and 10 w. % GLD from different paper mills.

Methods

Materials for the laboratory study

Three tills with different particle size distributions were used in the laboratory study. Till 1, a fine grained till (34 % < 63µm; 2.6 % < 2µm) was collected at a till carrier in Boden, northern Sweden. Till 2, a sandy till (14 % <63µm) was collected from another till carrier outside of Boden and till 3, also a fine grained till but with a higher clay content compared to till 1 (35 %<63µm; 4.3 %<2µm) was collected in Luleå, northern Sweden. The materials were collected in plastic buckets with lids.

The GLD used in the laboratory study came from the Smurfit Kappa paper mill in Piteå, northern Sweden. The GLD was collected in sealed plastic containers to preserve the water content of the material.

The total solid contents (TS) of the materials were determined with the SIS standard SS-EN 14346:2007.

The tills were sieved to below 20 mm and air dried to lower the water content. They were then mixed with 5, 10, 15 and 20 wt. % of GLD. The weight percent was calculated towards a dry till and a natural moist GLD. The mixing was carried out by hand with a small shovel until the mixture was homogenised. Till 3 was used naturally moist (TS 90.8 ±0.8 %, n = 6) when analysing hydraulic conductivity.

Particle size distribution

The till was washed and dry sieved according to SS-EN 933-1:2012 to obtain the weight percentage of fines in the material. The sieve used was a mechanical Retsch AS 200 sieve with amplitude 2.2 mm/”g”. The sizes of the sieves were 12.5, 10, 8, 5, 4, 2, 1, 0.5, 0.25, 0.125 and 0.063 mm.

Particle size distributions for the fines were done by laser diffraction analysis on triplicate samples of each material using a CILAS Granulometer 1064 (CILAS, Orléans, France). The particle size distribution was calculated using the CILAS software.

Proctor compaction

Proctor compaction was carried out according to standard SS-EN 13286-2:2010. For the proctor compaction experiments the till was air dried at least 24 hours prior to mixing with GLD. The GLD was naturally moist for till 1 and 2, but air dried for till 3.

Hydraulic conductivity

HC measurements were conducted on a moist till (TS 91±1 %, n=24) with 5, 10, 15 and 20 wt. % addition of GLD. The constant head-method was used in air tight cylinders with a volume of 943 cm^3. The walls of the cylinders were sealed with a thin layer of benthonite. The mixtures inside the cylinder were compacted with proctor compaction in five equally thick layers with a falling weight of 4.54 kg, falling 45 cm 25 times on each layer. Dry density and water content of the samples were calculated from the "left over mixture" when compacting the samples. The values are therefore only an estimation of the values in the actual sample. Water was lead to the bottom of the cylinder with a hydraulic gradient of 8.3 for till 1 and 2, 12.5 cm for till 3. The water passing through the cylinder was collected in a plastic bottle, sealed from the top to prohibit evaporation. The plastic bottle was weighed regularly and the time was noted to measure the velocity of the water passing through the sample. HC was calculated using Darcy's law.

Pilot cell construction

In August 2014 a 400 m^2 cell was constructed in Boden, northern Sweden as part of a pilot-scale study. The pilot cell consisted of 0.2 m foundation of till, 0.5 m sealing layer and 1.5 m protection layer (*Figure 1*). The sealing layer consisted of a mixture between till and 10 w. % GLD from different paper mills and were compacted with different number of passes with an excavator-mounted compactor. The TS of the different GLD ranged from 43 to 56 %, with the GLD from Metsä Board paper mill being wettest and the GLD from Domsjö being driest (*Table 1*). The protection layer consisted of a fine grained till (~30 % < 63 µm). Density was measured on the surface of the sealing layer by water volumetry and with a Troxler nuclear density gauge at a depth of 50 and 250 mm. Material was also compacted in the laboratory with the proctor compaction method.

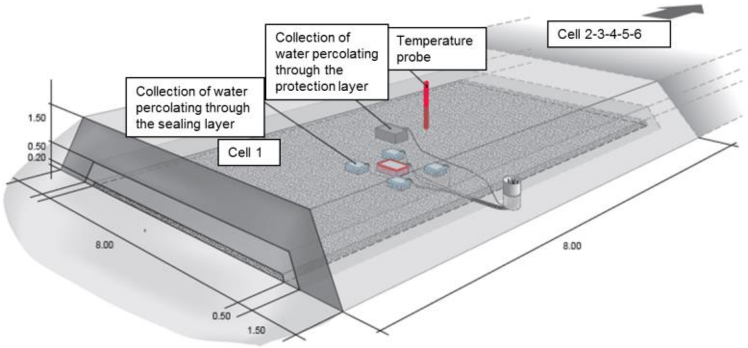

Figure 1 *The pilot cell at Boden, northern Sweden which consist of six different cells with a 0.5 m sealing layer and a 1.5 m thick protection layer on top of that. The sealing layer consist of till and 10 w. % of GLD from different paper mills. The protection layer consist of a fine grained till.*

Table 1 *Overwiew of the selected materials, the thickness of the sealing layers, the number of passes with an excavator-mounted compactor and total solids (TS) of GLD from different paper mills.*

	Cell 1	**Cell 2**	**Cell 3**	**Cell 4**	**Cell 5**	**Cell 6**
GLD (Paper mill)	Smurfit Kappa TS= 46±3 %	SCA Obbola TS= 49±3 %	Domsjö TS= 56±3 %	Metsä Board TS= 43±2 %	Metsä Board TS= 43±2 %	Metsä board TS= 43±2 %
Thickness of sealing layer (m)	0.5	0.5	0.5	0.5	0.5	0.25 GLD/Till 0.25 Till
Compaction (nr of passes)	6 and 9	6	6	6	3	6

Results

Laboratory study

The particle size distribution of the tills shows that the GLD has 100 % of fines (<63µm), of which ~ 10 % is in the clay fraction (<2µm; Mäkitalo et al. 2014). Till 1 is a fine grained till and consists of around 34 % fines of which 2.6 % is in the clay fraction. Till 2 is a sandy till and consist of around 14 % fines of which only 0.7 % is in the clay fraction. Till 3 is a clayey till and has the same percentage of fines as till 1, but a higher percentage of these are in the clay fraction, 4.3 % compared to 2.6 % in till 1 (*Table 2*).

The performed proctor tests shows that the highest dry density was reached with the pure till; 2.1 g/cm^3 in the fine grained till (till 1) and 2.0 g/cm^3 in the sandy till (till 2). The maximum dry density decreases with increasing addition of GLD in the mixture; from 2.1 to 1.9 g/cm^3 in the fine grained till, 2.0 to 1.9 g/cm^3 in the sandy till and down from 2.6 to 2.5 g/cm^3 in the clayey till (*Figure 1* and *Table 2*). The optimal water content after compaction increased from 8-16 % with increasing amount of GLD added to the till (*Figure 2*).

In the fine grained till (till 1) the HC first decreased from 3E-08 to 2E-08 m/s with 5 w. % addition of GLD to then increase up to c. 7E-08 m/s with 10 w. % or higher addition of GLD in the mixtures (*Figure 3*). In the sandy till (till 2) the HC decreased when adding up to 20 w. % of GLD (from 7E-8 to 4E-8 m/s), with the lowest values (2E-8 m/s) with 5 to 10 w. % of GLD in the mixture. The HC in the clayey till (till 3) increased from 3E-10 to 5E-09 m/s when adding up to 20 w. % of GLD (*Figure 3*). The dry density after compaction of the HC samples decreased with increasing addition of GLD to the till; from 2.01 to 1.65 g/cm^3 in the fine grained till, 2.04 to 1.64 g/cm^3 in the sandy till and 2.12 to 1.67 g/cm^3 in the clayey till when adding up to 20 w. % of GLD (*Table 2*). The molding water content of the HC samples increased with increasing percentage of GLD added, from 9 to 21 % for adding up to 20 w. % of GLD. The increase in water content was greater for the clayey till compared to the fine grained- and sandy till (*Table 2*). The water contents of the mixtures were greater than the optimal water contents which were determined by proctor compaction (*Figure 2* and *Table 2*). The molding water content of the samples tested for HC are for pure till 0-2 % wet of the optimum molding water content, 2-5 % wet of optimum for 5 w.% addition of GLD, 3-5 % wet of optimum for 10 w. % addition of GLD and 5-7 % wet of the optimum molding water content for 15 w. % of GLD addition.

Table 2 *Hydraulic condictivity (HC), compaction properties, fines/clay content and total solids (TS) of the materials used in this study.The dry density and molding water content of the samples tested for HC are an estimation from the soil left over after compaction.*

		Hydraulic conductivity (HC)			Compaction properties		Fines/clay content		TS (%)
	w. % GLD	Average HC (m/s)	Average dry density (g/cm^3)	Average water content	Average max. dry density (g/cm^3)	Average opt. water content	Fines (%<63µm)	Clay content (%<2µm)	
Till 1 (Fine grained till)	**0**	3E-08±3E-09 (n=3)	2.01 ± 0.05 (n=3)	9±0.5 % (n=3)	2.08±0.01 (n=3)	8±1.1 % (n=3)	34±5 (n=9)	2.6	91.5±0.4 (n=9)
	5	2E-08±5E-09 (n=3)	1.97±0.02 (n=3)	10±0.6 % (n=3)	2.05±0.01 (n=2)	8±0.9 % (n=2)			
	10	4E-08±5E-09 (n=3)	1.88±0.01 (n=3)	14±1.3 % (n=3)	1.99±0.01 (n=2)	9±1.4 % (n=2)			
	15	6E-08±1E-08 (n=3)	1.74±0.05 (n=3)	18±0.4 % (n=3)	1.95±0.00 (n=2)	10±0.0 % (n=2)			
	20	7E-08±1E-08 (n=3)	1.65±0.02 (n=3)	20±0.7 % (n=3)					
Till 2 (Sandy till)	**0**	7E-08±3-08 (n=3)	2.04±0.02 (n=3)	9±0.6 % (n=3)	2.03±0.01 (n=3)	8±0.5% (n=3)	14±1 (n=3)	0.7	91.7±0.4 (n=9)
	5	2E-08±3E-09 (n=3)	1.99±0.03 (n=3)	11±1.0 % (n=3)	2.01±0.00 (n=3)	9±0.2 % (n=3)			
	10	2E-08±3E-09 (n=3)	1.92±0.02 (n=3)	14±0.3 % (n=3)	1.98±0.02 (n=3)	11±1.3% (n=3)			
	15	3E-08±3E-09 (n=3)	1.78±0.05 (n=3)	18±1.0 % (n=3)	1.93±0.02 (n=3)	7±1.2% (n=3)			
	20	4E-08±1E-08 (n=3)	1.64±0.04 (n=3)	21±0.4 % (n=3)					
Till 3 (Clayey till)	**0**	3E-10±8E-11 (n=2)	2.12±0.01 (n=2)	10±0.1 % (n=2)	2.23 (n=1)	14 % (n=1)	35±1 (n=2)	4.3	91.1±0.8 (n=6)
	5	8E-10±3E-10 (n=2)	1.95±0.01 (n=2)	14±0.5 % (n=2)	2.16 (n=1)	15 % (n=1)			
	10	2E-09±2E-10 (n=2)	1.87±0.03 (n=2)	15±1.0 % (n=2)	2.10 (n=1)	20 % (n=1)			
	15	5E-09 (n=1)	1.67 (n=1)	21 % (n=1)					
GLD		1E-08±7E-09* (n=3)					100* (n=4)	~10*	43±4.3 (n=12)

*(Mäkitalo et al 2014)

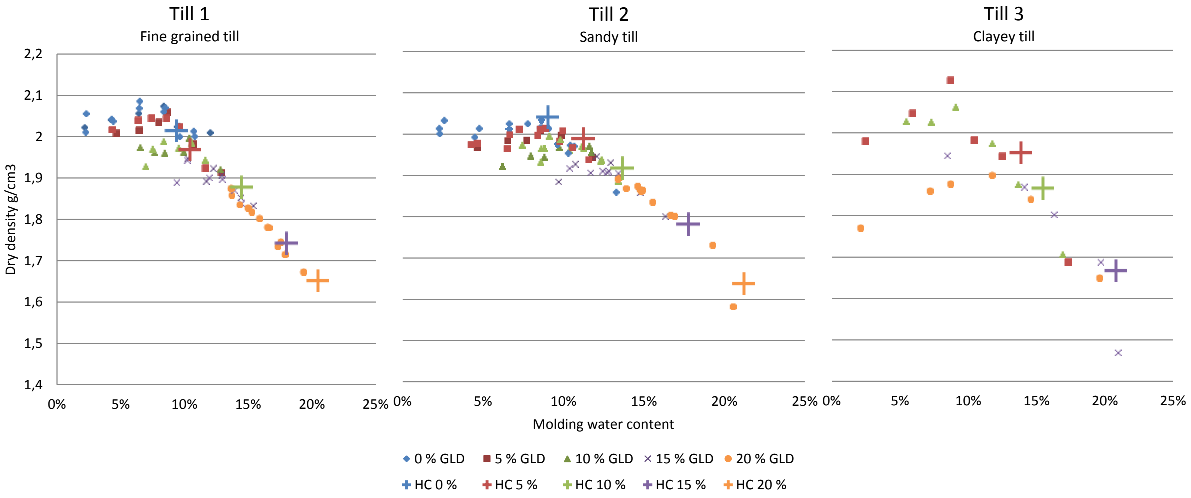

Figure 2 *Proctor compaction curves, with dry density (g/cm³) plotted towards molding water content of the different tills and till-GLD mixtures. The pure tills are plotted with blue rhombs, 5 w. % GLD-mixtures in red squares, 10 w. % GLD-mixtures in green triangles, 15 w. % GLD-mixtures in purple crosses and 20 w. % GLD-mixtures in orange dots. The plus-marks represent the estimated dry density and molding water content of the samples tested for hydraulic conductivity (HC).*

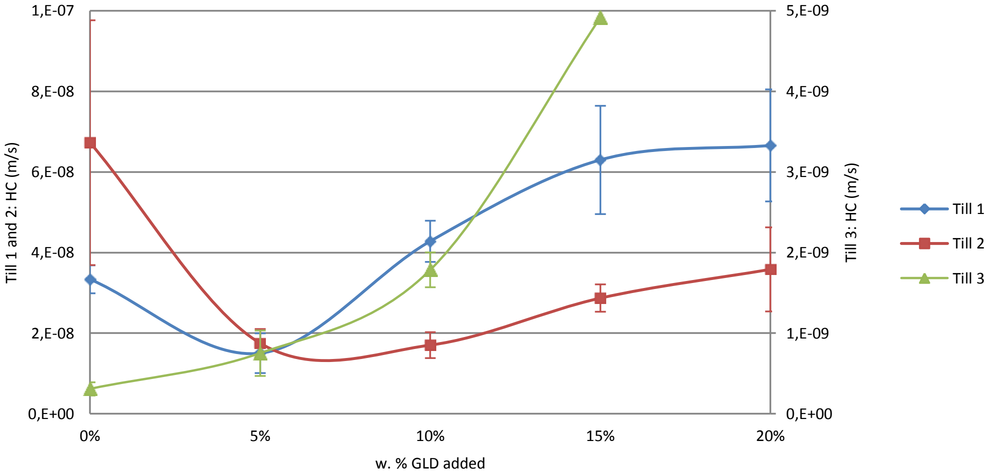

Figure 3 *Hydraulic conductivity (HC) of the different mixtures. Note that the HC for till 3 is on the right y-axis.*

Pilot cell study

Dry density is an indicator of the compactness of a material at a given volume. Based on the proctor compaction test performed on the different mixtures, a dry density of 1.8 g/cm^3 was set as a limit for a high degree of compaction. Density measurements of the sealing layer of the pilot cell shows that the dry density was above the required at a depth of 250 mm when using Troxler apparatus for all cells (*Figure 4*). Proctor compaction tests shows similar results as the Troxler. At the surface, the till alone reaches the required 1.8 g/cm^3, but the till and GLD mixtures does not reach up to this value. However, the compaction is expected to have increased after the application of the protection layer. The dry density at 50 mm depth is lowest in the cells with GLD from Metsä Board paper mill (cell 4-6), the GLD that had the highest water content (*Table 1*).

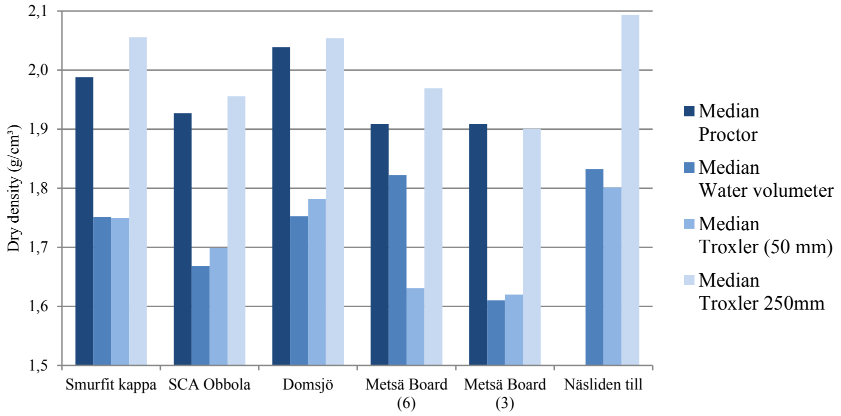

Figure 4 *Dry density of a till and a mixture of till and 10 % of GLD from different paper mills compacted in the laboratory using a Proctor hand hammer and in the field using a hydraulic plate compactor. The field samples were analyzed with both a water volumeter and Troxler apparatus.*

Discussion

The proctor compaction curve in *Figure 2* shows that the maximum dry density decreases as more GLD is added to the sieved till (<20 mm). This is likely due to the properties of the GLD, i.e. its high water content, porosity and flow stress. The high porosity and water content of the GLD leads to liquefaction when intensive compaction energy is applied and water is released which makes the material difficult to compact (Mäkitalo et al. 2015b). The proctor compaction curves also show that the maximum dry density increases with higher clay content in the tills, which is expected (*Figure 2)*. The dry density for the clayey till (till 3) is higher than for the fine grained till (till 1), even if the content of fines are similar (*Table 2*), which shows that a higher clay content is important to reach a higher dry density.

Only the mixture that consisted of a clayey till (till 3) had a HC below 1E-08 m/s (*Figure 3*), which is a required minimum for a sealing layer on top of mine waste in northern Sweden. The HC in this mixture also reached below 1E-09 with up to 5 w. % of GLD added, which is recommended by (Höglund et al. 2004) for a sealing layer on top of mine waste. A decrease of the HC was expected with an addition of GLD as the fine grained material in the mixtures increased (Benson et al. 1994; Benson and Trast 1995; Leroueil et al. 2002). A high amount of clay minerals generally corresponds to a decrease in the size of microscale pores which controls the flow in soil compacted wet of the line of optimums, which leads to a low hydraulic conductivity (Benson and Trast 1995). A decrease in HC is seen for the fine grained and sandy tills (till 1 and 2) with addition of GLD up to a w. % of 5-10 (*Figure 3*). The lack of decrease in HC with increasing amount of GLD for the clayey till (till 3) is likely due to that the clay particles in the till alone fill up the micropores leaving no place for the GLD. The addition of GLD is therefore only deteriorating the compaction degree of the mixture due to an increase in water content, which leads to a lower HC. The same mechanism is believed to be the reason to the increase in HC when more than 5 w. % and 10 w. % of GLD is added for the fine grained and the sandy till respectively. Composition of the soil has shown to be an important factor that can control the hydraulic conductivity of a soil, especially for compaction wet of the line of optimum water content where flow is controlled by the size, shape and connectivity of microscale pores (Benson et al. 1994). The reason for the much lower HC in till 3 compared to till 1 (*Figure 3*) is likely the higher clay content of till 3 (4.3 compared to 2.6 %), as the percentage of fines is similar in the two different tills (*Table 2*). A study conducted by (Benson et al. 1994) showed a strong relationship between clay content and hydraulic conductivity and a weak relationship between fines and hydraulic conductivity when studying clay. However, in contradiction to this (Benson and Trast 1995) also saw a weak relationship between fines and hydraulic conductivity in their study of different clays, but no relationship between clay content and hydraulic conductivity was found. The increase in HC in the clayey till (till 3) with an addition of GLD, and in the fine grained and the sandy till (till 1 and 2) with an addition of GLD above 5 and 10 w. % respectively is likely also due to the compaction properties of the mixtures. In addition to the clay content HC has also shown to be highly dependent on the degree of compaction, with decreasing HC with increasing degree of compaction (Benson et al. 1994; Leroueil et al. 2002; Watabe et al. 2000). However, low HC values cannot be reached if the material is unable to be compacted due to excessively high water content which is the case when adding more than 10 w. % of GLD (*Figure 2* and *Figure 3*). A study conducted by (Benson and Trast 1995) on thirteen compacted clays shows that HC is sensitive to molding water content, where the lowest HC was reached at molding water content of 1-2 % wet of the line of optimums. The molding water content of the samples tested for HC are for pure till 0-2 % wet of the optimum molding water content, 2-5 % wet of the optimum for 5 w. % addition of GLD, 3-5 % wet of optimum for 10 w. % addition of GLD and for 15 w. % of GLD addition the water content is 5-7 % wet of the optimum molding water content (*Figure 3* and *Table 2*). Around 10 w. % of GLD seems to be a threshold and with increasing amount of GLD above that the water content increases beyond the 1-2 % wet of optimum that according to (Benson and Trast 1995) generates the lowest HC. The properties of the GLD discussed in the beginning of this chapter are likely also contributing to the materials difficulties to be compacted.

The unexpectedly low decreases or no decrease in HC when adding GLD to the tills might be due to the method of compaction used, i.e. standard proctor compaction. Studies conducted by Mäkitalo et al. 2015b shows that mixing time and mixing effort increases the water content and porosity of the till-GLD mixtures used in that study. A result from this may be an increase in HC. A standard proctor compactor may not be the best choice when working with GLD. In future HC samples compacted with a lighter weight and a shorter falling height should be studied and compared to the results from this study.

Comparing the results from the laboratory studies and the materials compacted in the pilot cell shows that the dry density reached in laboratory is difficult to reach in the field (*Figure 2* and *Figure 4*). The lower dry density in cell 4-6, with GLD from Metsä Board is likely due to that this GLD had the highest water content of the GLD's used in the pilot cell (*Table 1*). However, as shown in the results from the hydraulic conductivity (*Table 2*) a decrease in dry density does not mean that the hydraulic conductivity will automatically increase. For the tills with low clay content (till 1 and 2) the HC decreases even if the dry density decreases when adding GLD to the till.

Conclusions

The HC of the different tills improves with addition of 5-10 w. % of GLD, except from the till that had a higher clay content and already a low HC without addition of GLD. The decrease in the tills with lower clay content was however not enough to reach below the required 1E-08 m/s. The decrease of HC in a till with an addition of GLD is limited by the decreasing compaction properties with an increase of GLD in the mixtures, mainly due to the higher water content of the GLD. The laboratory study further concludes that the percentage of fines in the till decreases the HC and increases the compaction properties of the till, but the clay content seems to play a major role in determining compaction properties and HC.

The pilot cell study concludes that it might be difficult to compact a sealing layer made of a till and 10 w. % of GLD in field to a high compaction degree. However, it does not necessary mean that the hydraulic conductivity of the sealing layer will increase. The laboratory study shows the opposite trend, a decrease in HC with a decrease in dry density for tills with low clay content.

The main conclusion of the study is that addition of GLD can be an alternative option to improve the properties of a local till that alone does not meet the requirements for HC. Using of GLD in a remediation of a mine is beneficial for both the mining company and the industry providing the industrial residue. However, the properties of the till are important to consider. For tills with a high HC, the improvement with an addition of GLD may not be enough to meet the requirements and for tills with a high original content of clay, addition of GLD is only detrimental. It is therefore crucial to characterize the materials that are to be used in a sealing layer before applying them. Long term effects of the material in a sealing layer needs further studies. Future studies will therefore include further evaluation of the pilot-scale study and a field study will be conducted on a waste rock dump covered with a sealing layer of a till/GLD mixture.

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Geochemical Evaluation of Cemented Paste Tailings in a Flooded Underground Mine

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Abstract

Two underground gold mines in the western United States recently received approval to use cemented paste tailings as backfill. Regulatory authorities required a rigorous evaluation of potential environmental effects of paste because of concerns about water quality after the mines flood with groundwater.

Preliminary testing of cemented paste tailings led to three important findings: 1) cemented paste must be cured prior to geochemical testing, 2) fragmenting cemented cylinders prior to testing alters their geochemical properties, and 3) conventional test methods such as static and kinetic tests do not adequately describe potential chemical releases from cemented paste. As a result of these findings, the Leaching Environmental Assessment Framework (LEAF Kosson et al. 2002) was used to evaluate cemented paste. LEAF consists of three primary testing protocols (EPA 2015a, 2015b and 2015c) to assess solubility across a range of pH (EPA 1313), chemical release by batch or column leaching (EPA 1314 and 1316), and diffusive release (EPA 1315). This testing framework originally developed in the EU for evaluating coal combustion waste has not been extensively used by the hard rock mining industry in the US (Van der Sloot and Zomeren 2012).

Geochemical tests were conducted on cemented cylinders that had cured for 56 days. Any test conducted on cylinders that had been crushed prior to testing yielded high pH values (pH 10 to 11.5), whereas tests on intact cylinders typically had pH values closer to neutral. Neutral pH is more typical of waters contacting aged cement that has undergone carbonation reactions that convert calcium-hydrate-silicates into calcium carbonate in the skin of the cemented material. Therefore, intact cemented specimens provide more representative chemical results for evaluating long-term environmental behavior of cemented paste.

Comparison of constituent levels in the various tests showed that concentrations measured by diffusive release tests were much lower than those found in leaching or pH-solubility tests. This finding indicates that diffusion limits the rate of release of constituents such as arsenic from cemented paste. Owing to the low permeability of cemented tailings, the diffusion release test was found to be provide the most representative data for evaluating releases from cemented paste. All

This paper provides details on the geochemical examination of cemented tailings and how they will interact with an alkaline groundwater. In addition, the paper suggests how LEAF can be applied to the environmental behavior of mining waste, specifically use of cemented paste for underground backfill.

Key words: Mine water, Underground mines, cemented paste, tailings, diffusion

Introduction

Cemented paste tailings are increasingly used for backfill of underground mines and open pits. Adding cement or other binders such as flyash to paste increases strength and also reduces chemical mobility of key constituents, especially metals. The unique geochemical nature of cemented materials poses a challenge to predicting the environmental behavior of cemented paste tailings. Conventional testing methods such a static and kinetic tests and simple solution batch tests fail to properly characterize the nature of water-rock interaction with cemented paste. The purposes of this study are to;

- evaluate the suitability of cemented paste tailings for use as backfill in an underground mine that will eventually flood with groundwater, and
- compare the LEAF protocol to traditional tests used for mine waste characterization.

Chemical and Physical Immobilization of Metals Using Cement

Solidification/stabilization is commonly used at metal-contaminated industrial sites to control chemical releases from contaminated soils and sediments (EPA 2000). In the US, solidification/stabilization is the second most commonly used remediation approach and has been applied to materials contaminated with lead, arsenic, cadmium, copper, nickel and other metals. Cement and flyash are among the most commonly used binders for waste remediation applications.

As cement cures, a series of chemical reactions occur that gradually lend increasing strength. The dominant minerals formed in cement, termed calcium-silicate-hydrates (CSH) are poorly crystalline but have a strongly cross-linked gel structure. CSH form at high pH levels (10 to 12) over a period of many weeks as cement cures in a process known as **hydration**. Metals become immobilized in cemented composites in a variety of ways including formation of metal oxide and hydroxides, sorption, or co-precipitation (Chen et al. 2009). Aluminum and arsenic solubility in untreated tailings, fresh and cured cemented paste (Figure 1) shows a progressive decline in ion solubility with increased hydration.

Cement forms in a strongly alkaline system with pH levels ranging from 10 to 12 SU. Soon after cement forms, the outside surface reacts with atmospheric carbon dioxide that breaks down CSH and forms a silica framework and calcite. The advance of the zone of **carbonation** is quite slow, often progressing only a few mm over many years. Two primary effects of carbonation are to reduce the pH of contact water by about 3 units from 11 to 8 (SU), and decreased permeability of the carbonation layer due to a slight volume increase where calcite plugs the pore space in the silicate matrix. Carbonation can either increase or decrease metal solubility relative to what occurs in the interior of the cemented form (Nath et al. 2012). For most metals tested in cemented paste tailings, however, the pH decrease from 11 to 8 causes a substantial reduction in metal mobility (Figure 2). When pH is decreased from 11 to 8, solubility of aluminum was reduced by a factor or a 20, 2.5-fold for arsenic, 5-fold for vanadium, and remained unchanged for copper (all copper values were below detection in this pH range). Given the importance of carbonation reactions, unbuffered tests that utilize crushed samples of cemented test forms are flawed in that they reflect the pH of the interior of the cement matrix rather than the protective layer formed by carbonation.

Mine Site and Tailings

A western US mine proposed to use cemented paste tailings as fill for primary and secondary stopes in their underground mining sequence. Tailings to be used as backfill are from an oxidized carbonate-hosted Carlin style deposit. Tailings have low levels of pyritic sulfur but are alkaline in pH, and are non acid-generating with net neutralization potential of +38.4 and a neutralization potential ratio of 6.9 (Table 1, Sobek et al. 1978). The tailings have low levels of base metals such as cadmium, copper and zinc but have elevated total and soluble arsenic and antimony. A key concern for using cemented paste for backfill at this site was the potential release of arsenic into groundwater when the mine resaturates during closure.

Test Protocols

A geotechnical testing program was conducted to determine the strength of cemented paste at different rates of binder addition. To evaluate potential environmental effects of cemented paste, numerous tests were conducted on the 15 cm diameter cemented test cylinders used for strength tests. Cylinders were cured for 56-days prior to testing. For tests requiring granular samples, the cylinders were crushed to less than 5 mm fragments.

Humidity cell tests (ASTM 2007a) were conducted on a crushed sample and an intact cemented cylinder. A Meteoric Water Mobility Procedure (MWMP, ASTM 2007b) extraction was performed on a crushed specimen. EPA 1313, 1314 and 1315 tests were also conducted (EPA 2015a, 2015b and 2015c). The leaching and diffusion tests were modified to reflect the nature of groundwater that will flood the underground mines. The diffusion test protocol was also based in part on an ASTM test (C-1308) for cemented radioactive waste (ASTM 2008). The chemical nature of the leachant is an important consideration when evaluating cemented materials because groundwater may chemically attack the cement (Baker and Bishop 1996). Groundwater in the vicinity of this carbonate-hosted deposit is strongly alkaline with a well-head pH of around 6.5 to 7 owing to elevated carbon dioxide partial pressure. Groundwater chemistry was approximated by creating a synthetic groundwater into which a mixture of air and carbon dioxide was bubbled to maintain near neutral pH. Although the local groundwater contains 0.12 mg/L arsenic in addition to other metals, the synthetic groundwater did not include added metals so that metal release from cemented paste could be more easily detected. The highly alkaline groundwater is not expected to degrade the cement.

Results

Humidity Cell and MWMP Tests

Humidity cell tests on intact versus crushed samples gave widely different results. Arsenic in the intact cylinder was 0.01 to 0.03 mg/L through most of the test, increasing to 0.09 mg/L in the final week. The pH of the unbuffered test began at 10 SU, but decreased after about 3 weeks to 8 SU. This relatively rapid change in pH reflects the initially rapid development of a carbonation zone that decreases the pH of contact water to equilibrium with calcite. Continuous aeration of the humidity cell provides ample carbon dioxide for the carbonation reaction. Crushed samples had much higher arsenic from 0.15 to 0.37 mg/L but similar pH. Both tests tended to increase in arsenic through time. This change is attributed to corrosion of the outside surface of the cemented grains by distilled water added each week to flush the humidity cell. The addition of large amount of water (water weight equivalent to 0.6 times the mass of the sample each week) may have removed calcite from the zone of carbonation, increasing the permeability of the outside layer of the sample leading to more rapid chemical exchange.

The MWMP extraction had 0.08 mg/L arsenic at a pH of 11.4 which was intermediate between the intact and crushed sample HCT results for week 1. The high pH of the MWMP test indicates that it reflects the interior of the cement sample rather than the protective layer.

pH-Solubility Tests

EPA 1313 tests (EPA 2015a, Figure 4) were conducted on tailings, cemented paste tailings (5 % binder) and on a composite of wall rock collected from the underground mine void. Metal levels were measured in a series of 10:1 extracts with synthetic groundwater. All samples exhibited minimum arsenic levels at near neutral pH levels with higher arsenic release at pH below 6 or above 9. Solution pH levels of 5.5 to 7 are near optimum for sorption of arsenate from solution by metal oxyhdroxides (Dzombak and Morel 1990). Arsenic solubility in cemented paste was about one order of magnitude lower than in untreated tailings across the entire gamut of pH values tested. This overall reduction in arsenic release was attributed to chemical reactions of arsenic with binder. Cemented paste had similar arsenic releases as wall rock so would have little net effect on dissolved arsenic during underground mine flooding.

Leaching Tests

EPA 1314 leaching tests (EPA 2015b, Figure 5 and 6) were also conducted on tailings, cemented tailings (5% binder) and mine wall rock. For soluble constituents such as sodium (Figure 5), the leaching test followed a traditional model of advective-dispersive solute transport. Advection displaces the majority of a soluble constituent within the first few pore volume of solution displacement in a column test with dispersion causing a gradual shift from the concentration of the interstitial solution to that of the eluent solution, giving the classical S-shaped breakthrough curve. Tests conducted on untreated tailings showed that sodium was mostly removed before an LS ratio of 8. Leaching results for arsenic were unlike sodium in that elevated arsenic persisted even after leaching 100 weight equivalents of synthetic groundwater. The persistent release of arsenic is typical of constituents with a high solid:liquid partitioning coefficient (Kd) and whose concentration in solution is more strongly controlled by equilibrium reactions that are pH-dependent (Kosson et al. 2002)

During early stages of leaching, cemented paste had much lower soluble arsenic (about 0.1 mg/L) than untreated tailings (about 0.5 mg/L), but above an LS ratio of 30, arsenic values for the two samples tended to converge at about 0.2 mg/L (Figure 6).

The gradual decrease in arsenic with increased leaching from the untreated tailings was attributed either to removal of a more soluble phase of arsenic or due to leaching the soluble sulfate which can compete with arsenate for limited sorption sites in the tailings solids. As the sulfate was removed, remaining arsenic became more strongly sorbed.

Arsenic levels in cemented paste were initially lower (0.1 mg/L) during the first 10 weight equivalents of synthetic groundwater leaching, but then increased to around 0.2 to 0.25 mg/L. During initial leaching steps, most bicarbonate was also removed from synthetic groundwater (bicarbonate reduced from 200 mg/L to less than 20 mg/L). The decreased bicarbonate was attributed to carbonation reactions on the fresh surfaces of cemented grains. The secondary calcite that would have formed as a result of these reactions may have reduced soluble arsenic through co-precipitation (Schafer et al. 2006). After leaching by about 30 weight equivalents of synthetic groundwater, the tailings and cemented tailings had similar arsenic results.

Leaching tests may overestimate actual arsenic release. The protective layer formed by carbonation is disrupted when a sample is crushed so that the high pH interior of the cemented material is exposed during leaching. Surface area is also greatly increased as a result of sample fragmentation. Diffusion tests, described below, provide a more representative means of testing release from intact cemented materials

Diffusion Tests

EPA 1315 diffusion tests (EPA 2015c, Figure 7 and 8) are fundamentally different than other analytical tests used for mine waste characterization. The test consists of sequentially placing an intact, cured cemented specimen into a series of batch solutions. The contact duration in each subsequent batch solution is carefully controlled so that the rate of mass release from the cylinder into the solution by diffusion can be determined. The primary purpose of the diffusion test is two-fold. Firstly, the test identifies whether the release of a constituent is diffusion-limited or not. Secondly, if constituent release is diffusion limited, the analytical data can be used to calculate the effective diffusivity of an ion in the cemented specimen. If apparent diffusivity is more than 100X slower than ion diffusion in water (e.g. about 4.4 x 10^{-6} cm^2/s for arsenate), the ion is considered diffusion-limited. Since the amount of a constituent measured in each batch solution depends on the batch duration and on the sequence of the test, the constituent concentration measured in solution is less important than the diffusion rate calculated from the results.

The equation for calculating effective diffusivity assumes that the test cylinder is a semi-infinite solid for which the cumulative fraction of any constituent leached (CFL) is a function of diffusivity, test duration and cylinder geometry from equation [1]. The CFL curve is fit to experimental data by varying the value of effective diffusivity (De) to minimize the mean square error in measured versus predicted CFL using an iterative solver.

$$CFL = \sum \frac{a_n}{A_0} = \sum IFL = 2\frac{S}{V}\left[\frac{D_e t}{\pi}\right]^{1/2} \quad [1]$$

Where a_n is the mass of constituent in the n^{th} batch solution (mg)
A_o is the total constituent mass in the cylinder (mg)
S is the cylinder surface area (cm^2)
V is the cylinder volume (cm^3)
D_e is the effective diffusivity cm^2/s
t is time in s

Diffusion test results (Figure 7) for paste cemented with varying binder amounts show a progressive reduction in arsenic release as binder is increased from 3 to 12%. For all binder levels, the effective diffusivity was more than 5 orders of magnitude slower than diffusion of arsenate in water.

Comparing all geochemical test results for a cemented paste (Figure 8), diffusion test results yielded much lower arsenic concentrations than leaching tests, pH-solubility tests, or humidity cells at a similar pH level suggesting that all other tests would overestimate constituent release for a diffusion-limited constituent such as arsenic.

Test Interpretation

Suitability of Cemented Paste as Backfill

Geochemical tests results showed that addition of as little as 3% binder to an oxidized tailing significantly reduced the mobility of all constituents evaluated. Owing to the low permeability of the cemented paste tailings matrix, release of all metal ions tested was controlled by diffusion. Extrapolation of test results to the flooded conditions after mining indicated that cemented paste used as backfill would have no adverse or measurable effect on water quality. Regulatory approval was received for the proposed use of cemented paste.

Applicability of LEAF Protocol for Mine Waste Evaluations

The LEAF series of tests provides a broad spectrum of information about mine waste that facilitates an in depth understanding of the nature of water-rock interactions. At least three fundamentally different categories of water-rock interactions are addressed by the suite of tests. Constituents can be categorized according to the factor that controls release from solid to aqueous phase (Kosson et al. 2009, Van der Sloot and Zomeren 2012)

- **Advection-Controlled** – This release mechanism includes more soluble constituents such sodium, chloride, nitrate and boron that are readily leached out of the solid phase (e.g. have a low Kd) with progressive rinsing. The leach test (EPA 1314, EPA 2015b) best describes the release of these constituents.

- **pH Dependent Control** – Constituents with high Kd values, which is the case for many metals in alkaline waters, are often not readily leached from a system because the constituent is very slowly depleted. Ions that form low-solubility solids or that are strongly sorbed onto mineral surfaces are included in this category. Determining the apparent solubility of these constituents is complex because small changes in pH or counter-ion concentrations can have large effects on constituent release. Where pH of the contact water is the primary factor affecting constituent release, EPA method 1313 provides insight into ion mobility.

- **Diffusion Controlled** – The concept of flow in granular porous media is the basis for much of the theoretical development of groundwater and transport models. In a homogeneous granular porous media, water contacts all mineral grains, so chemical equilibrium reactions can occur rapidly relative to the flow dynamics. In reality many systems exhibit two regions of flow: a rapid flow region and an immobile region where chemical flux is controlled by diffusion (van Genuchten and Wierenga 1976). Examples of two-region flow include preferred flow in waste rock, copper and gold leaching, fracture flow groundwater systems, and cemented paste tailings used as backfill. EPA test method 1315 (EPA 2015c) and related tests such as ASTM C-1308 (ASTM 2008) provide a basis for evaluating and quantifying the diffusive rate of release from monolithic waste fills or systems with preferred flow paths around large clasts.

The LEAF series of tests proved to be superior to conventional mine waste characterization tests such as static, humidity cell and simple batch tests (e.g. MWMP, ASTM 2007b) for evaluating the performance of cemented paste tailings backfill in an underground mine.

Tables

***Table 1**. Static tests, total and soluble metals in tailings.*

Static test Results		Constituent	Total (mg/kg)	Soluble MWMP (mg/L)
Paste pH	7.71	Arsenic	821	0.56
Total Sulfur (%)	0.22	Barium	1970	0.024
Sulfate Sulfur (%)	0.01	Cadmium	1.36	<0.001
Non-extractable Sulfur (%)	0.056	Copper	62.4	<0.05
Acid Neutralizing Potential (kg/t as $CaCO_3$)	45	Iron	21100	<0.01
Acid Generating Potential (kg/t as $CaCO_3$)	6.6	Antimony	106.5	0.078
Net Neutralizing Potential (kg/t as $CaCO_3$)	38.4	Zinc	131	<0.01
Neutralizing Potential Ratio (ANP/AGP)	6.9			

Figures

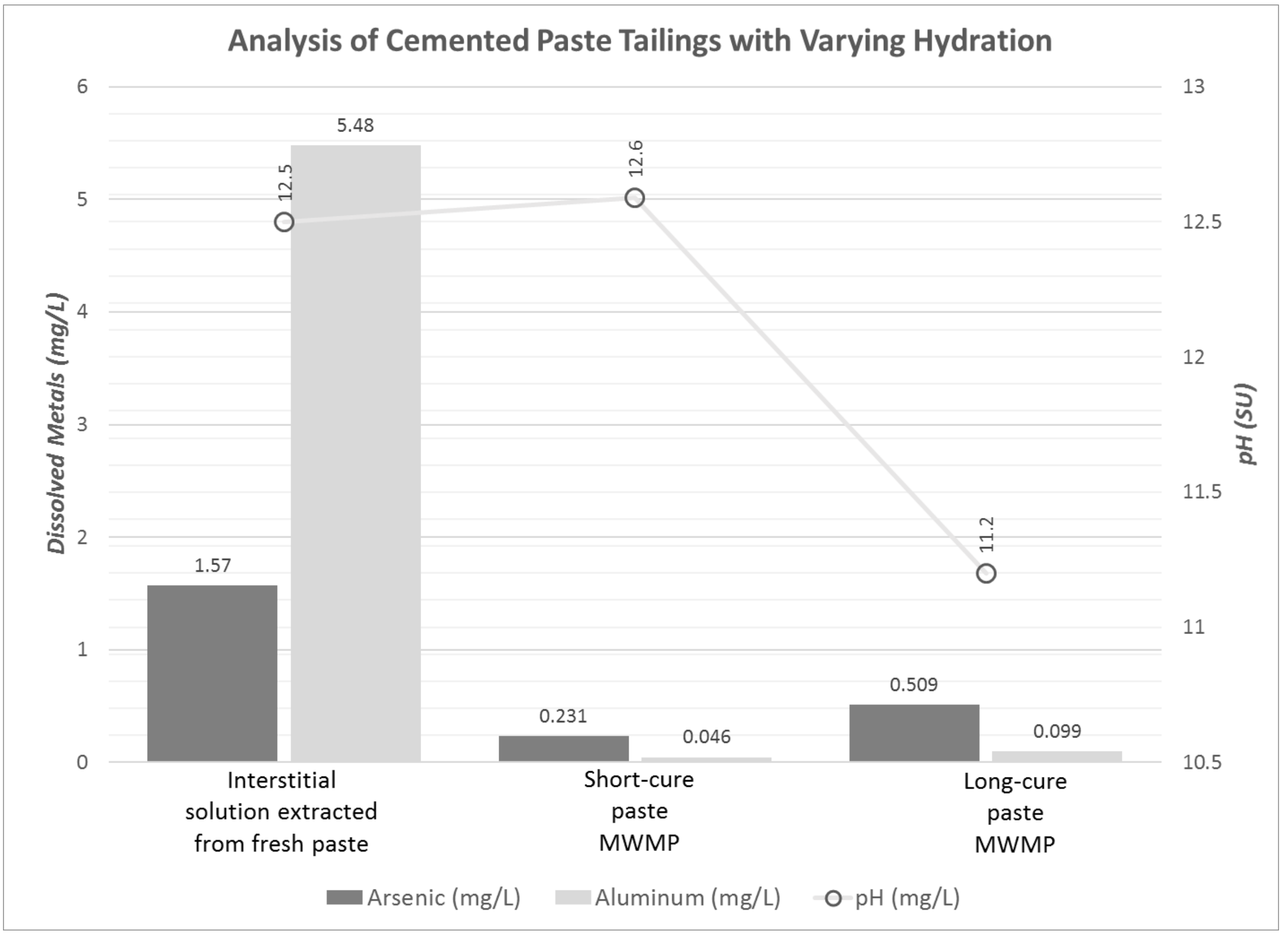

***Figure 1.** Solubility of arsenic and aluminum in groundwater, untreated tailings and in cemented paste tailings with increasing time for hydration.*

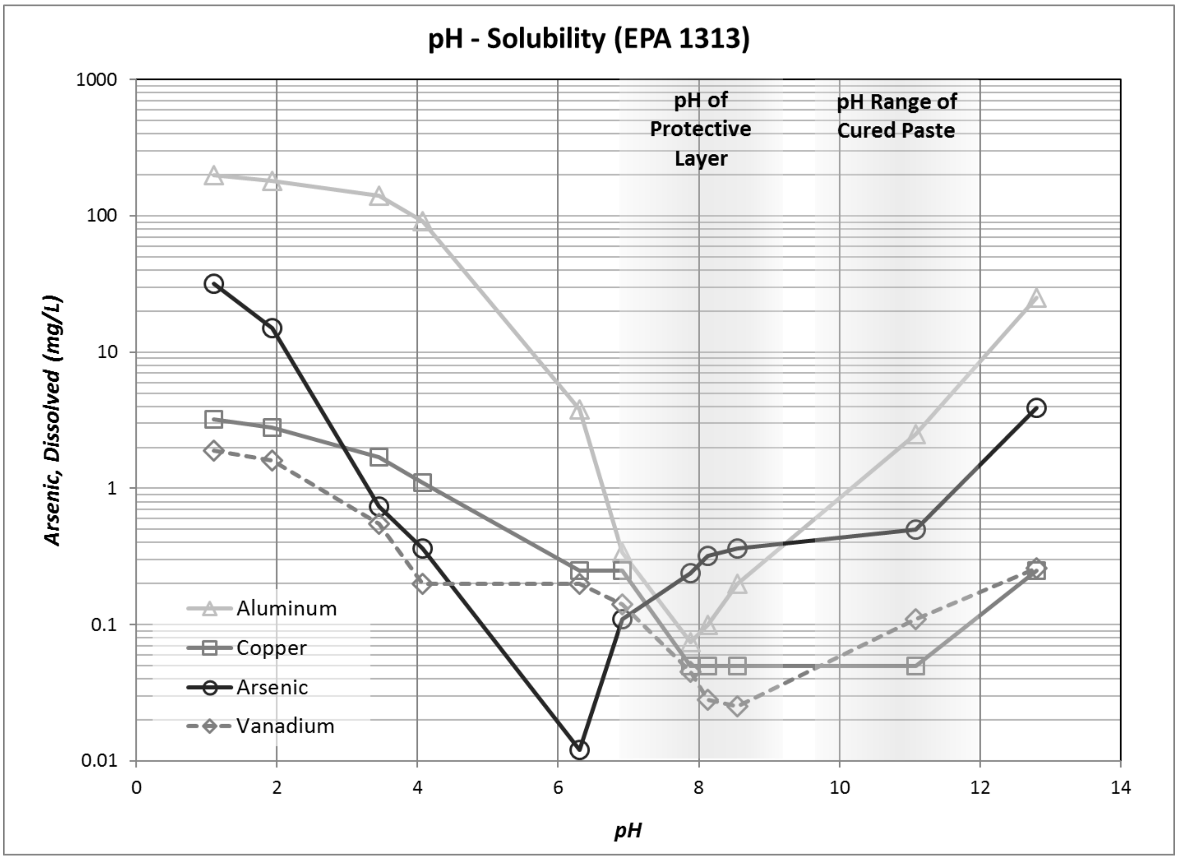

Figure 2. *Solubility of aluminum, copper, arsenic and vanadium in samples of 56-day cured cemented paste tailings at varying pH.*

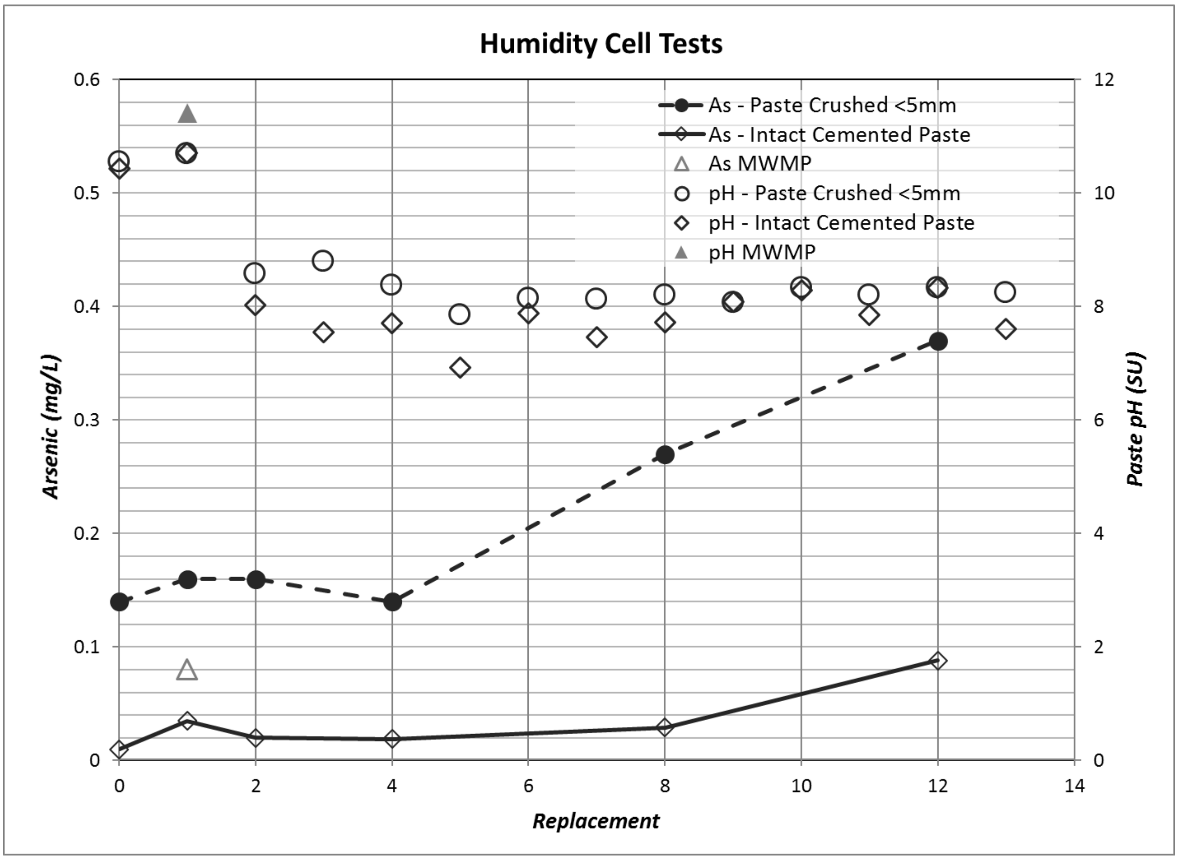

Figure 3. *Solubility of arsenic and solution pH for humidity cell tests of crushed and intact cylinders.*

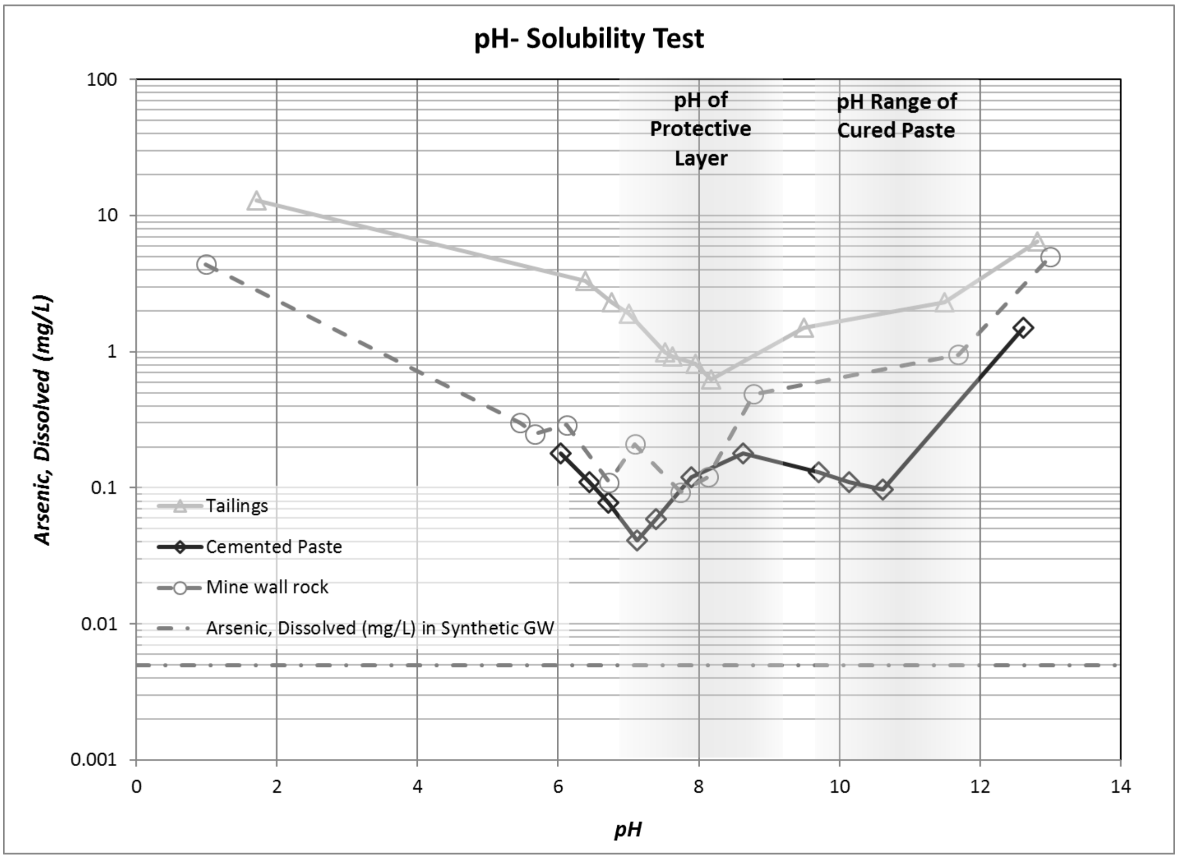

Figure 4. *Solubility of arsenic in tailings, cemented paste tailings and in mine wall rock as a function of pH.*

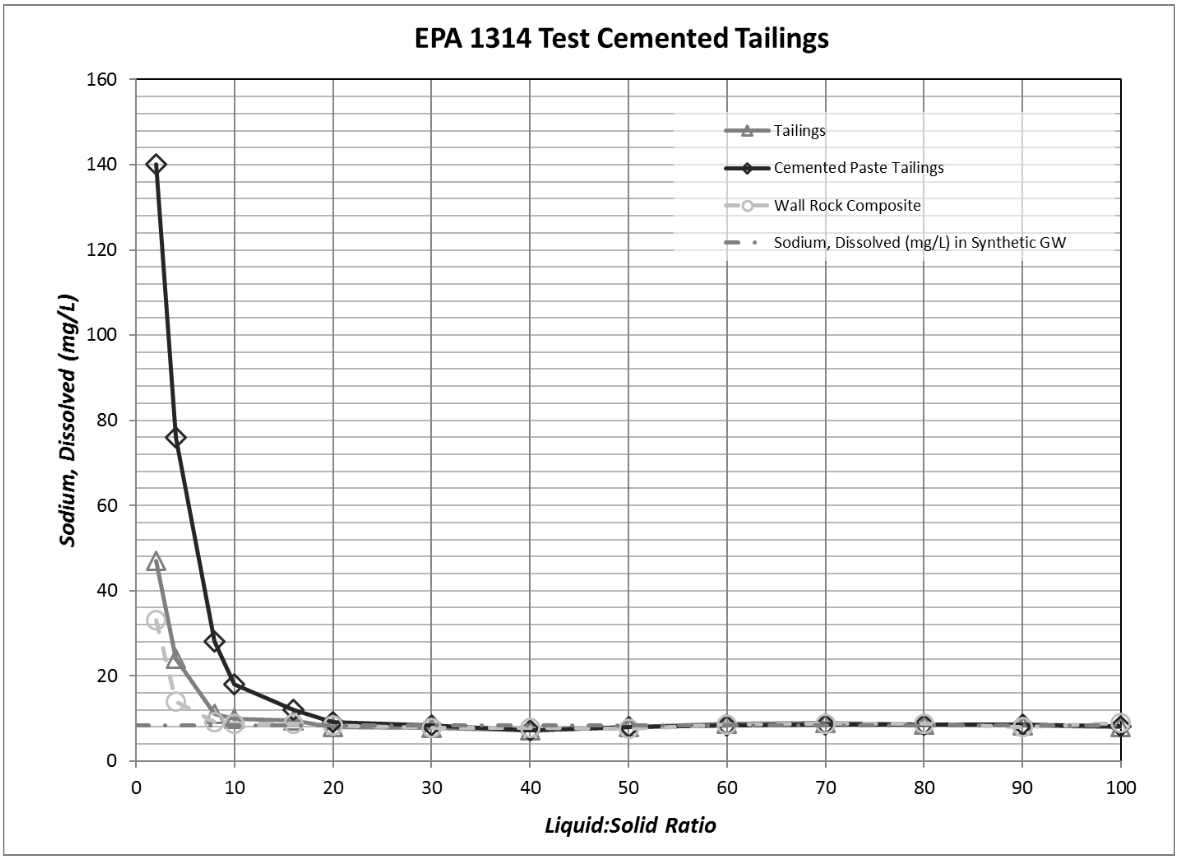

Figure 5. *Sodium leaching tests for tailings, cemented tailings and mine wall rock.*

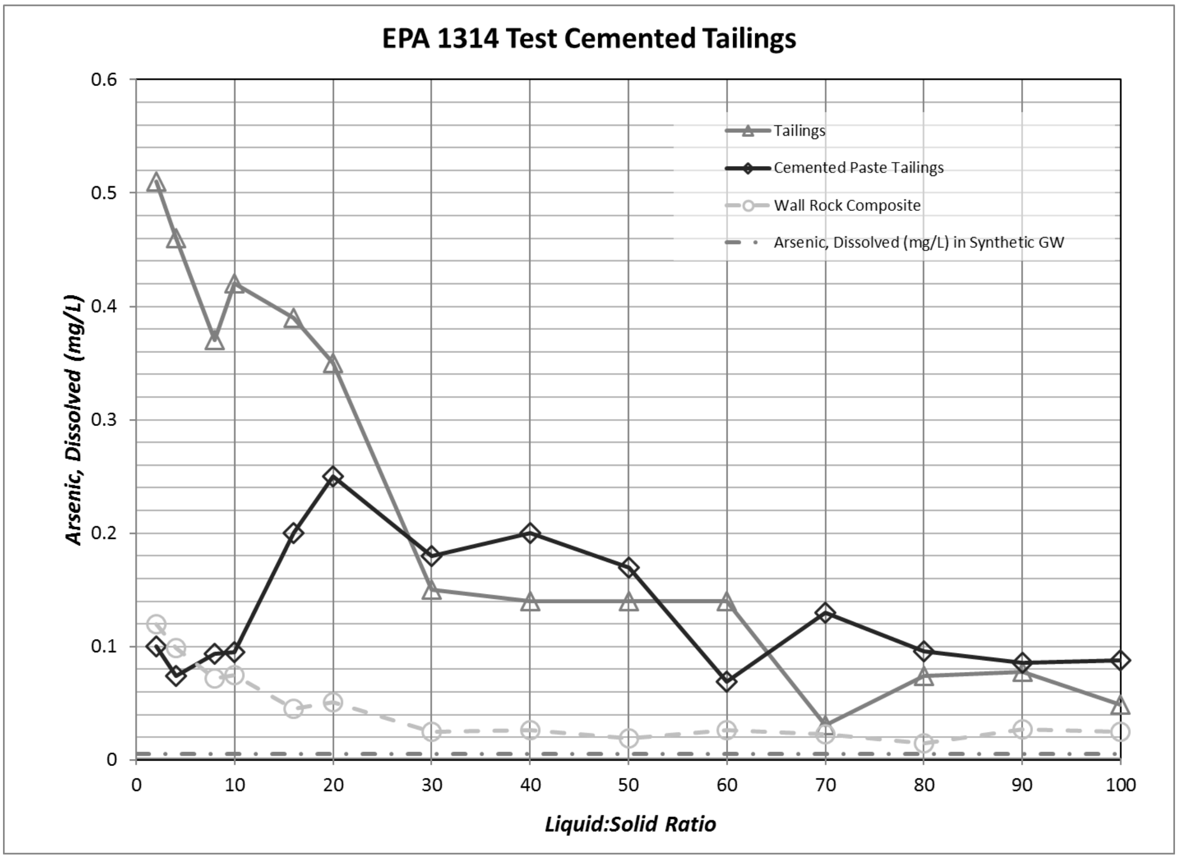

Figure 6. Arsenic leaching tests for tailings, cemented tailings and mine wall rock.

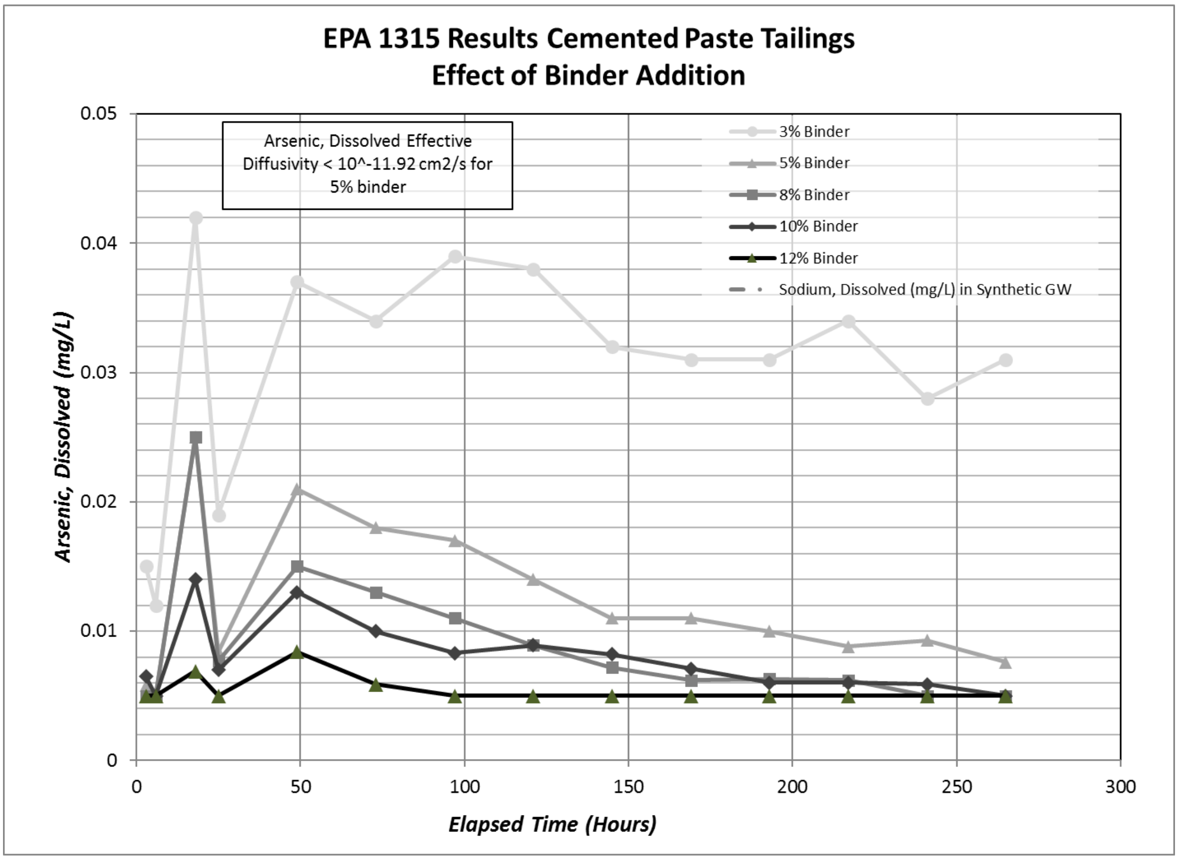

Figure 7. Arsenic diffusion tests for cemented tailings with varying binder addition (50 % Portland Cement and 50 % flyash).

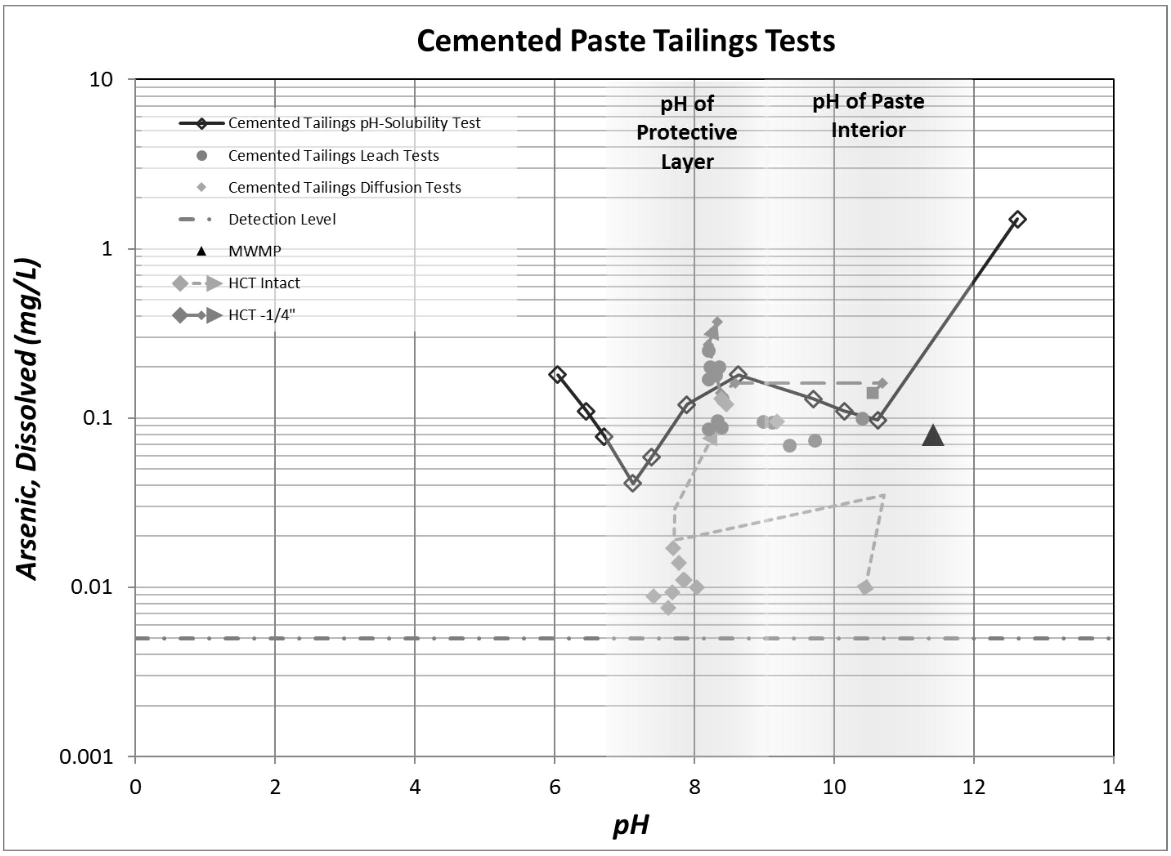

Figure 8: *Results of various tests for evaluating the environmental effects of cemented paste tailings.*

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Preliminary results from experiments with Cement slurries to control Acid Mine Drainage in Waste Rocks from Brukunga Mine in South Australia

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Abstract

The use of cements or grouts for geotechnical stabilization of mine voids is well documented, but the effectiveness of cements and grouts in controlling sulfide oxidation has received comparatively little attention from researchers.

In this study, a range of Portland cement slurries were applied directly to waste rocks from the Brukunga Mine in South Australia to test effectiveness in controlling acid mine drainage generation. This paper focuses on the results from three columns used as a control group with no cement application, and another three columns, subjected to application of a cement slurry with a water cement ratio of 1.0.

Cement slurry application caused the pH to increase to almost 12 in the first leach before stabilizing at around 8 after 2 months, at the same time reducing sulfur loads by around 75% and reducing acidity, iron, aluminium, magnesium, copper, zinc and manganese to undetectable levels. These improvements have been sustained for around 8 months since cementing, and monitoring is continuing.

Higher Calcium, sodium and potassium concentrations suggests in the leachates from the cemented rocks indicates that the cement is dissolving slowly whilst neutralizing the acidity produced by the lower rates of pyrite oxidation in these rocks.

Key words: Portland Cement Slurry, Acid Mine Drainage Control

Introduction

The use of cements or grouts for geotechnical stabilization of mine voids is well documented, but the effectiveness of cements and grouts in controlling sulfide oxidation has received comparatively little attention from researchers. Cements have been used for grouting of voids in underground mines (Guynn et al, 2010) as well as a component in covers used to prevent water from flowing through acid producing rocks (Jones and Wang,1994).

Many studies have investigated the potential of utilizing the useful properties of alkaline industrial waste products such as coal combustion by-products, lime kiln dust and green liquor dregs for controlling acid mine drainage (Bulusu et al, 2007, Perez-Lopez et al, 2007 Sahoo et al, 2013, Makitalo et al, 2015). There is little published work concerning the utility of Portland cement in controlling acid mine drainage.

The Brukunga Pyrite Mine in South Australia was mined between 1955-1972 for pyrite and pyrrhotite resulting in production of 8 million tonnes of waste rocks (Cox et al, 2006). The waste rocks continue to produce acid mine drainage, which is currently treated at a lime treatment plant on-site.

The main objective of this study was to test the effectiveness of directly applying a Portland cement slurry to acid producing waste rocks in reducing acid mine drainage generation.

Methods

Waste rocks and sludge samples were collected from the Brukunga mine in South Australia and the cement used was Cement Australia's General Purpose Cement product.

Six leach columns with 15.5cm diameter and 22.5 cm length were made from PVC pipe. A press on cap with a tap was used to seal the column at the base, and a screw on cap was used to seal the column above.

Each column was filled with 4.78kg of waste rocks from the Brukunga mine ranging from 2mm-26mm in particle size, with 13.6% in the 2-4.75mm size fraction, 69% in the 4.75-13.2mm size fraction and 17.4% in the 13.2-26mm size fraction.

The columns were leached with 1 liter of deionized water each fortnight for 6 months and then kept dry for 49 days before a range of cement treatments (Table 1) was applied to 3 columns with another 3 columns used as a control group.

Table 1 *Cement slurries applied to leach columns.*

Columns	Treatment	Cement Composition	Water/Cement Ratio
1	Control	-	-
2	Control	-	-
3	Control	-	-
4	Cement	250g cement, 250g water	1.0
5	Cement	250g cement, 250g water	1.0
6	Cement	250g cement, 250g water	1.0

Immediately before the cement slurries were applied to the columns, the columns were leached with one liter of deioinised water to remove a fraction of the sulfide oxidation products that had accumulated over the 49 day dry period.

The cement slurries were prepared in a clean 2 liter plastic beaker. For each column to which a cement slurry was applied, the procedure was as follows. The dry cement powder was first weighed into the beaker and mixed and pounded with a wooden spoon to ensure any lumps were broken up. Deioinised water was carefully added whilst the mixture was stirred vigorously to form a homogenous slurry, before the slurry was carefully poured over the rocks in the column with the aim of achieving a uniform coverage over the top surface of the columns and as deep penetration through the columns as the rheological properties of the slurries would allow.

One week after the application of cement slurries, fortnightly leaching was resumed. The fortnightly leaching has been continued for a further 8 months so far, with a 49 day break during the Australian Summer of 2015/16.

Initially leachate samples were collected one day after application of water, but this became problematic after the cement application reduced the permeability of the cemented columns. From 230 days onwards, samples were collected one week after application of water to allow sufficient volumes of leachate to be collected.

pH, electrical conductivity, redox potential and temperature were measured using TPS probes. Titrations were used to measure acidity for samples with a pH < 6.0, and alkalinity for samples with pH >4.0 with a Metrohm 888 autotitrator. Samples were preserved with nitric acid for analysis for Fe, Al, Ca, Mg, Si, Mn, Cu, Zn and S with a Perkin Elmer Optima 8000 ICP-OES and Na and K using a flame photometer. Since November 2015, samples were analysed for sulfate and thiosulfate using a Metrohm 883 Basic Ion Chromatograph.

Results and Discussion

Leachate composition prior to cement application

Prior to the application of cement, there was little variability in the leachates produced by the 6 columns (Table 2) with total loads of acidity ranging from 57.0 – 67.7 grams of acidity as CaCO3 equivalent for the six of columns, produced over a period of around 6 months.

***Table 2** Average pH, Total Loads of Ca, Mg, Al, Fe, S, Si, Cu, Mn, Zn and Acidity of samples collected from leach columns prior to application of cement slurries. Loads of elements calculated using concentrations measured using ICP-OES*

Column	Group	pH	SO4 (g)	Fe (g)	Al (g)	Ca (mg)	Mg (mg)	Si (mg)	Cu (mg)	Mn (mg)	Zn (mg)	Acidity (total) (g)
1	Control	2.37	42.8	11.2	1.9	936	263	295	17	247	668	44.2
2	Control	2.42	38.9	10.6	1.7	604	254	172	15	229	726	42.6
3	Control	2.37	43.7	12.2	1.8	799	264	238	18	231	700	47.3
4	Cement	2.41	39.6	10.8	1.8	721	252	208	15	228	707	43.1
5	Cement	2.43	37.3	10.2	1.8	598	235	136	42	293	615	41.0
6	Cement	2.40	40.4	11.5	1.8	721	205	169	42	272	584	43.5

Leachate composition after cement application

Since the application of cement slurries, the leachate compositions of the six columns have diverged (Table 3). The columns to which cement was added have become moderately alkaline (pH ~ 9.0), with reduced loads of sulfur and silicon, and undetectable levels of Fe, Al, Mg, Cu, Mn and Zn, while Na, K and Ca levels are greatly increased. The slightly sulfurous odors of the cemented columns also differ from those produced in the control columns, suggests the presence of sulfide in the cemented columns.

***Table 3** Average pH and total loads of Ca, Mg, Al, Fe, S, Si, Cu, Mn,Zn, and Acidity of samples collected from leach columns after to application of cement slurries. Element loads were calculated using concentrations obtained using ICP-OES for each element except for Sulfur, which was analysed by IC.*

Column	Group	Vol (L)	pH	SO4 (g)	Fe (g)	Al (g)	Ca (g)	Mg (mg)	Na (mg)	K (mg)	Si (mg)	Cu (mg)	Mn (mg)	Zn (mg)	Acidity (total) (g)
1	Control	12.6	2.34	64.9	17.9	2.6	0.9	534	29	21	404	26	145	376	64.7
2	Control	12.6	2.36	65.0	18.0	2.7	0.9	520	25	9	339	24	150	479	65.4
3	Control	12.8	2.32	65.2	18.2	2.5	1.0	496	28	9	440	25	136	429	63.8
4	Cement	8.0	9.21	20.6	0.0	0.0	5.5	0	235	872	150	0	0.0	0.0	-1.0
5	Cement	10.1	9.34	20.2	0.0	0.0	5.8	0	250	845	219	0	0.0	0.0	-1.8
6	Cement	3.0	9.26	12.4	0.5	0.2	3.0	0	198	728	18	0	0.07	0.31	-1.2

There is more variation in leachate compositions in cemented columns than in the control group after cementing, due to variations in the degree to which the cemented columns were made less permeable by the cement applications. Column 6 is the least permeable of the columns with only 23% of the water applied to the column draining through the column within a week, which automatically reduces the loads of sulfur, calcium and silicon produced by the column. The reduced permeability of this column also increased the fraction of total sulfur that is present as thiosulfate rather than sulfate in the leachates from this column (Table 4).

***Table 4.** Average Sulfate and Thiosulfate concentrations measured with Ion Chromatography (IC) for 9 samples measured from November 2015 til April 2016.*

Columns	Group	SO4 IC	S2O3 IC
1	Control	4844	0.0
2	Control	4902	0.0
3	Control	4818	0.0
4	Cement	1440	220
5	Cement	1380	115
6	Cement	1501	578

Stability of cement over time

Cement application resulted initially in a spike of alkalinity corresponding with high pH; over time, the alkalinity and pH declined and stabilized to ~ 8 and ~40mg/L (Figures 1 and 2).

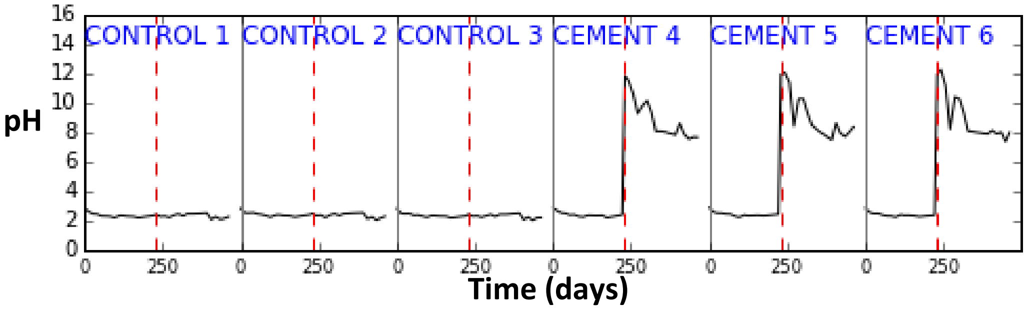

Figure 1. *pH*

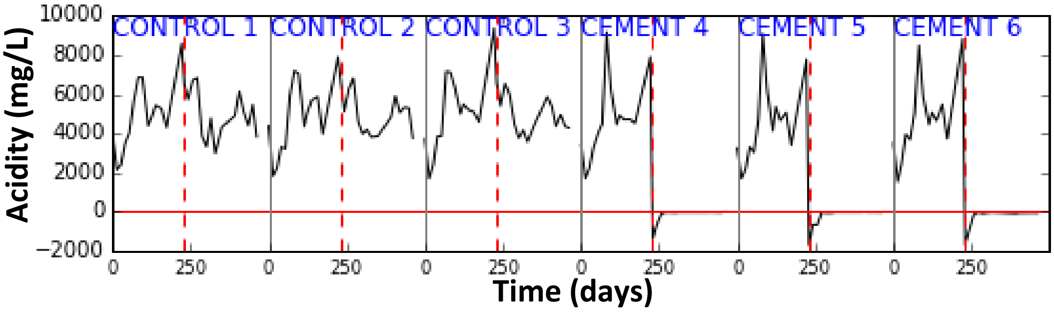

Figure 2. *Acidity (mg/L CaCO3 equivalent), Alkalinity plotted on negative y-axis with the same unit.*

Over time column 6 and to a lesser extent columns 4 and 5, have become less permeable as evidenced by decreasing weights of sample collected (Figure 3). To a lesser extent the permeability of columns 4 and 5 have also decreased over time. The higher concentrations of calcium, sodium and potassium in column 6 (Figures 4,5 and 6 respectively) probably reflects enhanced dissolution of these elements from the cement due to the longer contact time.

Assuming constant rates of cement dissolution based on the data in table 3 and using a typical CaO content for Portland Cement of 64% (Guirguis, 1998) predicts that 432 leaches would be required to completely consume all of the calcium in the applied cements. At the fortnightly rate of leaching used here, the calcium of the cements would be completely consumed in around 12 years.

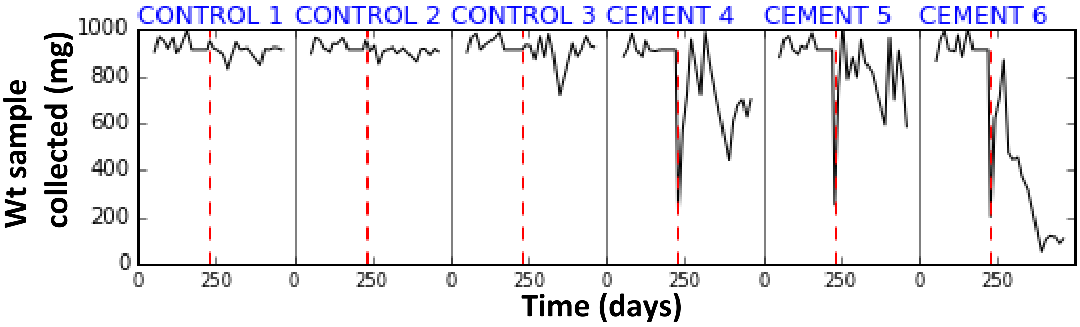

***Figure 3**. Weight of Leachate sample collected (mg). For the first 230 days, samples were collected after one day. After 230 days, samples were collected one week after water application to allow for the slower rate of drainage in the cemented columns.*

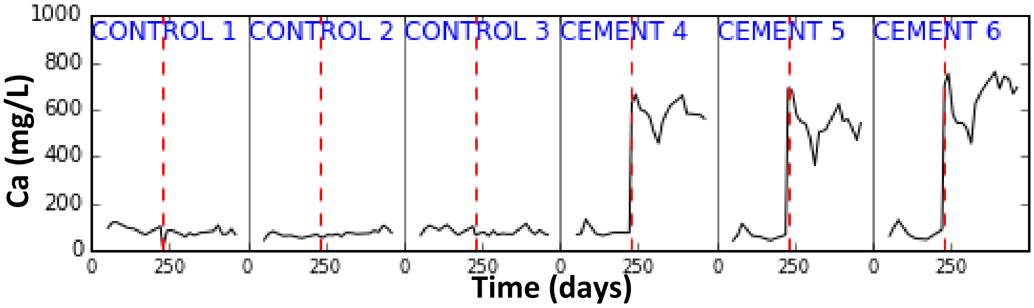

Figure 4. *Ca (mg/L)*

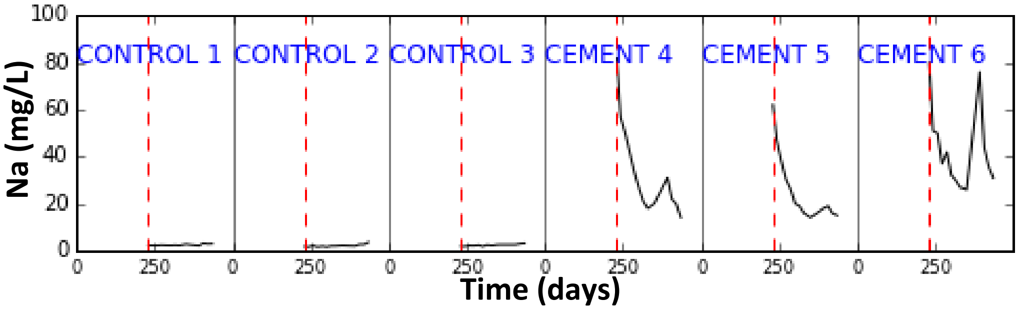

Figure 5. *Na (mg/L)*

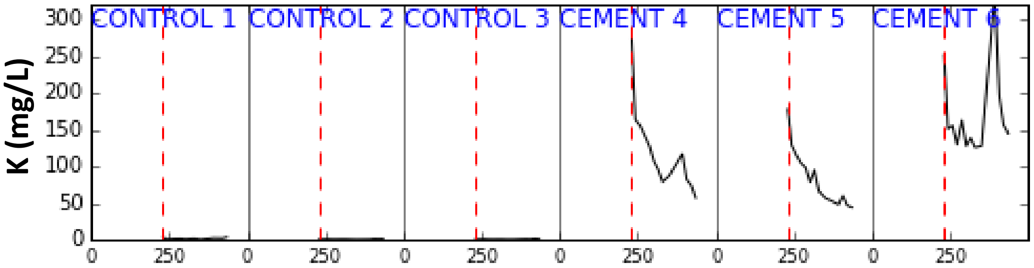

Figure 6. *K (mg/L)*

Silicon concentrations are higher in the controls columns than in the cemented column, reflecting likely due to sulfuric acid attack of aluminosilicate minerals in the waste rocks. Upon cement applications silicon concentrations decreased in the cemented columns, but in columns 4 and 5 have begun to increase as the pHs in these columns decreased, but this is not the case for column 6; Si is likely being released from the cement matrix, but in column 6, may be re-precipitating (Figure 7).

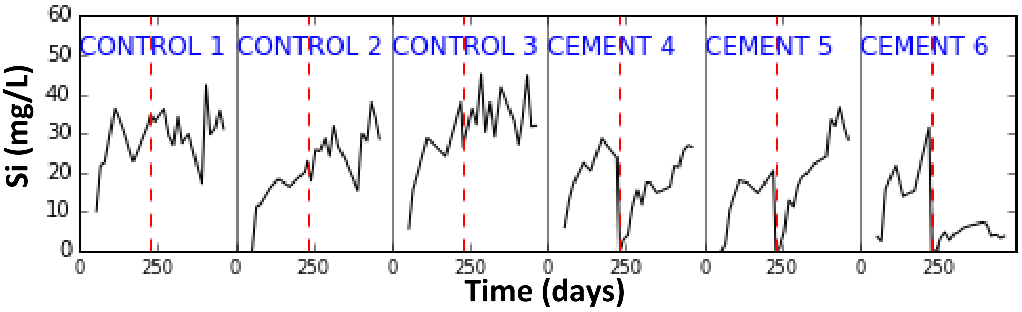

Figure 7. *Si (mg/L)*

Rate of pyrite oxidation in cemented columns

Sulfur concentrations in leachate from the cemented columns appear to be stable at around half the concentrations in the control columns (Figure 8), which suggests that the rate of pyrite oxidation has decreased due to the cement application. It is likely that the lower rate of pyrite oxidation in the cemented rocks is due to direct encapsulation of sulfide surfaces as well as the increased water retention in these columns (Figure 3), which would likely serve as a water barrier to oxygen.

Iron concentrations in the control leachates are over 1g/L, but have been reduced to below detection limit in the cemented columns, which suggests that the iron is being retained in the cemented columns, probably as precipitated ferrihydrite or schwertmannite (Figure 9). The steady release of sulfate in the cemented columns indicates that the precipitation of iron in the cemented columns is not presently inhibiting the oxidation of pyrite.

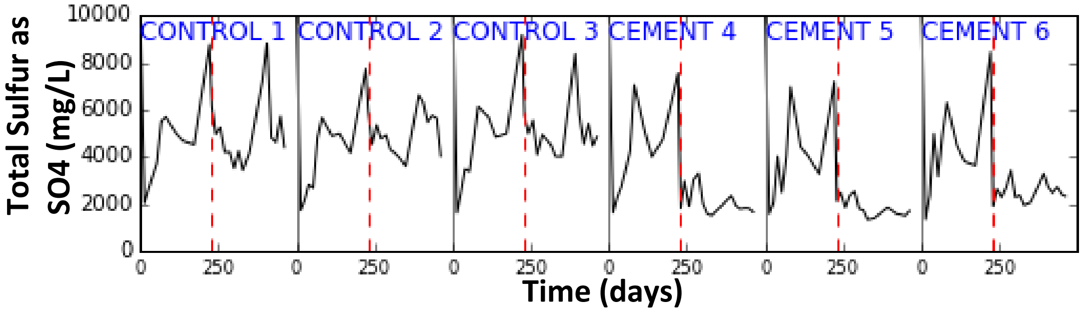

Figure 8. *Total sulfur as SO4 (mg/L)*

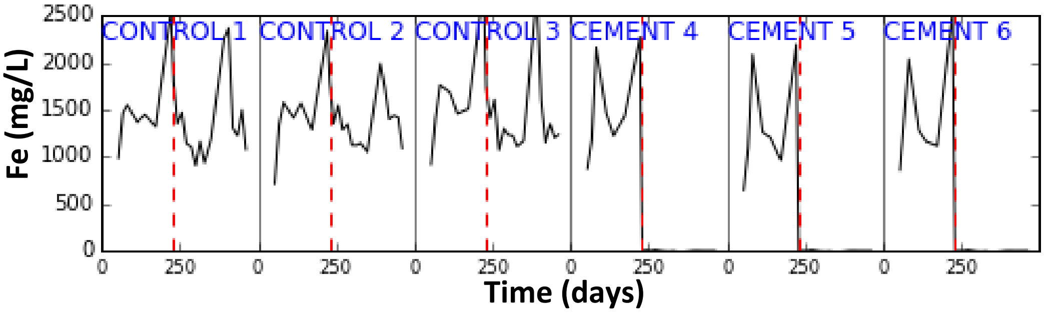

***Figure 9**. Fe (mg/L)*

Conclusions

Direct application of cement slurries to the Brukunga waste rocks in all cases greatly diminished acidity production and metal loads (iron, aluminium, copper, manganese and zinc).

Calcium, sodium and potassium concentrations are all increased in the cemented columns, which suggests that the cement is dissolving while neutralising the acid being produced by oxidizing sulfides in the waste rocks and leaching sulfate through the cement matrix. The rates of calcium dissolution measured in this experiment suggest that the cements would lose effectiveness after around 12 years due to complete dissolution of the calcium from the cement.

The lower rates of sulfur production in the cemented columns indicate that the continuing pyrite oxidation is occurring at around half the rate of pyrite oxidation in the control columns due to direct encapsulation of pyrite surfaces with cement as well as due to increased retention of water, which may serve as a water barrier to oxygen.

Future work will test the longevity of the cement slurry treatments on the waste rocks and compare the effectiveness of different cement slurry compositions in controlling acid mine drainage.

Acknowledgements

Thanks to Raul Mollehuara and Chris Henschke from Mineral Resources, South Australia for assistance with the collection of samples from the Brukunga Mine.

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Trace substances in ascending mine waters – environmental and social effects in urban areas

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Abstract

Germany will quit from black coal mining in 2018, the last two operating mines in the federal state of Northrhine-Westphalia are going to stop production by then. Nevertheless, post-mining operations will have to be continued endlessly (in the foreseeable future). The maybe most important of these so-called "eternity tasks" is the handling of large amounts of ascending mine water: in the Ruhr mining district alone, about 120 million m^3 of mine water per year have to be pumped from depths of several 100s of metres to the surface and discharged to adjacent receiving water courses to avoid flooding of former and still active mining drifts. This water has temperatures of up to 50° C and may contribute to a future geothermal energy supply of the region. On the other hand, the mostly saline waters also partly contain unwanted trace substances of potential environmental concern. These include radionuclides (esp. ^{226}Ra and ^{228}Ra) and polychlorinated biphenyls (PCB). The former are probably geogenic contaminants while the latter are suspected to derive from anthropogenic remnants left in the galleries. These substances´ sources, mobility and distribution in surface waters and sediments are hardly understood, associated social consequences of their occurrence in this densely populated area have not yet been discussed. The proposed interdisciplinary young researchers group "Dealing with an Eternity Task in the Ruhr Area" (DETRA) aims at addressing suchlike questions from natural scientific and social scientific points of view. In summary, we will address interdependencies of geoscientific findings and social consequences around a water-related environmental problem in a densely populated urban area, and contribute to understanding the impacts of a transforming water and energy landscape in the region.

Key words: Geothermal mine water use, trace contaminants, sustainability, corporate social responsibility

Introduction

In 2018, Germany will quit from black coal mining. However, post-mining operations will probably have to be continued forever. The maybe most important of these so-called "eternity tasks" is the handling of large amounts of ascending mine water: in the Ruhr mining district alone, about 120 million m^3 of mine water per year have to be pumped from depths of several 100s of metres to the surface and discharged to adjacent receiving water courses to avoid flooding of former and still active mining drifts (Wedewardt 1995).

This water brings along temperatures of up to 50° C and may therefore contribute to a future geothermal energy supply of the region. On the other hand, the mostly saline waters also partly contain unwanted trace substances of potential environmental concern. These include radionuclides (esp. ^{226}Ra and ^{228}Ra) and polychlorinated biphenyls (PCB). The former are assumably geogenic contaminants which are also known from Polish black coal mining districts (e.g. Leopold et al. 2007) while the latter are suspected to derive from anthropogenic remnants left in the galleries. Anyway, these substances´ sources, mobility and distribution in surface waters and sediments are not well understood. Table 1 shows ambient dosage rates for different rivers receiving the former mines´ runoff. Dosage rates tend to increase from the southern (Ruhr river) to the northern (Lippe river) Ruhr Area. This is probably caused by increasing percentages of highly mineralised, Ra-rich deep waters in the northern part, where mining was active below a thick Mesozoic overburden while the oldest mines in the southern part operated on, or close to the ground surface.

Table 1 *Ambient dose rates in former mines discharge, ordered by receiving rivers (data from Behrendt 2007).*

River	n (mines)	Ambient dose rate (nSv/h)
Ruhr	3	50-80
Emscher	6	50-600
Lippe	4	50-3000

Climate change is likely to have a significant effect on the quantity and quality of ascending mine waters due to changing amounts and distribution of precipitation. This will probably impact the occurrence and distribution/accumulation of trace substances in water and flooding sediments. Therefore, climate change scenarios and their consequences will be considered by the research group.

The consequences of handling the mentioned eternity tasks do not only have an impact on the natural conditions of an area. In densely populated areas they also affect areal social reality. The reason is that interrelations exist between natural and social conditions in a region like the German Ruhr area. This assumption is part of the discourse about (social) sustainability which occurred in the 1980s/1990s. Today the topic “sustainability” has reached the status of one of the contemporary mega trends in societies. A central concept thereby is the “triple bottom line” which identifies three dimensions of sustainability: economic, ecologic and social which are interrelated Deutscher Bundestag 1998; WCED 1987; Zimmermann 2016). It is also a complex issue that contains different perspectives on handling the different dimensions. In some views the economic (due to economic growth and sustainable management) or the ecologic dimension (in terms of protection and conservation of environmental resources) dominates the model (Zimmermann 2016). The social dimension is (usually) defined weakly. That is why there is no version in which the social dimension dominates. In other views the three dimensions are treated as equal. Anyway, although the subject has arrived in various disciplines, it is slightly becoming part of sociological research. Opielka states that there is a lack of "a sociotheoretical and time diagnostic sociology of sustainability” (Opielka 2016, 33) until now. Only since the 2000s sociological studies focus on the terms "sustainability" and "corporate social responsibility" (CSR) (Backhaus-Maul 2009; Backhaus-Maul/Kunze 2015). Thereby they are particularly referenced to sustainable organizational or economical actions (Deutscher Bundestag 1998; Backhaus-Maul/Kunze 2015; Brand & Jochum 2000; SRU 2002) – besides studies in the context of environmental sociology that concentrate on social contexts regarding relationships between nature and society as well as ecological problems.

Empirical studies on sustainability and sustainable organizational actions (in the field of organization sociology) usually can be characterized as explorative. That is because the topic still needs to be developed. Most of the works base on the sociological neo-institutionalism as one of the most popular and recent approaches concerning organization theory. The central assumption is that organizations (primarily profit-organizations) conform to environmental demands and expectations (of their stakeholders), implement e.g. CSR and sustainable strategies and thereby gain legitimacy which is important to facilitate organizational survival (e.g. Bluhm 2008; Bluhm und Geicke 2008; Brugger 2010; Hiß 2007). Today more than ever organizations act under a social legitimation pressure due to the fact that they are central actors of modern societies. Therefore they have to shoulder social responsibility and contribute significantly to the sustainable societal development (Brugger 2010; Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit 2006). Conforming activities of different actors to adapt to environmental demands also have impacts on the region in which they are located. Regions (this means social and natural conditions of an area) and actors (organizations, communities, interest groups) are interrelated with regard to a sustainable development. That contains chances as well as risks for both. On the one hand it holds chances and potentials when all relevant actors of an area are involved in planning and implementing sustainable strategies. On the other hand risks could evolve, when different interests and ideas are conflicting. The latter is an example for a perspective in which (usually) one dimension of sustainability dominates the other.

Against this background the project group „DETRA“ aims to combine a geological and an organizational perspective on sustainability in urban areas like the German Ruhr area. Due to the fact that the project still is in the planning phase the following chapter contains first ideas about the empirical work.

Methods and project goals

The proposed research group strives for the following goals:

- Implementing laboratory methods for the determination of radionuclides (γ spectroscopy) and organic contaminants (GC-qMS) concentrations in mine water, surface water and sediments,
- Describing and evaluating the current state of occurrence and distribution of the trace substances around selected mine water discharges: characterizing the problem´s extent,
- Studying behaviour and fractionation of trace elements in environmental media including the use of isotope tools (e.g., chlorine isotopes [Jin et al. 2011]): understanding the structure of sources and sinks,
- Creating suitable hydrogeochemical and climate change impact models to forecast future developments and transfer findings to other affected locations: formulating recommendations for dealing with the problem from a natural scientific point of view,
- Assessing social consequences of the problem: “good practice” in dealing with the problem, organisational sustainability and corporate social responsibility, consequences on reputation and identity, stakeholders´ self-perception and population´s social acceptance during the evaluation of an energy source with suchlike “side effects”: formulating recommendations for dealing with the problem from a social scientific point of view.

Conclusions

The proposed research group will evaluate the interdependencies of the different parts of the mentioned ascending mine water challenges: contamination with organic trace substances, inorganic trace elements (esp. radionuclide) occurrence, impact of climate change, and social consequences. It will therefore contribute to an improved understanding of the consequences of the transforming water and energy sectors in Northrhine-Westphalia.

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Assessing post-mining risks in the long term: ten years of hydrological monitoring in Liège (Belgium)

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Abstract

One of the major environmental changes observed after mine closure are associated to groundwater flow and the coupled stress redistribution in the subsurface. Flooding of the mined voids starts as soon as the extensive pumping required during mining activities stops. This process called “ground water rebound” continues until mine water levels equilibrate with the regional ground water surface or reach a point of discharge. In case no such point of discharge exists (e.g. due to the collapse of drainage adits) outbreak, flooding and/or stability problems can occur in the surrounding area (Wolkersdorfer 2008).

Management of risks associated to former mining activities is thus essential to ensure public safety where extraction activities have been intense for several centuries, e.g. in Wallonia (Pacyna and Salmon 2012). To assess these risks, flow rates at discharge adits and groundwater levels have been monitored for 10 years in an abandoned coalfield in the area of Liège (Eastern Belgium). A statistical study is conducted on the long term data, aiming at understanding groundwater behavior and improving the monitoring network. Annual trends calculated from time series decomposition are used to evaluate if groundwater rebound is still active or not in the study area. Spatial and temporal correlation analyses between piezometric levels and discharge rates allow identifying response time of groundwater to recharge events and to obtain indications on the storage capacity of the aquifer.

This study shows how statistical analysis of a long term database can be used as an efficient low cost tool to improve a monitoring network for mining risk management purposes since it helps understanding connectivity and reactivity of the groundwater table at different locations in the mine.

Key words: Abandoned mines, mining risk management, temporal analysis

Introduction

On February 27th 2002, an outbreak occurred North of the city of Liège (Eastern Belgium), in the Meuse valley where intense coal extraction activities took place during several centuries (Pacyna and Salmon 2012). Last pumping phases stopped in 1982 in this abandoned coalfield. The event of 2001 triggered the set-up of a monitoring system to assess risks of new outbreaks, floodings and/or stability problems in the surrounding area. Flow rates in drainage adits and groundwater levels in residual mine voids have therefore been measured for 10 years in this area.

Due to the presence of cavities and rubble zones, hydraulics within mine workings and within karst systems are considered to behave similarly (Burbey et al. 2000). Therefore, the use of time series analysis seems to be a valuable low-cost method to characterize flow processes in underground mines (Sahu et al. 2009), as it is a widespread method for characterizing karstic systems (Mayaud et al. 2014; Panagopoulos and Lambrakis 2006). Two main questions are addressed in this study: is the level of risk stable, and what is the response time in case of pressure anomaly? The level of risk is linked to groundwater rebound and increases if rebound is still active. Response times are linked to the storage capacity of the hydrogeological system, as it influences how fast groundwater pressure pulses propagate through the abandoned coalfield. Indeed, high transmissivity is observed as recharge events are drained on short period of time by quickflow processes (e.g. Padilla and Pulido-Bosch 1995) in systems characterized by low storage capacity. In contrast, baseflow is the dominant process controlling water release in systems with high storage capacity (e.g. Larocque et al. 1998).

Methods

Collected data was measured in a groundwater network of six piezometers (Pz4-Pz10 in Figure 1) monitored since 2003, with screens installed in mined out areas of the Carboniferous shales. Groundwater depths were either manually measured on a monthly basis or monitored with pressure sensors at an hourly resolution. Stream levels behind weirs with rectangular notch installed in two channels located in the valley were monitored with pressure sensors and used to calculate discharges at an hourly resolution. Daily means of piezometric data and of discharge values are used in this study.

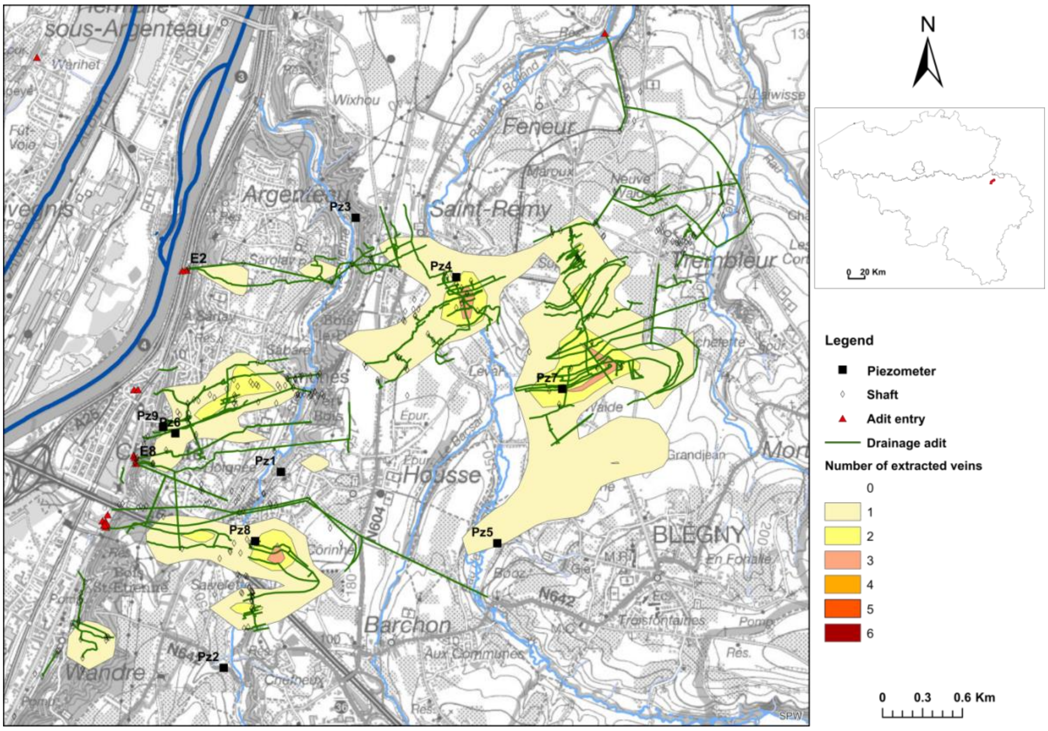

Figure 1: *Location of the study area, mining plans of the exploitations located above the level of the Meuse River (55m) and measurement setting*

Trend decomposition of water levels and discharge hydrographs, based on moving average calculations, allows extracting annual trends. These trends are used to evaluate if groundwater rebound is still active or not.

Correlation analyses are performed on the first derivatives of the time series, since stationary data are required. Consequently, conclusions of our study concerning spatial and temporal correlations refer to the *velocity* of groundwater level and discharge variation. Auto-correlation functions are calculated for each time series to identify memory processes in the data, considering that slow decreasing trends of auto-correlation function are attributed to slow mechanisms (e.g. seasonal recharge) and fast decreasing trends are induced by faster short term processes (e.g. reaction to single short recharge events). Finally, cross-correlation functions are evaluated to understand connections through the mined system at different time scales (long term vs. rain event) (Mayaud et al. 2014).

Results

Annual trends (Figure 2) calculated over ten years do not show any increase, suggesting that the groundwater rebound stopped before monitoring started.

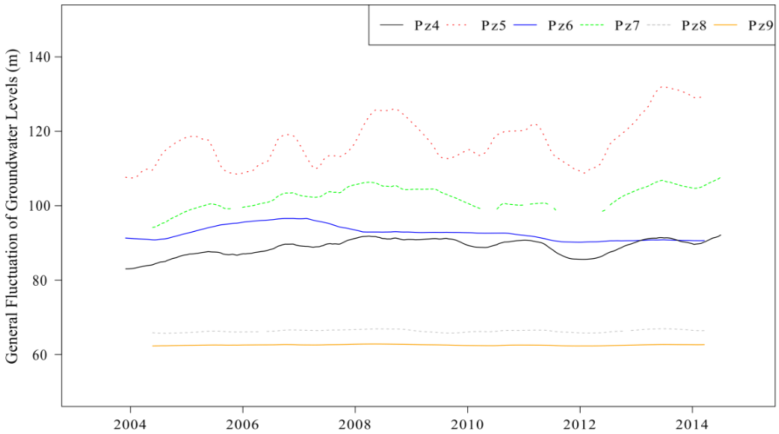

Figure 2 *General trends extracted from piezometric levels.*

Auto-correlation analyses allow differentiating locations in the mine influenced by slow and fast recharge processes, characterized by long and short decorrelation time, respectively. In general, short decorrelation times are observed in this study case. However slightly higher decorrelation times are calculated for Pz7 and Pz8, indicating these piezometers are probably located in areas with larger storage capacities than the other monitoring locations (d in Table 1).

The cross-correlation functions (ccf) indicate that some locations (Pz4, Pz7 and E8 – Table 1) in the mines are always connected to each other while no galleries connecting Pz4, Pz7 and E8 are reported (Figure 1), indicating that hydraulic pressure probably transfers through fractures or unknown rubble zones. In contrast, other locations are poorly connected to each other (low ccf for Pz6, Pz8, E2 in Table 1). Even if galleries seem to connect E2 with Pz4 and Pz9 with E8 (Figure 1), hydraulic pressures do not seem to transfer between these measurement points (low ccf in Table 1). However locations Pz4 and E2 are connected during rain events as maximum cross-correlation coefficients calculated for 14 selected rain events reached an average value of 0.61 within 2 days.

Table 1 *Maximum cross-correlations coefficients (ccf) between time series measured from 2003 until 2014 and decorrelation times (d in days) calculated by auto-correlation. All italic figures are related to coefficients >0.5 The underlined symbol « ns » stands for not significant values.*

	ccf							
	Pz5	Pz6	Pz7	Pz8	Pz9	E2	E8	d
Pz4	0.46	0.49	*0.65*	0.38	0.32	0.09	*0.51*	5
Pz5		0.22	0.33	0.24	0.2	0.22	0.17	7
Pz6			0.41	0.33	0.39	ns	0.46	4
Pz7				0.38	0.36	0.05	*0.66*	9
Pz8					0.26	0.11	0.27	9
Pz9						ns	0.23	6
E2							ns	2
E8								4

Conclusions

This study proved time series analysis is an efficient low cost tool to improve the understanding of groundwater fluxes through an abandoned coalfield. It helps understanding the interconnections between different zones and the reactivity of the groundwater table at different locations in the mine. The results show that outbreak risks due to groundwater rebound processes can be excluded in this area but that reported galleries from the exploitation maps (Figure 1) are not sufficient to understand the hydraulic connections between the different exploited zones. The statistical approach highlighted connections between measuring points that were not connected by galleries (Pz4-Pz7-E8) and showed that ancient galleries not always transferred hydraulic pressures (i.e. E2 - Pz4 and Pz9 - E8).

This study reveals that discharges in E8 evolve similarly to piezometric levels in Pz4 and Pz7, as cross-correlation analysis clearly proved hydraulic pressure must be transferred between these measurement locations. If data evolution differs between these points during future monitoring, investigations should be performed to know how pressure cannot be transferred by the usual way. In that case, further investigations should identify if pressure builds up somewhere in the coalfield or if it is transferred by another pathway. Hydraulic pressure can in that case be released by another pathway, as E2 drains this area at least during rain events. This observation proves that considering different time scales (whole monitoring period vs. event time scale) allows giving new insights on the active flux processes in the mine system (e.g. quickflow or not).

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Restoration, Governance and Regional Development in the South of Leipzig

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Abstract

In the region south to Leipzig, several surface mines and its associated infrastructure as power and briquetting plants had to be closed due to economic reasons after the German reunification. In the following years, the open holes altered into lakes with significant touristic and conservation potential: beaches, harbors and protected areas were created. The living quality of the region underwent an overall improvement.

This study aims to depict the current situation of this post-mining region considering the last 15 years and represents the notions of six local stakeholders of the governance sector. By means of semi-structured interviews, respondents described success factors and challenges in the regional development. Based on this, the landscape transformation is assessed on the basis of the sustainability concept.

The potential sustainability of the transformation is critical both in consideration of short- and long-term consequences: besides the pure technical and ecological aspects, the social dimension is a significant factor for a successful restoration (Metcalf et al 2015; Berkner, Thieme 2005). Also, restoration outcomes lie the basis of the further development of the region. Experts expect the lakes to exist for many thousands years (Berkner, Thieme 2005), creating a long-term influence.

This work contributes to the up-to-date limited knowledge of social aspects in mining restoration processes. It opens up insight into one post-mining region, which strives to transform into a touristic destination and describes factors facilitating and challenging such a transformation.

Key words: pit lakes, governance, success factors, sustainability

Introduction

In the past, the region south of Leipzig belonged to the most polluted areas in Europe. Dust, chemicals, and noise deteriorated the environment; recreation areas were lacking; residential buildings and infrastructure facilities were decaying (see, for example, Kabisch, Linke 2000). After the German reunification, surface mining economy closed down and an enormous transformation altered the landscape; giving rise to several lakes. Besides public safety and environmental aspects, that needed to be ensured, also the living quality for the residents was restored.

While studies on ecological and technical aspects of restoration processes are numerous, publications considering the social and economic dimensions are limited (Kabisch 2004). However, as the impacts of the restoration on the local population are extensive and the success of the restoration depends on social aspects, the human 'side' needs to be acknowledged. This fact is supported by academic results (for example Baker et al 2014; Metcalf et al 2015).

Following to what was said, this paper investigates the trajectory of the region depicted by six local experts and thus contributes to an increasing interest in the social dimensions of restoration by describing the process from a governance point of view.

Methods

Using semi-structured interviews, six local experts illustrated the current situation and development in the region. Four experts represented municipalities (Borna, Großpösna, Leipzig, Markkleeberg) and two respondents associations (Kommunales Forum Südraum Leipzig, Tourismusverband Leipziger Neuseenland). At the beginning, the intention of the study was to focus on stakeholders acting close to the former open pit Espenhain. These actors belonged to various spheres and were chosen in agreement with Prof. Dr. Andreas Berkner, head of the Regional Planning Department of West Saxony. However, during the study a re-arrangement took place as a close connection to other lakes and a potential conflict situation between municipalities was identified. Thus, business representatives were omitted and instead, the cities Leipzig and Borna added. The interviews were transcribed and analyzed.

Results

Tab. 1 and tab. 2 give an overview of success factors and challenges in the region. Named by all interviewees, the horizontal cooperation between policy makers revealed to be the most important success factor. Also, vertical cooperation between politics, owners, users and stakeholders of other sectors, as business or NGO is crucial. Further, certain special conditions distinguish the studied region from other post-mining landscapes: the allocation of funds by means of administrative agreements shared between national state and the corresponding federal state facilitated the implementation of many projects. The planned application of the city Leipzig for the Olympic Games in 2012 caused the creation of the Canoe park Markkleeberg, currently being one of the unique selling points in the region.

***Table 1** Success factors. Middle column: number of references in six interviews. Own translation.*

Success factor	#	Example of statement
Cooperation	6	'Without cooperation we would not be where we are right now.'
Special conditions	4	'Applying for the Olympics was a gift.'
Approach of governance	4	'We are learning something new every day.'
Work across levels	4	'It is not possible to think only within one term of office.'
Human approach	3	'There was an euphoria in the early 1990ies.'
Ownership structure	2	'If a lake is owned by one municipality, less agreement is needed.'
Planning preconditions	2	'We have good planning documents.'

Success factor	#	Example of statement
and earliness		

With similar weight, the approach of governance (flexibility, good negotiation and being open to uncertainty) as well as the work over temporal and local levels is needed to ensure a sustainable transformation. Other success factors, mentioned more seldom, were the ownership structure and the planning preconditions and earliness.

In comparison to the success factors, descriptions of challenges in the region were more heterogeneous. Interviewees agreed in particular on the serious financial situation with money missing for planned projects and decreasing funds in the future. Combining these two facts over long-term might exacerbate the situation. Challenges based on natural conditions as the quantity and quality of water and discharge especially during flooding conditions are openly communicated, acknowledged and overcoming them is imagined relatively easy by some experts. One issue, considered to be more challenging, are inter-municipal conflicts, as for example, the question of motorboat use on lake Zwenkau. This case is often named and assessed to be difficult to solve. Plus, some respondents named a general deterioration of the atmosphere of pro-active and constructive policy making. Also, the engagement of the population is degrading. Adding a decreasing 'need for action', this complex of challenges might weight harder than professional risks as the above mentioned natural conditions. Interestingly, half of the respondents named the extent of the German and EU legislation and bureaucracy as hindering a faster development and implementation of projects.

Table 2 *Challenges. Middle column: number of references in six interviews.*
Own translations.

Challenge	#	Example of statement
Decreasing funds and budget	5	'We will have more and more problems to [financial] maintain the things [which we created].'
Natural conditions – quality and quantity of water	4	'With groundwater (...) quality we have new problems, which we though to be already solved.'
Inter-municipal conflicts	4	'There are contrary opinions of municipalities on the use of the lakes.'
Bureaucracy / Legislation	3	'One gets partly drowned in formalities.'
Engagement of the population	2	'There is an approach of being a 'protest citizen'.'
Need for action decreases	1	'There are less real troubles now.'
Approach to governance	1	'There is a regress in how we communicate and argue.'

Discussion

Following, the interview results are discussed on the base of the sustainability concept. It is a normative concept aiming to consider and fulfill rights and demands of all and in particular vulnerable groups over long-term. Often used is the so-called three pillar model, which demands to balance the ecological, social and economic dimensions within one generation (intra-generational) and within a longer time frame (inter-generational). Thus, sustainability implies a temporal and a spatial transferability (Paech 2006).

Examining both the interviews and other resources, a clear aim to balance various dimensions can be found (interview data; Berkner, Thieme 2005). Tourism, jobs and the quality of living for the local people are striven to be harmonized. However, a number of examples reveal difficulties. So is the Floßgraben, a brook connecting Lake Cospuden with the water ways in the city of Leipzig, in a controversial position as it is on the one hand an important part of the touristic water way system and on the other hand a figurehead for local nature conservation. Also, in general, tensions between inhabitants and tourists as well as a differentiation of the population itself can impede local governance and development.

In comparison to other locations, as the Spanish case As Pontes, described in Pérez-Sindín, Hähnel (2016), the social openness and public acceptance in the Saxon case is higher while the centrality is lower than in Spain.

Differently, long-term consequences and trends were largely omitted in the interviews. Only one interviewee gave details about future financial risks and difficulties. She expressed the fear that facilities, which have been created during the transformation process, will need to be closed again due to lacking municipal budgets. According to her, towns and villages keep problematic issues at the back of their minds without approaching the issues as potential problems. They are steamrolled by smaller, current tasks, which they need to manage, so their approach is to 'handle a potential problem at the point, when it is a real problem.' Other potential long-term trends as population aging and decrease and its connection to the transformed landscape were not described. As ignorance grows with an increasing time horizon and the future does necessarily evolve linearly, the lacking reflection of the long-term development can be justified to a certain point. In contrast, the "greatest potential influence for shaping the future may often be precisely over those time scales where our gaze is most dim" (Lempert et al, 2003, p. xvii) and thus, supportive work by various institutions as the District Offices, Planning Associatons or the Federal State and research is recommended to anticipate the future.

Conclusions

The landscape transformation is assessed by all interviewees positive. Hence, a consistency among those institutional actors can be concluded. Such a consistency represents a positive base for the further regional development. Also, all respondents highlighted the importance of cooperation between policy makers. This comprehensive cooperation is especially striking considering the large spatial and temporal extent of the landscape transformation process.

Differently, challenges of the regions are viewed more heterogeneous. On the one hand, open acknowledged and communicated problems exist. On the other hand, some interviewees highlighted less obvious trends, as a worsening of the atmosphere of pro-active and constructive policy making between stakeholders, decreasing engagement of the population and less urging problems.

Considering the sustainability of the transformation, it can be stated that balancing ecological, economic and social aspects is one goal of the local governance. The implementation of such a balance is naturally complicated and does not proceed without conflicts and tensions. The results from this study indicate a relative high equilibrium among the ecological, social and economic dimension.

However, the majority of interviewees did not elaborate long-term questions and developments. Only one respondent acknowledged and described potential future financial straits and lack of human and time resources. Accordingly, support by external institutions and research is recommended to anticipate the future.

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Water resources monitoring and mine water control in Portuguese old uranium mines

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Abstract

Environmental rehabilitation of old abandoned mines in Portugal in done since 2001 by EDM - *Empresa de Desenvolvimento Mineiro*, a state-owned company, of 175 abandoned mining areas, 61 of which in radioactive minerals and 114 in polymetallic sulphides. By the year of 2015, 95 mining areas have been intervened of a total of 175 and ten are with ongoing remediation works.

Monitoring the water environment is a relevant activity in the work developed in radioactive mines, started since 2002, which includes measuring *in situ* parameters and laboratory analysis of chemical and radiological parameters as total uranium, radium-226, sulphates, chlorides, manganese, calcium and sodium, these already identified in previous studies to be the best indicators of hydrochemical contamination related to the old uranium mining areas. Water resources monitoring plan covers upstream and downstream surface water samples, groundwater samples through wells, boreholes and piezometers in the surrounding mine area, together with the quality control of mine water before and after treatment. Per year a total of around 1260 water samples are collected in 61 radioactive mines. Denser monitoring plan in terms of sampling points and monitoring frequency is dependent on the level of contamination of each mine.

The main objective of this paper is to present some details and example results of the work performed by EDM regarding the water resources monitoring plan and control of mine water effluents implemented in the radioactive mines. One of the main focus of remediation design projects is the control and treatment of mine water using passive treatment systems. EDM is implementing this type of systems with demonstrated success, in some cases associated with groundwater natural attenuation processes for uranium, radium-226 and other metals.

Key words: Environmental monitoring, water resources, mine water control, passive treatment systems

Introduction

Portugal has an important legacy of old abandoned mining sites with clear environmental and public health impacts and safety problems. Since 2001 they are being subjected to environmental rehabilitation operations by EDM - *Empresa de Desenvolvimento Mineiro*, S.A., a state-owned company, under a legal regime of concession assigned by the Portuguese State and approved by the Decree-Law Nº 198-A/2001. EDM is covering the environmental rehabilitation of 175 abandoned mining areas, 61 of which in radioactive minerals and 114 in polymetallic sulphides. In the radioactive mines the most relevant are Urgeiriça, Quinta do Bispo, Cunha Baixa, Bica and Vale de Abrutiga, all located in the Beiras Granitic Region (EDM, 2011), in the central part of Portugal. By the year of 2015, 95 mining areas have been intervened of a total of 175 and ten mining areas are with ongoing remediation works.

During the first years of the environmental concession the main areas of activity were the development of the inventory and detailed characterization studies of abandoned and degraded mining areas, followed by a risk ranking assessment, as well as the development of environmental remediation projects and its implementation tanking in to consideration the risk assessment prioritization.

The main environmental impacts in radioactive mines are acid water drainage, mostly a direct result from exploitation methods with static leaching and/or *in situ* and from ore concentrates production, from the radiations susceptible to produce air, soil and water pollution and the presence of waste dumps tailings ponds liable to produce chemical and radiological contamination by leaching phenomena, dust dispersal and radiation emissions. Common solutions in the remediation process are confinement and sealing of mining wastes and adequate mine water management, ensuring control and treatment either through active or passive systems, or both.

Actually, main strategic missions of EDM are the development of remediation works of the remaining mining sites, the development of safety actions and the development of medium and long term monitoring and maintenance actions before and after remediation in air, water, soils and sediments.

The objectives of the water monitoring plan are to obtain and maintain an integrated data base established for all the 61 radioactive mining areas of continuous records that will allow to compare water conditions before and after environmental remediation and to analyze the performance of the developed actions, also to ensure the accompaniment of active and passive treatment of mine effluents during and after post-remediation phases, and in the future during the transition phase from the active treatment to the new passive systems.

In this paper a few results examples of the water resources monitoring plan and the control of mine water effluents implemented in the radioactive mines are presented in terms of water quality and discharge flow and the water quality evolution in already rehabilitated mines regarding surface water, groundwater, active and passive treatment systems of mine water.

Methods / Monitoring Plan

Monitoring the water environment is a relevant activity in the work developed in radioactive mines, started since 2002, which includes measuring *in situ* parameters (pH, electrical conductivity, redox potential and temperature) and laboratory analysis of chemical and radiological parameters as total Uranium, U234 and U238 radionuclides, Radium-226 activity, sulphates, chlorides, manganese, calcium and sodium, these already identified in previous studies to be the best indicators of hydrochemical contamination related to the old uranium mining areas. Water resources monitoring plan covers upstream and downstream surface water samples, groundwater samples through wells, boreholes and piezometers in the surrounding mine area and in the upper and depth aquifers, together with the quality control of mine water before and after treatment. Piezometric levels and river flow are also measured at the water sampling locations.

Per year a total of around 1260 water samples are collected in 61 radioactive mines. Denser monitoring plan in terms of sampling points and monitoring frequency is dependent on the level of contamination of each mine area. Additionally continuous monitoring of *in situ* parameters (pH, electrical conductivity, redox potential, temperature, total suspended solids and discharge rate) is implemented in treated mine water before watercourse discharge.

In radioactive old mines 34 were already recovered including most of the old mines with more significant negative environmental and public health impacts and the environmental liabilities. At the end of 2015 there were ongoing efforts to conclude the remediation of another six radioactive mining areas and there were 21 remaining areas with remediation works to be carried out until 2022, when the concession contract expires. Table 1 presents the distribution scope of the monitoring plan per each mine.

***Table 1** Monitoring plan scope distribution per radioactive mines, in 2015*

Monitoring plan scope	Radioactive mines	Total
Mine water control and monitoring (ATS)	Urgeiriça, Cunha Baixa, Quinta do Bispo, Bica	4
Passive treatment systems (PTS)	Urgeiriça (*Shaft 4*), Cunha Baixa, Bica, Freixiosa, Vale de Abrutiga	5
Surrounding environmental monitoring pre- and post-remediation	Urgeiriça, Cunha Baixa, Bica, Vale D´Arca, Freixiosa, Carrasca, Vale de Abrutiga, Prado Velho, Senhora das Fontes, Other mines	34
Surrounding environmental monitoring pre-remediation	Quinta do Bispo, Castelejo, Mortórios, Other mines	21

The periodicity of the water samples collection as also the number of sampling locations is dependent on the historical quality data and environmental risk of those mines. The monitoring plan is revised before and after the remediation takes place. Table 2 presents the number of sampling places and samples collected in each mine, ranging from an more intensive plan in Urgeiriça with 264 water samples/per year to a lesser intensive plan in Vale d´Arca with 32 water samples/per year. Also 36 small mines or with less environment impacts and low risk mines are monitored, ranging from one to five sampling points with biannual periodicity.

Table 2 *Monitoring plan regarding water resources and mine water control in radioactive mines*

	A	B	C	D	E	F	G	H	I	J	K	L	M
	Number of sampling places in each radioactive mine												
	A	B	C	D	E	F	G	H	I	J	K	L	M
Mine water control	2	2	2	-	2	1	-	-	-	-	-	-	-
Passive treatment	11	10	11	16	-	-	3	-	-	-	-	6	-
Groundwater	48	2	24	2	22	4	-	14	12	12	13	-	-
Surface water	6	18	3	-	2	7	3	6	4	4	3	2	57
	Number of samples in each radioactive mine per year												
	A	B	C	D	E	F	G	H	I	J	K	L	M
Mine water control	24	24	24	-	24	12	-	-	-	-	-	-	-
Passive system	132	120	132	192	-	-	12	-	-	-	-	24	-
Groundwater	96	4	48	4	44	8	-	28	24	24	26	-	-
Surface water	12	36	6	-	4	14	12	12	8	8	6	8	114
Sub-Total	264	184	210	196	72	34	24	40	32	32	32	32	114
Total	1266 water samples/year												

A-Urgeiriça; B-Cunha Baixa; C-Bica; D-Freixiosa; E-Quinta do Bispo; F-Castelejo; G-Carrasca; H-Vale de Abrutiga; I-Mortórios; J-Senhora das Fontes; K-Prado Velho; L-Vale d´Arca; M-Other 36 mines

Continuous monitoring of mine water

In addition to monitoring and to periodic quantification of the several parameters, based upon laboratory analysis, the need was felt to adopt a system that would allow a closer interaction with the phenomena occurring as a consequence of the ongoing control actions regarding the mine water treatment. For this purpose it was considered important to adopt a continuous monitoring system that would allow to control and possible correction in real time of the actions carried at the mine water ATS.

With the objective of following up in real time the process of neutralizing the liquid effluents generated in some of the radioactive minerals mining areas, EDM conceived and developed a monitoring system that allows determining and recording continuously some of the quantities and expedite parameters that qualify the conditions in which the treatment is processed and the conditions under which the treated mine water is fed into the water courses.

The central system installed in the head office of EDM in Lisbon, was conceived and commissioned in order to receive (from the remote system), process and store all the information relative to all the facilities for monitoring physical and chemical parameters, and equally to lodge and manage command applications and technically manage the facilities and equipment located next to such systems that comprise, in each location, a set of equipment and analytical instruments for the acquisition, grouping and transmission of data. All the collected information is subject to treatment and kept on record.

Water sample collection

Regarding conservation and preparation of water samples for laboratorial analyses, they are acidified with acid nitric (65%, v/v) to $1<pH<2$ after collection for total metal analysis, major cations and uranium. For radium-226 they are previously filtered using a 0,45 micron glass fiber filter and then acidified with nitric acid (65%, v/v) to $1<pH<2$. In case of this radionuclide only the dissolved form is analyzed. This is related to historical data and with the necessity to maintain comparable water samples results. Radiological analysis are performed by spectrometry by liquid scintillation supported in ultrasensitive spectrometer *PerkinElmer Quantulus*; with variable degree of uncertainty according the activity of radioisotopes, on average 15% of the calculated value. Metals and major cations are usually determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Compliance criteria

Compliance verification of the monitoring plan water quality results is performed accordingly to the water quality standards according to their uses (Portuguese Decree-Law nº 236/98, August 1st), namely Annex XVIII *Effluents discharge limits*; Annex XXI *Environmental objectives for surface water*; Annex XVI *Standard water quality used for irrigation*. Concerning radioactive elements compliance verification uses USEPA 40 CFR *Parts 9, 141, and 142 "National Primary Drinking Water Regulations Radionuclides, Final Rule";* USEPA CFR440.32 "*Effluent limitations for mine drainage from open pit and underground uranium mines*". The used references, mainly drinking water regulations for Uranium and Radium, point out the observance of water limit of 30 µg/l and 0,185 Bq/l, respectively. In case of discharge effluents monthly average limits are 2000 µg/l for total Uranium and 0,37 Bq/L for Ra-226.

Mine Water Active treatment system

Active treatment is performed in the following mining areas: Urgeiriça, Cunha Baixa, Quinta do Bispo and Bica. The active treatment system is based on addition of sodium hydroxide to increase pH, barium chloride to precipitate the radium and decantation ponds to precipitate metals. Water control before treatment includes mensal collection of mine water or leached and after treatment sample biweekly collection of composite samples meaning two samples per month. Before discharge in the watercourse *in situ* parameters are continuously registered (pH, electrical conductivity, temperature, redox potential, total dissolved solids and discharge rate). Figure 1 shows the temporal variation of discharge rate and conductivity average values at Bica monitoring station.

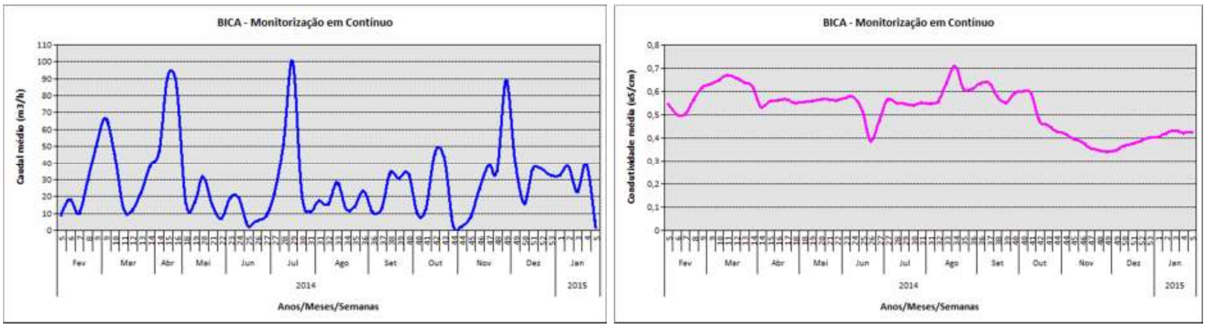

Figure 1 *Temporal variation of discharge rate and conductivity average values – continuous monitoring of treated mine water – Bica mining area*

Removal efficiency rates of active treatments were calculated based on most recent available laboratory results from chemical and radiological analysis and considering main contaminants and metals (Table 3). Removal efficiency varies from 60% to 100% for iron, 96% to 51% for manganese, 49% to 75% for Utotal and 85% to 96% for Ra-226.

Table 3 *Removal efficiency rates of active treatments systems (average values)*

Mining area/ data period	pH initial(final)	Removal efficiency	Iron (mg/L)	Manganese (mg/L)	Utotal (µg/L)	Ra-226 (Bq/L)
Urgeiriça	3,54(7,66)	RE (%)	100%	94%	74%	91%
(2012-2015)		C*i*(C*f*)	37,89 (0,12)	50,56(3,05)	522(137)	0,348(0,030)
Quinta do Bispo	3,69(7,91)	RE (%)	99%	76%	75%	96%
(2012-2015)		C*i*(C*f*)	41,1(0,31)	12,7(3,04)	2316(570)	0,494(0,021)
Bica	5,13(7,69)	RE (%)	98%	96%	49%	85%
(2014-2015)		C*i*(C*f*)	10,3(0,16)	2,49(0,09)	16,9(8,6)	0,274(0,040)
Cunha Baixa	5,00(8,15)	RE (%)	60%	51%	52%	97%
(2014-2015)		C*i*(C*f*)	0,68(0,27)	3,81(2,47)	1111(529)	1,070(0,029)

RE - Removal efficiency (%); C*i* - initial concentration; C*f* - final concentration, after active treatment

Thus, the discharge of treated mine water meets the regulatory standard limits for effluents discharge into watercourses, including the more restrictive limits the use for human consumption in case of Ra-226. Manganese concentrations are still one gram per liter superior to the legal effluent discharge limit value of 2 mg/L, nevertheless this is not considered a relevant exceedance because of the mining framework of the area and background geochemical composition of groundwater's.

An important aspect relating to mine water treatment is that normally it has gradually improved its quality over time, even before the interventions of environmental recovery they have started. This situation explains the lower concentrations of untreated mining water in case of Bica and Frexiosa. Figure 2 show for Bica mining area the temporal variation of pH and total Uranium in mining water, treated mining water and in downstream water course; after environmental remediation in 2013 concentrations of uranium in mine water decrease to <100 µg/l.

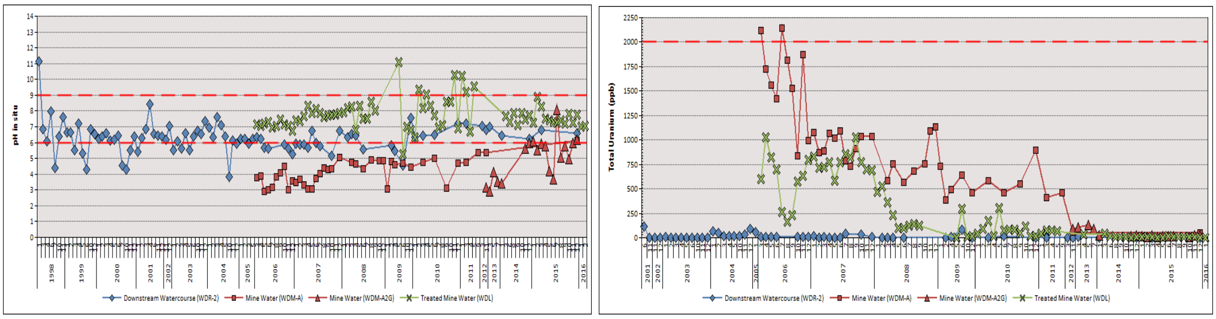

Figure 2 *Temporal variation of pH and total uranium in mine water before and after active treatment and in downstream watercourse – Bica mining area*

Mine water passive treatment systems

PTS are recently implemented in the following mining areas, with already concluded or ongoing environmental remediation actions: Urgeriça, Cunha Baixa, Bica, Freixiosa and Vale de Abrutiga.

In **Urgeiriça** a PTS was installed in 2012 in the old mine *shaft* nº 4 to decontaminate seepage water that outflows and as a result of the controlled mine flood. The monitoring results in the last three years proved that this system is efficient by promoting the decrease and significant removal of radionuclides and heavy metals concentrations to levels below regulatory standard limits (this issue is presented at IMWA2016 by Pinto *et al*. (2016) *Passive Treatment of Radioactive Mine Water in Urgeiriça Uranium Mine, Portugal*). Figure 3 presents the system removal efficiency by comparing initial and final average concentrations along treatment path (medium values in the first semester 2015). The calculated removal efficiency rates are greater than 90% for Fe, Mn, Utotal and Ra-226.

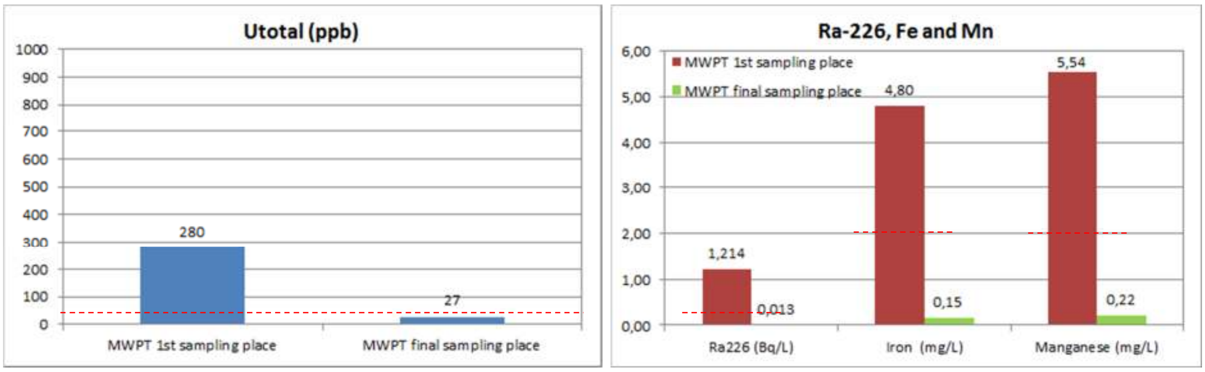

Figure 3 *Mine water PTS efficiency by comparing initial and final concentrations along treatment path (medium values in the first semester 2015) in Urgeiriça mine - Shaft4*

In **Cunha Baixa** the PTS started operating in March 2014 after environmental remediation works were completed. It is located in the old open pit where mine water from galleries outflows. It comprises various large ponds with aerobic treatment by aquatic *macrophytes*, anaerobic treatment with planted *macrophytes* and connecting sectors with limestone and barite. The primary results from monitoring data reveal the necessity of spatial increase the retention times of mine waters. So a complementary

PTS was constructed in 2016 and collection of water samples flowing by treatment tanks and ponds began in April, 2016. No results from this new passive treatment phase are yet available.

In **Bica** mining area the environmental rehabilitation took place from September 2011 to November 2013 and included the construction of a confined cell for heaps of leached material and sterile materials and the construction of ATS and also PTS. Mine waters drain preferably by a gallery located at a lower point. Mine waters and landfill leachate produced in the confined body are treated before discharge into the watercourse. The ATS is based on addition of sodium hydroxide to increase pH and barium chloride to precipitate the radium. After chemical treatment, the water is routed to a settling system comprising two ponds, which promote the sedimentation of radium and some metals. The PTS by physical-chemical and biological processes comprises a first tank that enables water circulation downwardly through a layer consisting of gravel, barite and activated carbon and a second tank with *macrophytes* in order to capture heavy metals that are still present in the water. The system has a number of *bypass* paths that allows conducting the water to different stages of treatment depending on its quality, which is continuously motorized by a monitoring station before watercourse discharge. The mine water quality has been subject to monitoring since 2002, when the underground galleries were flooded. Main elements present in mine water are uranium, radium, iron, manganese, sulfur, oxides and hydroxides of iron. Since this date it was possible to observe an improvement in the mine water quality, which is materialized by an increase of pH and conductivity decrease, which corresponds to a decrease in the acidity of water and a decrease of dissolved ions, in particular Fe and Mn. The PTS begins to work on its full mode since November 2014 and monitoring is done on a monthly basis (Figures 4 and 5). Figure 6 shows results of pH, Mn, Utotal and Ra-226 along treatment path, before watercourse discharge, with lower concentrations comparing to initial mine water concentrations.

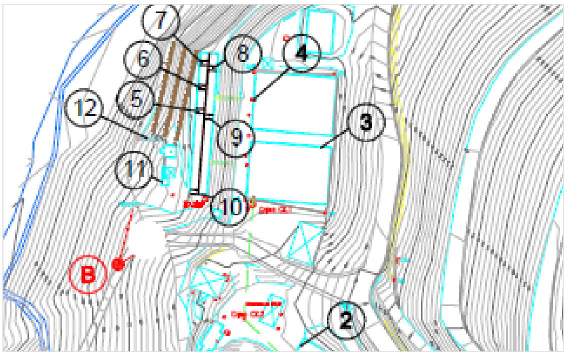

Figure 4 *Sampling points location at Bica PTS*

Figure 5 *Photo from the Bica PTS*

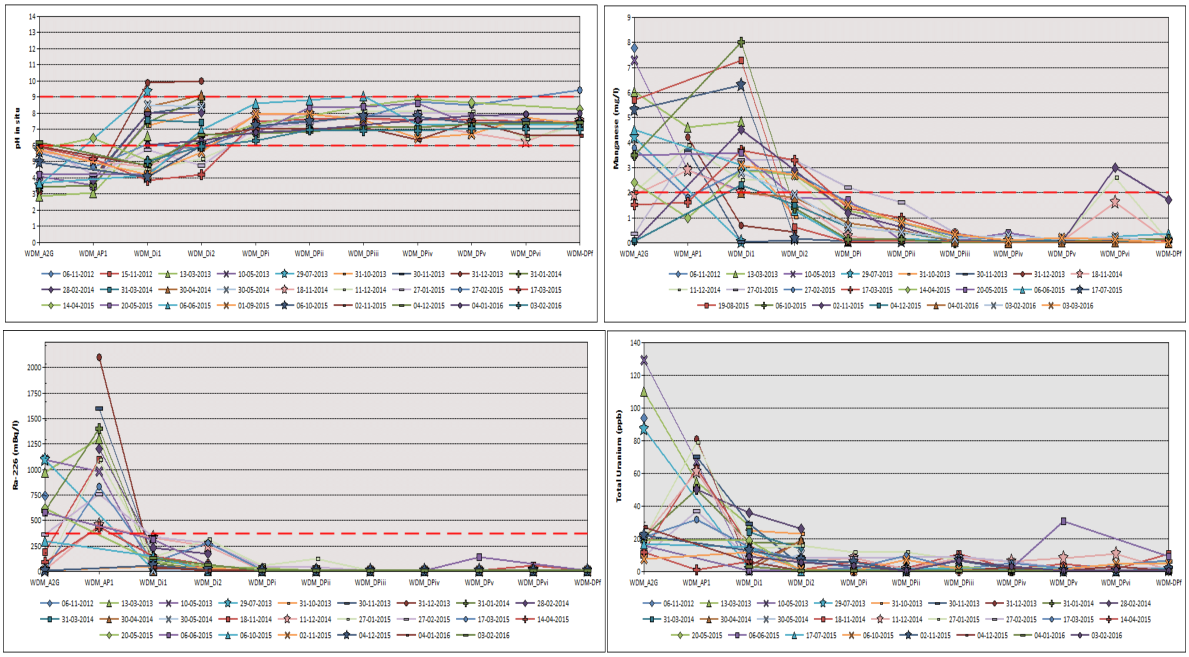

Figure 6 *Spatial and temporal variation in pH, Mn, Utotal and Ra-226 along PTS path - Bica mine*

In **Freixiosa** mining area the PTS was constructed in 2012 to treat seepage water with high concentrations of iron and some Ra-226. This seepage water naturally discharges in a small stream giving color to water due to iron oxides. The PTS is composed by a first stage with a cascade system and tanks that promote the precipitation of chemical species present in the effluent, namely the iron and manganese and a second stage with sequential seven decantation ponds, a barite tank and two *macrophytes* basins. At the end of the treatment pathway and before river discharge concentrations are low and below the regulatory values limits for Utotal, Ra-226, Fe and Mn.

In Vale de Abrutiga mining area it is under construction a new PTS to replace de old one that needed to be reformulated due to the appearance of new seepage water and also because it was clogged after six years.

Removal efficiency rates of PTS were calculated based on most recent available laboratory results from chemical and radiological analysis and considering main contaminants and metals (Table 4). The results have to be analyzed individually per mining site. In case of Urgeiriça removal efficiencies rates are >89% for the analyzed elements and compliance of regulatory limits is assured. In case of Bica and Freixiosa the same conclusion can be pointed out, but with exception for iron, initial concentrations are lower than in Urgeiriça-*Shaft4*. In case of Cunha Baixa contaminants removal did not produced the excepted results and the existing PTS was recently improved and enhanced.

Table 4 *Removal efficiency rates of passive treatments systems (average values from first semester 2015)*

Mining area	pH initial(final)	Removal efficiency	Iron (mg/L)	Manganese (mg/L)	Utotal (µg/L)	Ra-226 (Bq/L)
Urgeiriça (*Shaft4*)	6,37(7,47)	RE (%)	97%	96%	89%	99%
		C*i*(C*f*)	4,80(0,15)	5,54(0,22)	250(27)	1,214(0,013)
Bica	4,67(7,76)	RE (%)	98%	97%	89%	99%
		C*i*(C*f*)	10,48(0,22)	4,08(0,12)	45,5(4,86)	0,853(0,010)
Freixiosa	6,20(7,09)	RE (%)	90%	37%	89%	99%
		C*i*(C*f*)	6,46(0,67)	0,78(0,49)	8,97(1,00)	0,690(0,010)

RE - Removal efficiency (%); C*i* - initial concentration; C*f* - final concentration, after PTS

Groundwater and surface water monitoring

In terms of groundwater monitoring it is essential to previously determine the groundwater flow directions and to locate sampling points downstream and upstream from the mining area. Also groundwater monitoring must be performed before remediation actions are implemented, during the remediation and after works in the same locations. Special care must be taken to avoid piezometers destruction during the remediation works. An historical data base must be set up in terms of groundwater quality in a few piezometers that are correctly located and well-constructed and isolated regarding the aquifers that are monitored without interferences between them.

Figure 7 show for Cunha Baixa the spatial and temporal variation of total uranium concentrations in boreholes located downstream of the mining area. Is is important the note despite the variations the decrease in concentrations after the recovery actions. Also piezometric levels are measured in the groundwater monitoring points. Figure 8 shows historical series of depth to the water level measured in wells in the vicinity of Urgeiriça mine when the mine was flooded in 2003.

Meteorological Data

Meteorological data are gathered from two automatic stations located in Urgeriça and Cunha Baixa mining areas. Measured data are total precipitation, temperature, wind direction and velocity, solar radiation, evaporation and evapotranspiration calculation. All data is acquired in real time by telemetry. This type of data is used to calculate water balance in the study areas, especially for long term control and management of the PTS and to evaluate the discharge rates from seepage waters. Figure 9 shows an example of the data form Urgeiriça automatic meteorological station.

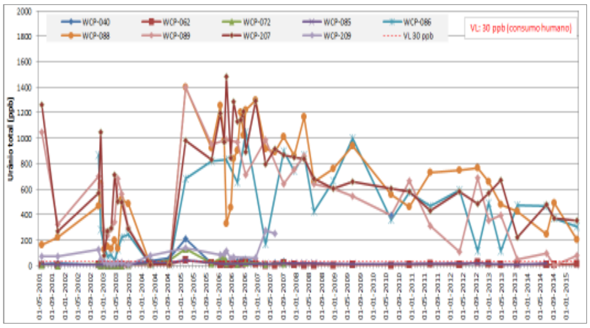

Figure 7 *Groundwater monitoring of total uranium - Cunha Baixa*

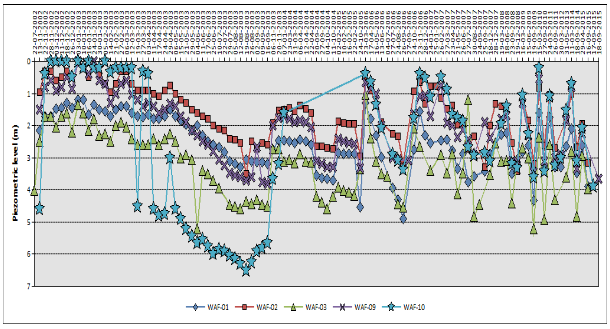

Figure 8 *Piezometric level – Urgeiriça*

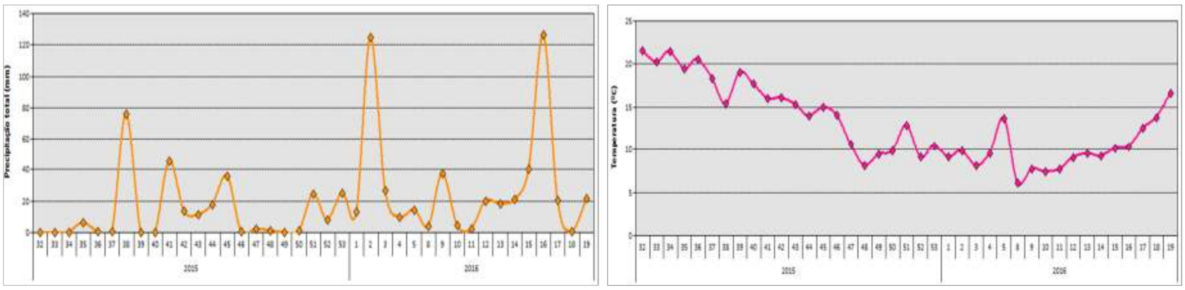

Figure 9 *Meteorological data from Urgeiriça mining area (precipitation and temperature)*

Conclusions

This paper briefly presents some details and results of the water resources monitoring plan and mine water control implemented by EDM in the 61 old radioactive mines located in Portugal, of which 34 are already recovered. Per year a total of around 1260 water samples are collected for chemical and radiological laboratory analyses and *in situ* parameters register. This activity is essential to compare the water conditions before and after the environmental remediation actions and to analyze its performance improvements in terms of downstream groundwater and surface water bodies. One of the main focus of remediation design projects is the control and treatment of mine water using passive treatment systems. Long term maintenance of these areas considerers a gradual transition from active treatment plants to passive treatment systems of mine water and leachates having as a perspective of more sustainable management post-remediation mining areas and also the decrease in contaminates concentrations. Preliminary results of removal efficiency rates of these systems are presented, although they have been recently implemented. EDM is implementing this type of systems with demonstrated success, in some cases associated with groundwater natural attenuation processes for uranium, radium-226 and other metals.

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Derivation of natural background values for groundwater in conjunction with the remediation of a sandstone-hosted uranium mine

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Abstract

The former uranium underground leach operation at Königstein, Germany is related to a sandstone-hosted uranium deposit situated in the lowermost of four Cretaceous aquifers. Since 2012 the mine is closed and partially flooded, mine water is controlled by a pump-and-treat-operation. In conjunction with the further prospects of mine water management the derivation of groundwater background values for uranium and radium deemed necessary for the deposit area. Since reliable information could not be derived from regional data sets due to the limited extension of the deposit (2.5 km x 10 km) and its geological setting in a deeper aquifer, local background values had to be generated by a combined evaluation of historical records and data from recent groundwater monitoring. Background values were calculated for the 3rd and 4th aquifer based on the determination of observation point related arithmetic means and a test for Gauss distribution. The calculated local uranium background values were found to be 20 µg/L for the 3rd aquifer and 140 µg/L for the deposit-hosting 4th aquifer. Those values differ significantly from data reported in the literature. For radium natural background values of 1,000 mBq/L for the 3rd and of 17,800 mBq/L for the 4th aquifer were derived. The information gathered will have to be thoroughly considered in the ongoing licensing procedure regarding the long-term water management strategy at the Königstein mine site.

Key words: Uranium mining, natural background values, data evaluation

Introduction

Natural background values for groundwater are one prerequisite for the evaluation of any anthropogenic groundwater impact. According to the German water legislation background values are defined as the 90 percentile of any concentration which is not or only insignificantly affected by human activity. For entire Germany groundwater background values are available for the uppermost usable aquifer in form of a hydrogeological general map called HÜK 200 (BGR 2015). Thereby, deeper aquifers and deposit related anomalies are only considered in a very generic form. Especially at ore deposits the natural groundwater composition can differ substantially from that of the surrounding area. In the case of historic mine sites natural background levels are mostly unavailable, and pre-mining water quality data are only insufficiently documented. Such values are, however, important for the definition of remediation targets, but also for the prescription of tolerable remaining emissions in the post-closure phase.

The present contribution aims to derive natural, pre-mining background values for groundwater at Wismut's uranium mine at Königstein, Germany, namely in conjunction with mine flooding, final site restoration and the prospects for long-term water management.

Site characteristics

The uranium deposit at Königstein is located in the Elbe Sandstone Mountains, some 20 km southeast of Dresden, close to the Elbe river. It is classified as typical roll-front sandstone hosted uranium deposit with an extension of about 2.5 km x 10 km (Tonndorf 2000). Workable uranium mineralization is exclusively associated to the so-called 4th aquifer of cenomanian age, the lowermost of four cretaceous Sandstone aquifers of the Pirna sediment basin (Fig. 1). The overlying turonian 3rd aquifer, however, is classified as the region's most important local drinking water reservoir.

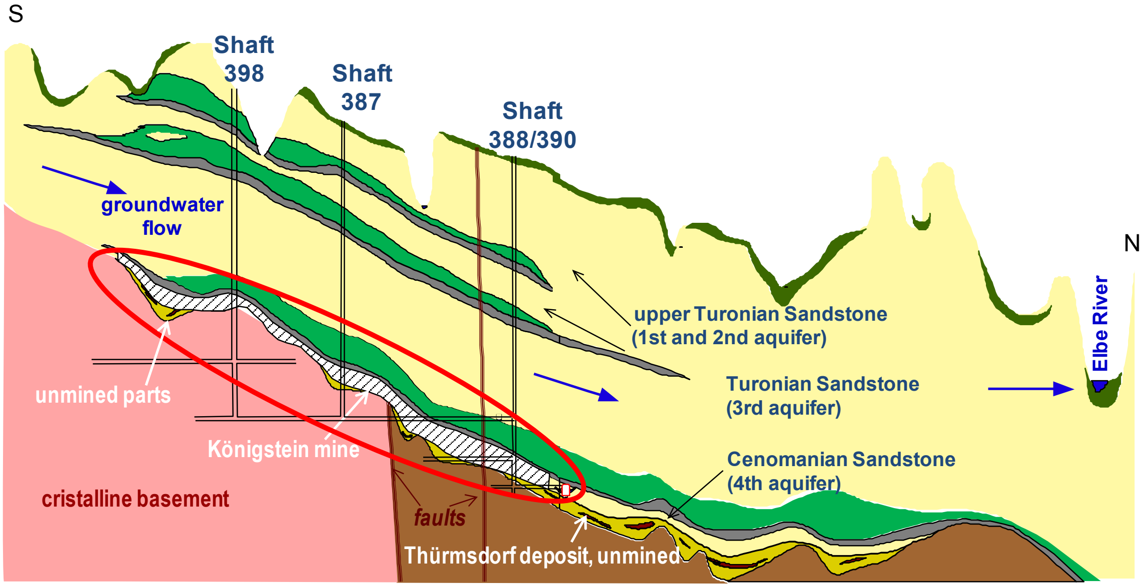

***Figure 1** Geological cross section of the Königstein mine site*

Between 1967 and 1990 the Königstein deposit was exploited by SDAG Wismut, first using conventional mining methods, from 1984 until 1990, however, exclusively applying an acid underground leach operation using sulphuric acid. Production totaled some 19,000 metric tons of uranium. In conjunction with the termination of the East German uranium industry, the Königstein mine was decommissioned in 1990. As per 1991, remaining resources were reported to be about 8,500 t U, including those at the unmined sub-deposits of Thürmsdorf and Pirna. Remediation activities were focused on the safe closure of the underground mine and preparation for flooding. Due to the substantial quantities of sulphuric acid applied during production, mine water was strongly acid and revealed very high concentrations of sulphate, heavy metals and radionuclides. In 2004, mean mine water quality was characterized as follows: pH 2.5, SO_4 2,100 mg/L, Fe 600 mg/L, Al 70 mg/L, Zn 24 mg/L, As 0.6 mg/L, U 30 mg/L, ^{226}Ra 8 Bq/L (Jenk et al. 2004).

Controlled flooding of mine section I commenced in January 2001 and was stopped in January 2013 when the preliminary target water level of ca. 139.5 m had been reached. At this water level accidental discharge of contaminated mine water into the downstream portions of the 3rd and 4th aquifers can be safely excluded. Insofar, continuation of pump-and-treat operation is imperative until further notice. In parallel, monitoring data gained and, in particular, modelling tools developed were used for design planning and permit application regarding the final flooding step, focussing on the further mine water rise to a natural water level (mine section II). Flooding of section II could enable a complete and conclusive remediation of the site but would, irrespective of any planned source-term control measures, be unavoidably linked with limited emissions of pollutants into the surrounding aquifers. With regard to the maximum permissible impact on groundwater quality, further decision making must refer to the natural, pre-mining groundwater background concentrations of key contaminants, in particular uranium and radium-226.

In this context, uranium background levels of 3.55 µg/L as derived by (BGR 2015) or 4 µg/L (Sohr & Lankau 2008) cannot be applied without critical review. BGR (2015) represents an overview map of regional scale, not suitable for decision making for a local problem. The map's digital version at Web Map Service "Background values in groundwater" presents hydrochemical data for the uppermost usable aquifer only, without any clear differentiation between the four known cretaceous aquifers. Due to its regional scale the hydrochemical anomaly of the Königstein uranium deposit has not been considered. Moreover, no uranium background level is reported for the unit 'Turonian quartz sandstone' (09M 5.2) which is by far covering the largest portion of the deposit (Fig. 2). The data presented by Sohr & Lankau (2008), on the other hand, were based on a very generic approach for the entire territory of Saxony, without taking specific geological site conditions into account. Data for radium-226 are not available at all in any of these publications.

Therefore, a systematic re-evaluation of local groundwater data was urgently needed in order to derive local background levels for the Königstein mine site. The work had to be executed in a comparable manner to BGR (2015), with separate handling of the data sets for the 3rd and 4th aquifers. Any reliable pre-mining data had to be taken into account in addition to appropriate data from recent groundwater monitoring.

Methodology

Data Base

Intensive research was invested into the compilation of the data base. In doing so, hydrogeological reports from the pre-mining period had been searched through for water quality data, in particular for uranium and radium-226. The research included documents from the first prospecting activities in the 1950ies as well as reports from the exploration phase (1961-1968).

Hydrochemical data from the first prospecting activities were derived from groundwater samples in the uppermost quaternary aquifer, the 1st and 2nd cretaceous aquifer or the palaeozoic unit only. Hence, these data proved unsuitable for the purpose of this investigation. By contrast, most data of the exploration phase of the 1960s could be definitely assigned to the 3rd or 4th aquifer, respectively. Samples with unclear assignment were excluded from further processing. The groundwater samples had been taken as bailed samples from open drill holes, observation wells or water supply wells around or within the Königstein deposit. The drill holes from the prospecting period were utilized for pumping tests used for the design of mine dewatering facilities as well as for investigations in the context of shaft sinking. Furthermore, the samples were also used for hydrochemical exploration. Most samples were analyzed by laboratories of SDAG Wismut, a minor part was processed by National Institute of Hygiene, Dresden or Water Lab, Freital. Radium-226 activity concentrations were determined by emanation. Uranium was analyzed by a luminescence method with uranium adsorption on active charcoal. The results are still reproducible and the analytical methods used are comparable to recent methodologies. From the exploration phase a total of 52 uranium and 48 radium-226 values for the 3rd aquifer could be derived. A respective data set for the 4th aquifer comprised 44 values for both uranium and radium. All data selected can be explicitly attributed as being unaffected by mining activities, due to the historic groundwater flow regime. Data from the 4th aquifer refer to the deposit hosting Pirna basin only, whereas those for the 3rd aquifer are related to both the immediate deposit area and its surroundings.

The historical data were complemented by a data sub-set derived from recent groundwater monitoring related to the period 1997-2011. This time interval refers to both the pre-flooding phase and the flooding period itself. Data from that period were subject to a multistage quality assurance program for sampling, lab investigations and data management. Individual records were only selected for further processing if any mining impact could be safely excluded. Data which showed a possible mine influence or might be impacted by waste rock seepage from a local waste rock dump had to be excluded from further evaluation. From recent groundwater monitoring a total of 1,652 uranium and 776 radium-226 values for the 3rd aquifer could be included into the data base. For the 4th aquifer, 334 uranium and 294 radium-226 values passed the quality checks. The data for the 4th aquifer refer to the Pirna basin only. Data for the 3rd aquifer are also spatially concentrated above the uranium deposit and its immediate surroundings, as a consequence of the monitoring approach which is very much focused on the Königstein mine as the main remediation object.

In conclusion, the final data base contained predominantly data from recent groundwater monitoring and only a low percentage of historical pre-mining data. However, all data used for the following assessment have not been impacted by mining activities and represent the natural background situation.

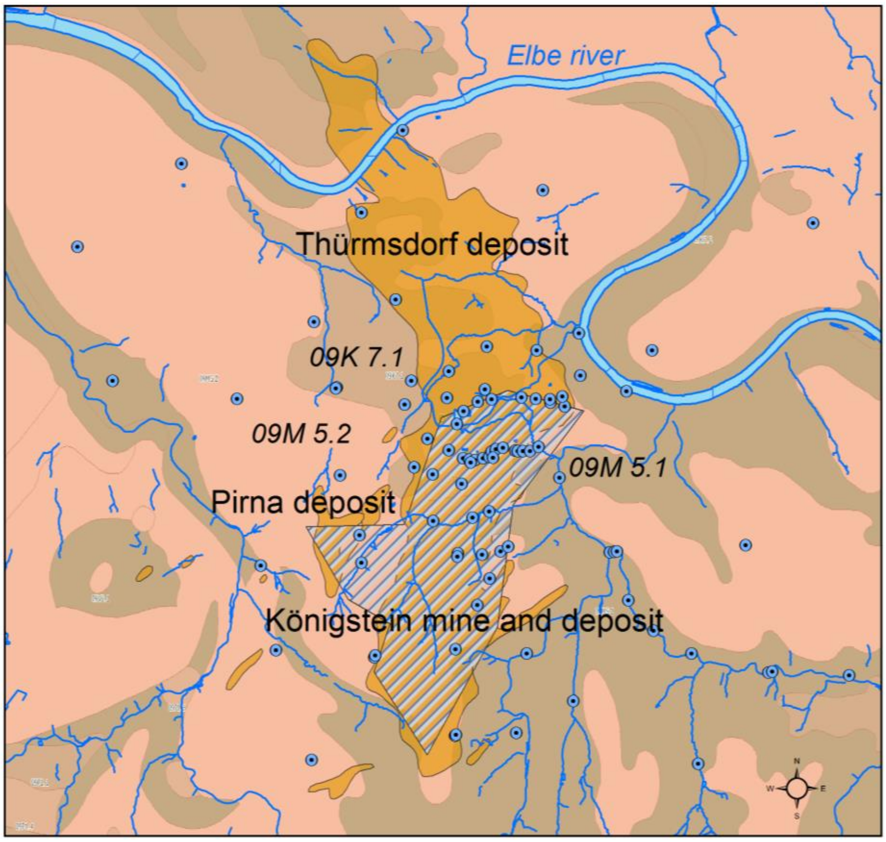

Figure 2 *Section taken from HÜK 200 (BGR 2015) with the Königstein mine (dashed area) and surrounding sub-deposits. Contour of the uranium deposit (brown) according to Tonndorf (2000). Blue spots are observation points in the 3rd aquifer. Aquifer characteristics: 09K7.1 – Quarternary gravels and sand; 09M5.1 – Turonian marlstone/sandstone, calcareous; 09M5.2 – Turonian quartz sandstone, siliceous*

Statistical Methods for the derivation of natural background levels

The methodology chosen for the derivation of natural background levels was similar to the approach of Wagner used for the HÜK 200 regional maps (BGR 2015). In so doing, the results of this study are comparable to the regional data in terms of methodology.

At a first step the entire data set was arranged by observation point. We found that some observation points had more than hundred values for uranium concentration while others had only one. If a number weighted background level would be determined, areas with most values would have the highest weighting. To receive a more uniform areal weighting arithmetic means for each observation point were calculated. Values below detection limit were equalized to the limit. The percentages of such values were as follows: uranium 4.9 % (3rd aquifer), 6.3 % (4th aquifer); radium 0.2 % (3rd aquifer), 0.0 % (4th aquifer).

For derivation of natural background levels the population must have a Gauss distribution. Hence, the population of observation point related means of uranium and radium concentrations was subsequently checked for Gauss distribution using the Shapiro-Wilk-test. Since the data populations were not Gauss distributed the observation point related means had to be logarithmized. The new check for Gauss distribution was positive for both populations (see Fig. 3). From the logarithmized data pools the 90 percentiles of uranium and radium were determined. To re-calculate real concentration values, the logarithmized parameters had to be potentiated.

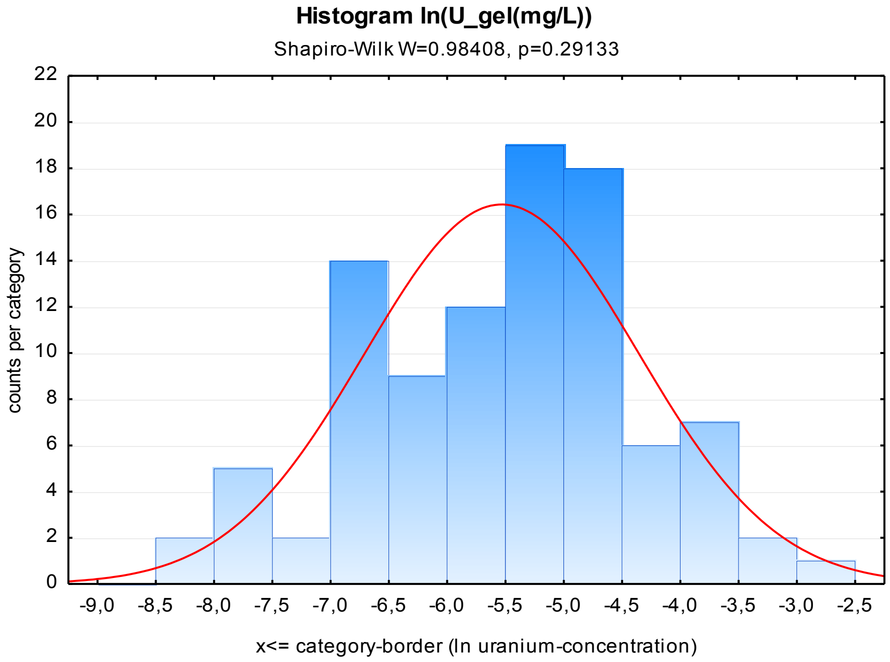

Figure 3 *Histogram of logarithmized observation point related uranium concentrations in the 3rd aquifer*

Results

The results of the calculations are listed in Table 1. The local natural background levels for uranium and radium-226 in the 3rd aquifer were found to be 20 µg/L and 1,008 mBq/L, respectively. In the 4th aquifer background levels of 140 µg/L for uranium and of 17,829 mBq/L for radium-226 were derived. Significantly higher values for the 4th aquifer are plausible since this formation is hosting the roll-front uranium mineralization which is still untouched in parts of the deposit.

Table 1 *Characteristic statistical values for uranium and radium-226 based on observation point related data*

Parameter	Number of records	Min	Max	Mean	Median	10 Percentile	90 Percentile = Background value
			3rd aquifer				
Uranium [µg/L]	97	0.3	50	4.0	4.5	1.0	20.0
Radium-226 [mBq/L]	92	19	1,887	207	215	33	1,008
			4th aquifer				
Uranium [µg/L]	61	0.2	470	9.5	11.4	0.5	140
Radium-226 [mBq/L]	60	22	72,890	1,715	1,725	126	17,829

Absolute maxima are considerably higher than those shown in Table 1, since the values represented in the table are based on observation point related arithmetic means. Absolute maxima were as follows: uranium 170 µg/L (3rd aquifer) and 810 µg/L (4th aquifer); radium 3,030 mBq/L (3rd aquifer) and 40,000 mBq/L (4th aquifer), respectively.

In summary it can be concluded that the calculated natural background level for uranium is substantially higher than the previously proposed ones of 3.55 µg/l (BGR 2015) or 4 µg/l (Sohr & Lankau 2008). The primary reason for lower values reported in the literature was the non-consideration of data from the Königstein deposit and its close surroundings, caused by the generalizing character of those studies.

Conclusions

In order to derive natural background levels close to a mine site it is essential to get concentration values of groundwater from the deposit, its un-mined parts and the surroundings. Mostly, the hydrochemistry in the surrounding aquifers is influenced by the geochemical anomaly of the deposit. Only groundwater data, which are not influenced by any mining activity must be used for the calculation. In particular, historical pre-mining data and data from the active mining period are valuable and have to be thoroughly considered. For the latter, a sound evaluation is necessary to exclude data which might have seen any mining influence.

The methodology of Wagner (BGR 2015) proved suitable for the calculation of natural background levels for the Königstein mine site. Both historical data from the pre-mining period and data from actual groundwater monitoring were available and could be included. The results revealed with regard to uranium substantially higher natural background values in comparison to regional data sets. Also, the background concentrations obtained for radium-226 prove that the pre-mining groundwater quality was characterized by significant radium activity concentrations well above recent water quality criteria.

Especially during licensing procedures in conjunction with mine remediation such hydrochemical anomalies surrounding mined deposits have to be considered. This approach is substantial for the determination of a maximum tolerable human impact during and after the remediation process and the flooding of the mine. Due to the geochemical anomaly of the deposit, natural background values and therefore the maximum tolerable impacts could be significantly higher than in the surrounding host area. With regard to the Königstein case this fact will have to be carefully acknowledged in the ongoing licensing procedure for the post-closure water management strategy.

Acknowledgements

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A Conceptual Surface Model for Rehabilitation of Nyala Mine Terrain and Improvement of the Pit Lake Safety Status

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Abstract

Historic mining of magnesite at Nyala Mine left behind terrain characterized by scattered mine waste dumps and open excavations that pose threat to public safety. These are aesthetically unpleasant. In this work conceptual terrain models that depict areas of cut and fill for rehabilitation of the landscape of the Nyala Mine and improvement of the safety status of the mine pit lake were created. The models were used to analyze the slope angles of the pit lake and rain water accumulation in the lake. Based on the study it has been established that the most stable slope angle that has potential of reducing erosion considerably was 14° (≈24.99% grade). In order to reduce the amount of sediments deposition at the pit lake floor, approximately 20m length pit slope was designed with gabion protected reverse bench of 1m width and the steepness of up to 1.72°. The 3D surface models that depicts areas to be graded to create flat topography around the pit lake and the entire mine was developed by superimposing the design terrain models on the models of the present topography of the mine. The cut and fill volumes were accurately calculated using the extended trapezoidal, extended Simpson's, and Simpson's 3/8 rules. The calculated total cut and fill volumes in the reshaping of the whole Nyala Mine terrain were 2269377m^3 and 2095037m^3 respectively. The surface models provided the technical basis for effective analysis of the mine terrain and making sound decisions on the areas to be cut and/or fill when creating the final post-mining topography. The work done in this research has provided the essential information necessary for estimation of cost of earthwork required for the improvement of the aesthetic beauty of the landscape of the abandoned Nyala Mine and safety status of the pit lake.

Key words: Pit Lake, Abandoned Mines, 3DTerrain Modeling, Mine Rehabilitation, Nyala Mine

Introduction

Surface mining if not conducted in a more responsible manner can lead to extensive land disturbance and barren landscape (Lin *et al.,* 2005). Historic magnesite mining at Nyala Mine left behind extremely altered landscape characterized by scattered heaps of mine waste (*i.e.* spoils and tailings dumps) and excavations (Mhlongo, 2012). Rehabilitation of Nyala Mine will require that some of the dangerous excavations be filled with different mine waste. Moreover, the improvement of the safety status of the existing pit lake is also to be considered. According to Lund and Blanchette (2014), the development of pit lakes is the goal of mine closure that focuses on the use of excavations left by surface mining to create new pit lakes as a way of trying to avoid restoring and rehabilitating the landscape. Such pit lakes can have several uses which include recreational and tourism, wild-life conversation, aquaculture, irrigation, livestock and industrial water sources and chemical extraction (Deupe and Lymbery, 2005).

The Nyala Mine is located at 22°31'20″S and 30°37'10″E along the far north eastern corner of the Limpopo province of South Africa. It is situated 50km north east of Thohoyandou Town and 31km south east of Musina Town. Figure 1 show the location of Nyala Mine within the Limpopo province and the areas of Nyala Mine affected by historic magnesite mining. The magnesite deposit at the mine is hosted by metamorphosed shales and sandstones of the Ecca Group and weathered olivine dolerite (Strydom, 1998). According to the Mineral Potential and Mining Development in the Black Homelands of South Africa (1977) and Strydom (1998), in 1965 the Nyala Mine orebody (≈270 000 tonnes to the depth of 21m) was estimated to be consisting of 12% magnesite. The mine was abandoned in 1975 without any rehabilitation of the mined out land. Historic mining of magnesite at affected an area of about 212ha. Such an extensive area of the mine landscape hosts several large mine waste deposits (*i.e.* both tailings and spoil dumps) and open excavations. These excavations contain water of volume varying from one season to another. Generally, the water in the pit lakes is used by domestic animals from nearby communities as drinking water. However, the water in the major pit lake of the Nyala Mine is also used by the community of Zwigodini Village for different domestic purposes that include washing of cloths, swimming (recreational purposes) and fishing (Mhlongo and Amponsah-Dacosta, 2014). The major safety hazards of this lake are unstable walls and fine sediments accumulation in the pit lake. This study used conceptual terrain models to create a physically stable post-mining landscape that is geomorphological, hydrologically and visually compatible with the surroundings of the mine. The concept of creating a digital elevation model (DEM) or terrain model is new, however; the use of DEM in the evaluation of rehabilitation strategies for areas disturbed by mining is fast growing (Al-Ruzouq and Al-Rawashdeh, 2014). In the case of Nyala Mine, models were used to identify the areas of the mine to be graded in order to improve the safety status of the Pit Lake and aesthetic appearance of the mine landscape around the pit lake. In order to limit the effects of over extrapolation of data, the abandoned Nyala Mine terrain was modeled in five segments denoted as Area-1 to 5 as shown in Figure 1.

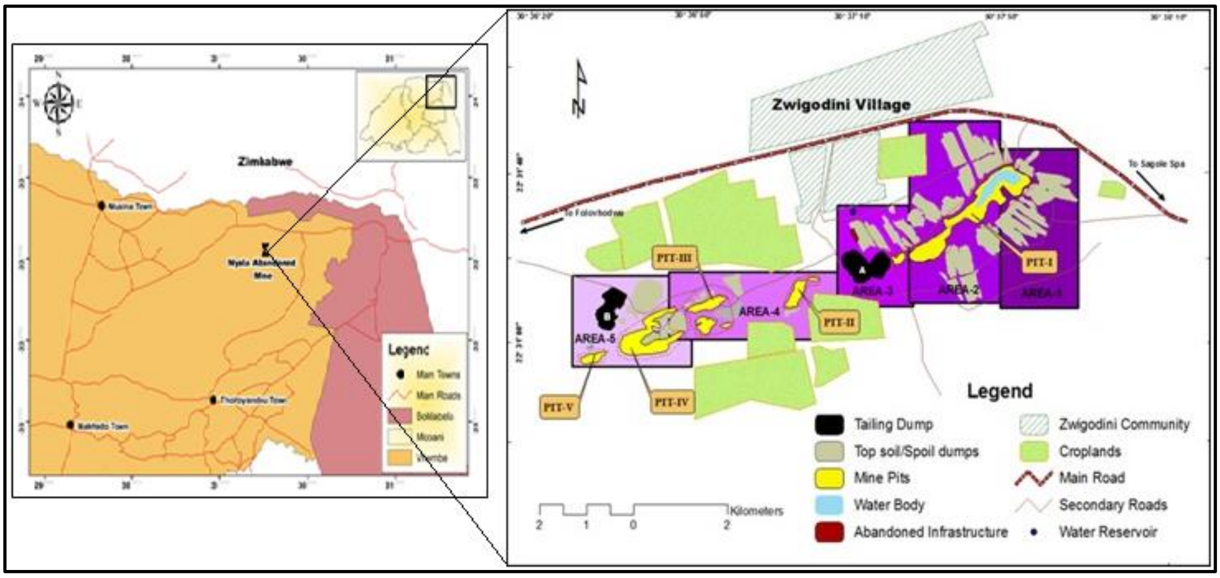

Figure 1 *The location of the abandoned Nyala Mine and the delineated areas for simulation of the mine terrain rehabilitation*

Methods

The height data needed for the development of the terrain models was collected using the Real Time Kinetics Global Positioning Systems (Hi-Target V9 GNSS RTK Surveying system). The setup of the system began with placing the base of the GPS at a known point satuated at about 50m away from features such as tall trees and high voltage power lines that are likely to affect the communication and accuracy of the system. The base point was localized to the nearest trig station (*i.e.* Lwandze trig) with the XYZ coordinates of -22.55431S; 30.6949E and 633.6m respectively. The receiver of the GPS base was set at elevation musk of 15° and placed on the fixed height tripod. On the other hand, the rover receiver was mounted on the 2m fixed height rod and set at elevation musk of 10º to enhance accuracy of the survey points. For data projection purposes, both the base and rover heights were set-up under the World Geodetic System 1984 (WGS-84) ellipsoid. The survey points were marked at every 1 to 2m vertical interval along the traverse lines designed to be 15m apart. About 15550 points were stored in the mobile PC and downloaded for processing and development of the models of the Nyala Mine terrain using the surfer®11 software.

Prior to actual development of the terrain models, the raw height data was processed to remove noise caused by poor communication between the base and rover receivers during the data acquisition process. This was also done to make the data compatible with the software. The kriging interpolation technique inbuilt within the software was used in producing visual maps from the data acquired from field survey. The average height of the natural topography around the mine was used to make adjustments to the data for the purpose of creating engineering terrain models which were then superimposed on the terrain models shown on the present topography of the mine. This allowed that the cut-and-fill areas and volumes are accurately determined. The volumes were computed as average of volumes calculated using the extended trapezoidal, extended Simpson's, and Simpson's 3/8 rules expressed mathematically as shown in equation (i), (ii) and (iii) and inbuilt in the software. In these equations, Δx represents the grid column spacing, Δy represents the grid row spacing, and $G_{i,j}$ represents the grid node value in row i and column j. The accuracy of the determined volume was judged by the difference in the volume computed using the three methods. Where the three estimated volumes were reasonable close to each other, the overall volume estimate was considered accurate. In cases where a huge discrepancy between the estimated volumes was identified, the computed volume was considered not reliable thus the computation was repeated.

Extended trapezoidal:

$$\mathrm{A_i} = \frac{\Delta \mathrm{x}}{2}[\mathrm{G_{i,1}} + 2\mathrm{G_{i,2}} + 2\mathrm{G_{i,3}} \ldots + 2\mathrm{G_{i,nCol-1}} + \mathrm{G_{i,nCol}}]$$

$$\mathrm{Volume} \approx \frac{\Delta \mathrm{y}}{2}[\mathrm{A_1} + 2\mathrm{A_2} + 2\mathrm{A_3} + \cdots + 2\mathrm{A_{nCol-1}} + \mathrm{A_{nCol}}] \qquad \text{(i)}$$

Where: the pattern of coefficients is: 1, 2, 2, 2,…, 2, 2, 1

Extended Simpson's:

$$\mathrm{A_i} = \frac{3\Delta \mathrm{x}}{3}[\mathrm{G_{i,1}} + 4\mathrm{G_{i,2}} + 2\mathrm{G_{i,3}} + 4\mathrm{G_{1,4}} + \cdots + 2\mathrm{G_{i,nCol-1}} + \mathrm{G_{i,nCol}}]$$

$$\mathrm{Volume} \approx \frac{\Delta \mathrm{y}}{3}[\mathrm{A_1} + 4\mathrm{A_2} + 2\mathrm{A_3} + 4\mathrm{A_3} \ldots + 2\mathrm{A_{nCol-1}} + \mathrm{A_{nCol}}] \qquad \text{(ii)}$$

Where: the pattern of coefficients is: 1, 4, 2, 4, 2, 4, 2,…, 4, 2, 1

Simpson's 3/8 rule:

$$\mathrm{A_i} = \frac{3\Delta \mathrm{x}}{8}[\mathrm{G_{i,1}} + 3\mathrm{G_{i,2}} + 3\mathrm{G_{i,3}} + 2\mathrm{G_{1,4}} + \cdots + 2\mathrm{G_{i,nCol-1}} + \mathrm{G_{i,nCol}}]$$

$$\mathrm{Volume} \approx \frac{3\Delta \mathrm{y}}{8}[\mathrm{A_1} + 3\mathrm{A_2} + 3\mathrm{A_3} + 3\mathrm{A_3} + \cdots + 2\mathrm{A_{nCol-1}} + \mathrm{A_{nCol}}] \qquad \text{(iii)}$$

Where: the pattern of coefficients is 1, 3, 3, 2, 3, 3, 2,…, 3, 3, 2, 1

The terrain slope map of the pit lake and the surroundings was developed and used to analyze the average steepness of the slopes of the lake. In this case, the pit lake slope map was developed to provide the necessary understanding of the general steepness of the pit lake slopes. In addition, the pit-lake catchment area and vector map were developed and used to identify the areas contributing to the accumulation of runoff and sediments deposition in the pit lake. This was used as a way of locating areas that contribute significantly in the deposition of safety hazardous fine sediments in the pit lake bottom.

Results

The modeled terrain of the mine covered the whole 212ha area of the mine and depicted the two large tailings dumps, five well defined surface excavations and several heaps of spoil dumps. Area 1 and 2 covered the area that is mainly occupied by the only pit lake at the mine site. Several piles of spoil material dumped around the pit lake have changed the previously flat and enviable terrain to a rugged landscape (see Fig2*a* and *b*). The area covered by the lake was estimated to be 11ha and its deepest part was estimated to be approximately 22m. According to the pit lake slope model shown in Fig2*c*, most of the pit lake slopes are generally physically stable with the majority of slope angle ranging from 15° to 20°. However, it is necessary that these slopes be graded to relatively flat angles in order to reduce the amount of fine materials that are deposited at the bottom of the pit lake due to various processes including erosion. The vector map shown in Fig2*d* illustrates that the pit lake accumulate much of surface run-off from the areas that are highly disturbed by mining and occupied by highly erodible magnesite tailing material. According to Sibanda *et al.* (2013), the mine tailings at Nyala Mine comprise of 43% gravel, 53% fine sand and 5% fines (*i.e.* silt and clay). In generally, soils that are dominated by fine sands and silt and lack organic matter are the most erodible soils (O'Geen *et al.*, 2006). The erosive property of fine materials coupled with the high slope angles directly influence surface runoff from the slopes of the tailings dump to the lowest part of the pit lake. This therefore explains the presence of fine sediments that deposited at the floor of the lake. It needs to be noted also that other factors such as slope length and unprotected nature of the slopes of the tailings dumps have influence on the soil erosion problem.

According to Qing-quan *et al.* (2001), the amount of surface runoff decreases with the decreasing slope angle while the flow velocity increase and decrease before and after the maximum slope of 40.9° respectively. The fact that the walls of the pit lake are made up of rippable metamorphosed shales and sandstones, based on the Maryland Standards and Specifications for soil Erosion and Sediment Control (2011), the grading of these slopes to angle of 14° (*i.e.* 4:1) was found appropriate. This slope angle will assist in curbing excessive erosion of the pit lake walls and subsequently control the amount of sediments deposited in the lake. It is expected that this slope design stretch the slope length to about 20m (maximum length) thus it necessary that a 1m reverse bench be introduced to divide the slope length into two equal halves. This slope design is expected to further reduce the runoff velocity or speed and indirectly reduce the rate of erosion of the slopes of the pit lake. This slope design approach is supported by Gilley *et al.*(1978) and Qing-quan *et al.* (2001) that in general, the runoff rate and velocity, sediments concentration, and rate of soil loss increase with an increasing slope length. This concept of introducing reverse bench in the design will channel runoff water to more stable (*i.e.* gabion protected) inflow channels to be placed along the shallow parts of the pit lake. In view of this, the reverse bench is to be constructed with a maximum slope angle of 1.7° to allow easy flow of runoff water to the protected inflow channel.

In order to further limit or eliminate the continuous supply of fine sediments to the pit lake, it is suggested that a flat topography be created around the lake. This will involve grading of about 737068m³ material over an area of about 23ha to fill a 610264m³ void that covers approximately 5ha area. The areas of cut and fill in the reshaping of the terrain around the pit lake are shown in Fig3.

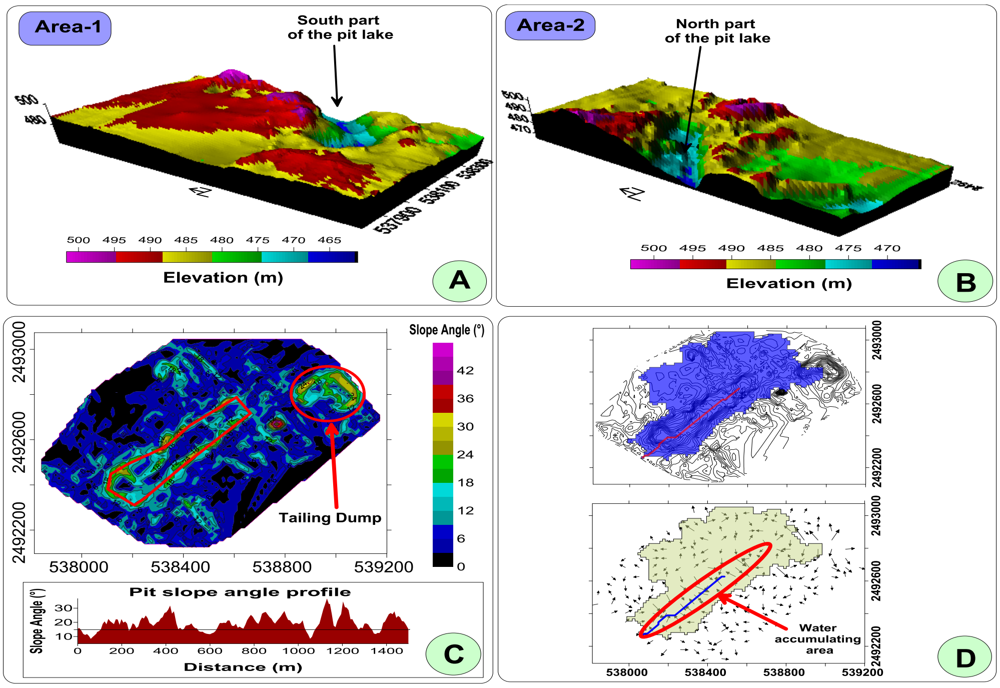

Figure 3 *(A) and (B) are the models showing the current terrain in Area-1 and 2, (C) is the pit lake slope analysis model, and (D) is an illustration of surface run-off accumulation flow to the pit lake.*

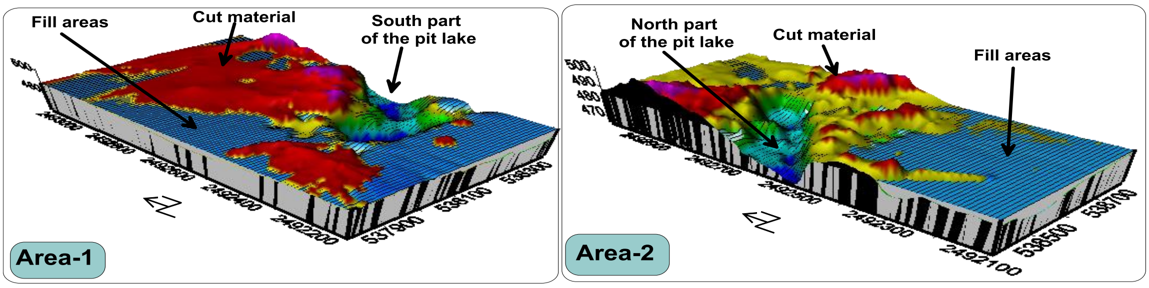

***Figure 3** A simulation of cut and fill areas in Area-1 and 2 occupied by the pit lake.*

The other three modeled areas (*i.e.* Area 3, 4 and 5) cover the portion of the mine where four pits, two tailings dumps (denoted as Tailing-A and B) and several heaps of spoil material are located. Tailing-A shown in Fig4a was estimated to be about 279448m^3 and covers an area of about 10ha. The volume and area covered by Tailing-B in Fig4*b* were estimated to be 534115m^3 and11ha respectively. Both tailing dumps at Nyala Mine had deep erosion gullies which are evidence of effect of excessive water erosion. The deposition of these alkaline and sandy magnesite tailings in the surrounding farmlands, orchards and woodlands by erosive forces of water and wind is likely to have serious effect on the soil structure and quality in these areas (Sibanda *et al.,* 2013). This is due to the fact that they are characterized by high pH value (mean = 9. 2) that has potential to affect the availability of plant nutrients such as phosphorus, iron and zinc thus reducing the productivity of the agricultural fields around the mine (Mhlongo, 2012; Quibing *et al.,* 2006).

In view of the problems posed by the two tailings dumps, it was proposed that the two tailings dumps be removed. This will involve using some of the tailings material to fill the shallow part of the pit lake and the other abandoned mine excavations. The filling of the shallow part of the pit lake (Pit-I) with the Tailing-A material will reduce the volume of the dump by 78% and that of the pit lake by 16%. The remaining 22% of the material will be used to fill the relatively small Pit-II (shown in Fig4*c*) located in less than 100m distance from the dump. Some of the spoils and Tailing-B material will be used to fill Pit-III, IV and V (shown in Fig4*c*) characterized by high (18m maximum) and unstable walls with the pit slope angle that in some areas was found to be greater than 90°. Filling of these pits will ensure that public safety hazards presented by the walls of the pit lake and exacerbated by the fact that they are open to the public and animals that graze around the abandoned minesite are removed. The proposed areas of cut and fill in the reshaping of this part of the mine are shown in Fig5.

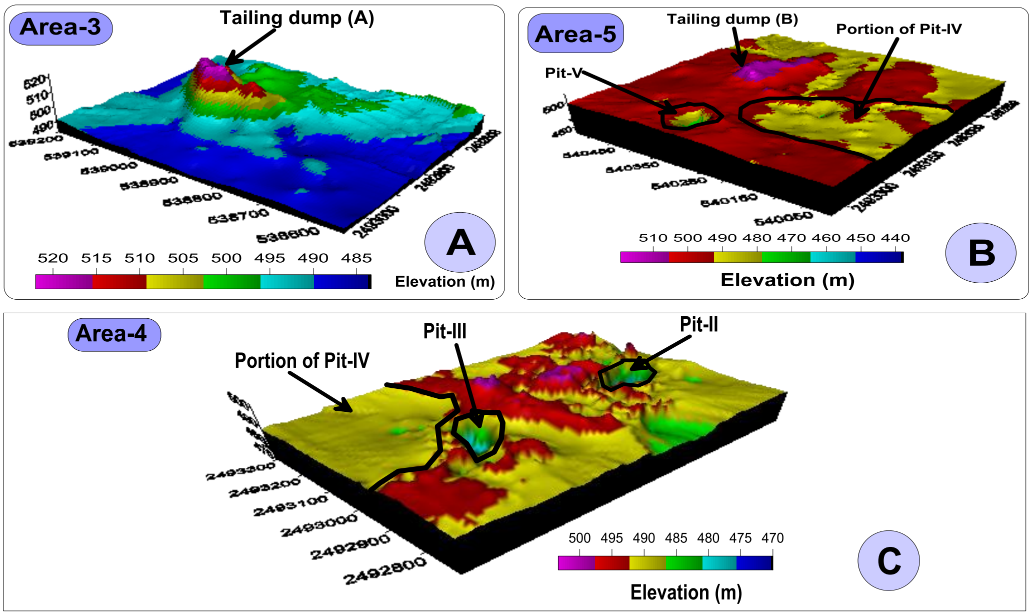

***Figure 4** Models showing the present terrain of Area-3, 4 and 5 of the abandoned Nyala Mine*

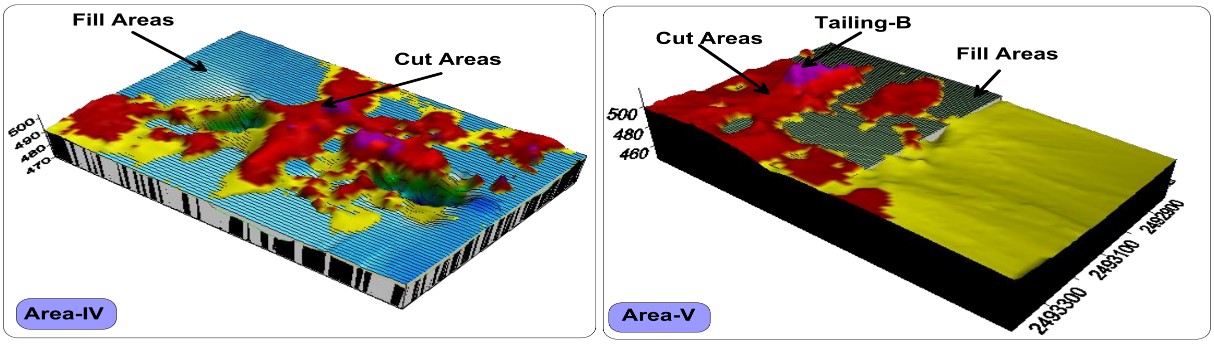

Figure 5 *A simulation of cut and fill areas in Area-4 and 5 of the mine*

Conclusions

The mapping of the slopes of the pit lake showed that the majority of the slopes were generally stable with the maximum angle of 48°. However, in order to minimize the effect of erosion on the slopes of the pit lake and reduce deposition of fine sediments in the pit lake floor where they present safety hazards to the animals who drink the water in the lake, it was deemed expedient that the slopes of the pit lake are reduced to 14° and be designed with a reverse bench. Such a design of the pit lake walls will play a crucial role in reducing the velocity of water runoff and ensure that the runoff inflow into the lake is controlled.

Based on calculations regarding cut and fill volumes and areas from the developed surface models for the mine, it was established that the reshaping of the Nyala Mine terrain will require a total of 2269377m^3 materials to be graded to fill a void of about 2095037m^3. It was also established that the grading of the Nyala Mine terrain with the purpose of creating a flat topography that blends well with the surroundings will leave a footprint of about 72ha which will require ripping of the soil to allow easy growth of vegetation.

In general, the surface models for the rehabilitation of the Nyala Mine terrain provided the technical base for the analysis of the mine terrain and determination of excavation and filling of areas and volumes. This provided the most needed information for estimation of the amount of earthwork required in the improvement of the aesthetic beauty of the landscape of the abandoned Nyala Mine and safety of its featured pit lake.

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The Kizel Coal Basin (the Western Urals, Russia): Environmental problems and Solutions

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Abstract

Coal mining usually causes severe anthropogenic changes by which the ground- or surface water might be significantly polluted. One of the main problem of coal mining industry is acid mine water containing high concentration of metals that have harmful consequences for aquatic life and the environment. Mine closure is not the solution of the environmental problem – waters discharging from abandoned coal mines, as well as those draining mine wastes containing pyrite are acid and highly enriched with soluble iron, sulfate, and metals.

Mining in the Kizel coal basin (the Western Urals, Russia) had been carried out for more than 200 years. Over 35 million m^3 of waste rocks had been accumulated in more than 70 tailingspiles. Since the 1980s the authors have been working on the problem of acid mine water and tailingspiles' drainage water neutralization and purification. This paper presents authors' experience in geochemical barriers using for environmental protection in the Kizel coal basin.

Laboratory and field-scale experiments have demonstrated the possibility to neutralize both discharging acid mine water and tailingspiles' drainage water using geochemical barriers filled with industrial wastes as reagents. Application of geochemical barriers demands considerably less costs and allows to avoid building of expensive cleaning constructions and to realize another measures of environment protection.

Key words: Acid mine water, tailingspile, drainage water, geochemical barriers

Introduction

Coal-bearing formations occupy 15% in the earth continental crust and have a complex structure – limestones, argillites, siltstones, sandstones, and other rocks occur between the coal beds. Almost 80 elements have been found in coal, 12 of which have 10–1,000 times higher concentration in coal than in background strata. Total sulfur content can be as high in coal as 20 weight percent. Average sulfur content in the Russian European coal basins is 3.8%. Sulfur occurs in forms of sulfides and sulfates, as well as of organic and elementary ones (Kler 1988).

These geochemical features can significantly influence the environment in coal mining areas: the oxidation of sulfur and iron containing minerals releases iron-rich, acidic solutions (acid mine water) which may contain elevated level of metals (Nordstrom & Alpers 1999a, Winland *et al.* 1991). Overall rates of sulfide oxidation and metal release in areas affected by mining are estimated to be orders of magnitude faster than natural rates (Nordstrom & Alpers 1999b). Sulfide-bearing mine tailings are known for their potential to form acid drainage water upon weathering (Dold & Fontboté 2002, Graupner *et al.* 2007, McGregor & Blowes 2002, Moncur *et al.* 2005, Sergeev *et al.* 1996). When acid mine and drainage waters enter natural waterways, changes in pH and the formation of ochreous precipitates can have devastating effects on aquatic ecosystems (Furrer *et al.* 2002, Gray 1998, Nordstrom *et al.* 2000, Sivakumar *et al.* 1994, Tiwary & Dhar 1994, Younger 1997,). So, coal mining can result in a significant deterioration of the environment.

Investigations in the UK, Japan, India, the USA and other coal basins revealed that the closure of mines could result to uncontrolled discharge of contaminated water to the surface (Burrel & Whitworth 2000, Donovan *et al.* 2003, Maksimovich & Gorbunova 1990, Okamoto *et al.* 2006, Siddharth *et al.* 2002, Younger 1993). Mine drainage may persist for decades, making the necessity to protect and improve the environment in coal mining regions is extremely important.

This paper presents authors' practical experience in geochemical barriers using for environmental protection in the Kizel coal basin (the Western Urals, Russia).

Regional settings and mining-associated problems

The Kizel coal basin (the Western Urals, Russia) occupies area of 200 km^2 and is located within West Urals folding zone adjacent to the pre-Ural boundary deflection. Folds have meridional and close to meridional orientation, are elongated for tens of kilometers, and are complicated by numerous disjunctive dislocations. Rocks of Palaeozoic (Middle Devonian – Late Permian) age are developed in the area. Rocks are represented by sandstones, mudstones, siltstones, shales, limestones, dolomites, marls, coals, and others and have a thickness column of 3–4 km. Carbonate rocks are intensely karsted, especially in the upper part of geologic column. Quaternary deposits are mainly represented by sands, loams, and clays and have often a high content of gravel and pebbles. Coal of the basin exhibits elevated content of sulfur (mainly as pyrite) – 5.8% (Kler 1988).

Mining in the Kizel coal basin had been carried out for more than 200 years. Over 35 million m^3 of waste rocks had been accumulated in more than 70 tailingspiles. Mine water was pumped out to the surface without any cleaning or pre-treatment during mining. Mines were closured in the 1990s, but the closure haven't solved the environmental problems.

The cessation of mining has led to gradual restoration of watertable level to it natural value, so 12 adits of abandoned mines have started to discharge acid mine water to the surface. Chemical interaction between acid mine water and surrounding rocks and grounds has resulted in high concentrations of iron, aluminum, and metals in discharged water flowing into 19 rivers, 15 of which were water sources for human use in the area. Several tones of sediments which consisted of amorphous iron and aluminum hydroxides and have a high content of Mn, Cu, Ni, Zn, Pb, and other metals have been accumulated in rivers' bottom. These sediments were washed downstream to the Kama and Chusovaya rivers, where they become a secondary source of water pollution.

Tailingspiles of the Kizel coal basin are composed of fragments of argillite, sandstone, and limestone with inclusions of coal. The content of pyrite in tailingspiles reaches 4%. Processes of physical weathering, oxidation, hydrolysis, hydration, and metasomatism occur within tailingspiles. The oxidation of pyrite releases sulfur acid and is accompanied with heat production. So, self-ignition of tailingspiles, roasting and melting of their rocks, and fumarole processes within tailingspiles were detected. Rainfalls drained tailingspiles are enriched in soluble compounds (sulfate ions – up to 30 g L^{-1}, iron – up to 8 g L^{-1}) and have a high salinity (up to 50 g L^{-1}). Infiltration of these waters into underlying grounds changes physical-mechanical and filtration properties of grounds and pollutes groundwater.

Solutions of the Problems

Since the 1980s the authors have been working on the problem of acid mine water and tailingspiles' drainage water neutralization and purification using geochemical barriers filled with industrial wastes as a reagents.

1. Acid mine water neutralization

At the end of the 1980s alkaline waste products from the Bereznikovsky Soda Factory (Russian Federation), so-called ''white seas'', were tested as potential reagents for acid mine water neutralization and appropriate technique was developed (Maksimovich *et al.* 2007, Maksimovich 2010, Maksimovich & Khayrulina 2014).

Alkaline waste products consist of calcite mainly (70–80% $CaCO_3$) and have pH 9–12. The quantity of waste suitable for use as a reagent exceeds 1 million m^3. Soda waste recycling and acid mine water purification are based on neutralization and precipitation reactions. Theoretically the main reagent, that is calcium carbonate, reacts with acid mine water as follows:

$$H^+(aq) + CaCO_3(s) = HCO_3^-(aq) + Ca^{2+}(aq) \quad (1)$$

$$SO_4^{2-}(aq) + Ca^{2+}(aq) = CaSO_4(s) \quad (2)$$

$$H^+(aq) + CaCO_3(s) + SO_4^{2-}(aq) = HCO_3^-(aq) + CaSO_4(s) \quad (3)$$

$$CO_3^{2-}(aq) + Fe^{2+}(aq) = FeCO_3(s). \quad (4)$$

Hydrogen ions are consumed, and sulfate ions form a precipitate of less soluble calcium sulfate as a result of reactions. Rise of pH value enables precipitation of iron and aluminum hydroxides.

We applied the developed technique to neutralize discharging acid water of the “40th Anniversary of the October” Mine. Samples of mine water were taken in summer when water was characterized by maximal values of salinity and concentration of pollutants. Laboratory studies involved a series of experiments to determine optimum amount of alkaline waste products and required period of time to neutralize mine water. Chemical composition of water samples before neutralization and after it was also examined. It was found that vigorous stirring accelerated neutralization.

Then the field-scale experiment was conducted (fig. 1). The part of discharging mine water was pumped in simple construction where it was mixed with paste-shaped alkaline waste products of the Bereznikovsky Soda Factory to form more fluid reagent. Appointed amounts of resulting pulp were periodically added directly in the stream of discharging mine water, where chemical reactions began to proceed. This reacting mix flowed to the pond of preliminary sedimentation, where chemicals formed sediment. The final cleaning of water from precipitate occured in the second pond, where water was cleaned up to standards and then entered into river. Chemical content of the mine water before the experiment and after it is presented (tabs. 1–2).

One of the main problem of mine water neutralization process is the disposal of formed sediment. Laboratory experiments to determine the phytotoxicity of sediment were conducted. It was established that a mixture of sediment and rocks of mine tailingspiles provided the most favourable conditions for growth of perennial grasses (timothy, fescue, couch grass, and alfalfa), especially with fertilizers addition. So, the sediment obtained in the course of neutralization process was suitable for remediation of mine tailingspiles.

The field-scale experiment has demonstrated the possibility of alkaline geochemical barrier using to neutralize acid mine water and to decrease the content of chemical elements in it. Moreover, this technique helped to solve the urgent problem of alkaline waste products disposal. Calculations have shown that the cost of 1 m^3 of acid mine water neutralization was about 0.03 $.

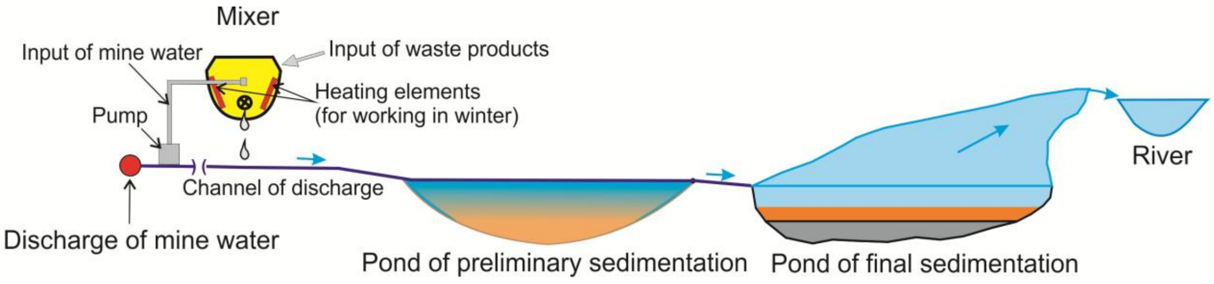

Figure 1 *The schema of the field-scale experiment to neutralize discharged acid mine water*

Table 1 *Change of chemical content of the "40th Anniversary of the October" Mine water during the experiment (mg L^{-1})*

Sample no.	Sampling conditions	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^++K^+	Fe^{3+}	Al^{3+}	Salinity	pH
1	Before neutralization	b.d.l.	329.49	5.67	24.05	12.15	9.89	30.72	10.79	426.38	2.81
2	Before neutralization	b.d.l.	355.43	21.27	36.07	12.15	32.72	40.00	14.39	516.35	2.85
3	Before neutralization	b.d.l.	320.37	14.18	24.05	12.15	4.14	32.11	14.03	427.55	2.89
4	After neutralization	73.22	348.22	5.67	140.28	14.58	7.82	0.23	b.d.l.	594.12	6.70
5	After neutralization	73.22	376.56	9.93	156.31	14.58	6.90	b.d.l.	b.d.l.	639.67	7.32
6	After neutralization	73.22	357.83	12.76	150.30	14.58	6.90	b.d.l.	b.d.l.	617.70	7.26

b.d.l. – below detection limit

Table 2 *Change of metals content in the "40th Anniversary of the October" Mine water during the experiment (ppm)*

Sample no.	Sampling conditions	Ni	Co	Cr	Mn	V	Ti	Sc	Cu	Zn	Pb	Mo	Be	Ga	Y	Yb	Nb
1	Before neutralization	0.25	0.17	0.025	8.28	0.008	0.12	0.008	0.075	0.75	0.005	0.0015	0.012	0.0017	0.17	0.017	0.008
2	After neutralization	0.05	0.03	b.d.l.	3.60	b.d.l.	b.d.l.	b.d.l.	0.007	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.

b.d.l. – below detection limit

2. Neutralization of groundwater polluted with tailingspiles' drainage water

An alkaline geochemical barrier was used to clean groundwater polluted with drainage water of tailingspile. Cabonate rocks are wide distributed on the territory of the Kizel coal basin, so waste of limestone mining was used as a reagent. Laboratory studies have demonstrated the efficiency of carbonate rocks usage to neutralize tailingspiles' acid drainage water.

The field-scale experiment was conducted near of one of tailingspiles, whose drainage water polluted groundwater (fig. 2). Trench works were done crosswise the groundwater flow to the depth of confining layer bedding (1–1.2 m). The trench was filled with wastes of limestone mining, two observation wells (before the trench and behind it) were done to monitor neutralization process.

As a result, the pH value of groundwater increased from 1.8 to 6.8 and maintained nearby values during a year. The chemical composition of water changed to sulfate-hydrocarbonate-calcium, water salinity decreased from 28 to 3.5 g L^{-1}, and the content of main polluting components decreased also. Filtration properties of grounds changed – there was an intensive precipitation of iron and aluminum hydroxides, as well as some sulfates and hydrosulfates – the formed precipitate filled the pore space and impeded filtration. The modulus of grounds deformation increased two times and more. So, the field-scale experiment has demonstrated the possibility of alkaline geochemical barrier using to clean groundwater polluted with tailingspile's drainage water.

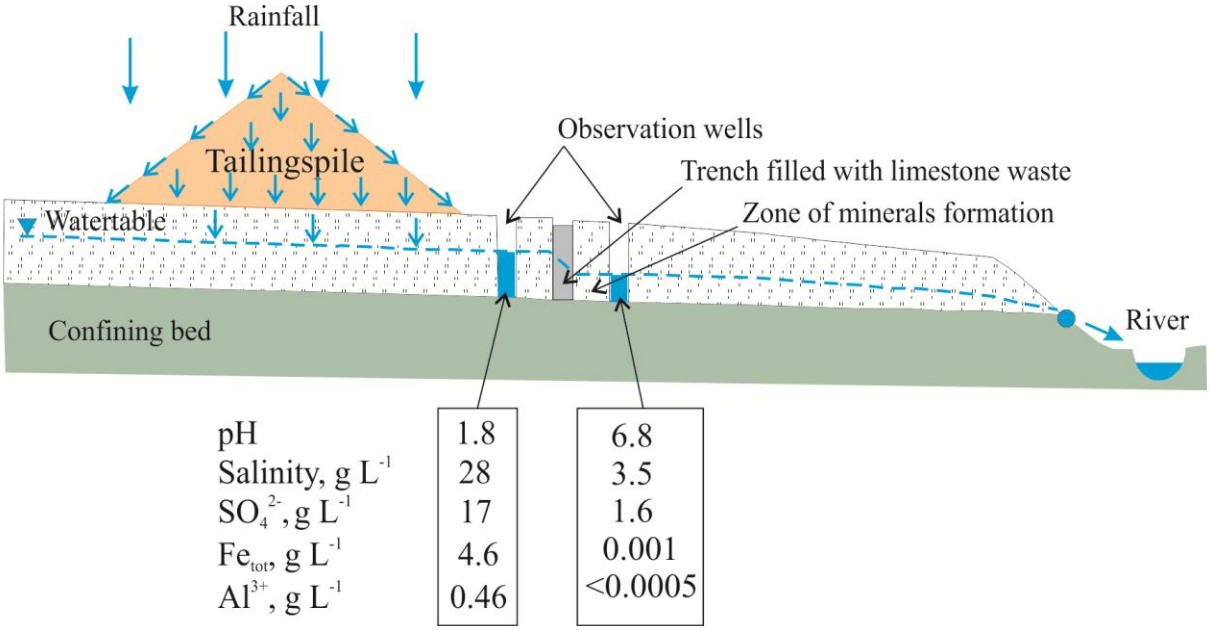

Figure 2 *The schema of the field-scale experiment to neutralize polluted groundwater*

Conclusions

Geochemical barriers could be effectively used to solve environmental problems in coal mining regions. The application of geochemical barriers demands considerably less costs and allows to avoid building of expensive cleaning constructions and to realize another measures of environment protection.

Aknowledgements

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Reduction of seepage outflow from potash tailings piles by improvement of greening: Results of a hydrological simulation

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Abstract

Groundwater and surface water in the Südharz potash mining district are influenced by high chloride salt outflow from waste piles due to leaching, erosion and subrosion. Surface and ground water do not meet ecological standards, especially in terms of the European Water Framework Directive (WFD) as well as German water laws. We elaborated an ecological solution to reduce the percolation water from the five studied piles. For reaching the prior restoration target, to decrease the seepage water formation, a functional combination of mineral coverage system with high water storage capacity and subsequent greening with high evapotranspiration rate is necessary. We assume that complete coverage of potash tailing piles with forest vegetation is able to maximize the evapotranspiration rate. For analyses, the potash tailings piles were subdivided into hydrotopes which are areas with similar hydrological properties. For each hydrotope we collected data of the current vegetation cover and the soil conditions. The results show that about 3.3 % of the potash tailings piles are already afforested and 53.7 % are covered with shrubs, grasses and herbs. The soil conditions are mainly alkaline and cemented by carbonate precipitation. For estimating the effect the percolation water rates (percentage of percolation water on rainfall) of three scenarios of greening were modeled with BOWAHALD: 1) status quo, 2) temporary greening and 3) complete forest vegetation. The hydrological modeling shows only a marginal decrease of percolation water by temporary greening (mean 7 %). Depending on local conditions, a reduction of the percolation water down to 31 to 67 % of the current percolation water is expected by afforestation. In conclusion, complete forest vegetation as a greening concept of potash tailings piles is able to decrease a substantial part of percolation water. However, the formation of seepage cannot be stopped totally and further efforts are necessary to reduce the impact on ground and surface water.

Key words: Potash tailings piles; evaporation of greening; coverage systems; recultivation; chloride charge; water protection

Introduction

Continuous weathering and leaching of potash tailings piles is a long term problem for groundwater and surface water in the Südharz potash mining district around the town of Sondershausen in Thuringia. Due to precipitation, easily soluble chloride is leached by percolation water. Insoluble and slightly soluble components, which mainly consist of anhydrite, gypsum and clay (Schmeisky and Lenz 1998), remain at the pile surface.

In Germany, surface water has to be continuously in a good ecological condition, according to the Water Resources Act of Germany (Wasserhaushaltsgesetz 2009). In the Südharz potash mining district, this standard is difficult to achieve at present. This is particularly true for the river Wipper because of its high chloride charges. This is caused by the catchment's geology as well as the chloride piles' drainage water. Retention basins collect a part of the pile's wastewater and control the release of chloride into the Wipper. The method is insufficient because of the large volume of contaminated pile water, which needs to be diluted in rivers with temporarily low runoff rates and high background salt loads.

A sustainable solution seems to be the avoidance of percolation water formation (Kloss et al. 2014). By decree of the Mining Authority of Thuringia, potash tailings piles have to be covered by a range of materials according to a treatment recommendation (TLUG 2013). While, the recommendation specifies the quality of the cover materials, less emphasis are given to aspects of greening such as tree species selection given the specific conditions on potash tailings piles.

In this study, we developed appropriate greening concepts for five potash tailings piles in the Südharz potash mining district. Our aims were to identify appropriate intermediate and final vegetation types that (1) can deal with the local conditions and (2) reduce the percolation water volume due to increase evaporation rates. For this purpose, we use the BOWAHALD software and assess the percolation water rate of the current and final (complete covered and afforested) conditions for each hydrotope.

Methods

Study site

The five studied potash tailings piles are located in the Südharz potash mining district next to the towns of Bleicherode, Menteroda, Rossleben, Sollstedt and Sondershausen (in the following, the pile's name is identical to the town's name). The pile body mainly consists of sodium chloride (67-77 %). The potash tailings piles Bleicherode, Sollstedt and Sondershausen are located in the Wipper catchment area, while Menteroda is part of in the Helbe and Rossleben of the Unstrut catchment area. Since the German re-unification in 1990, the piles are continuously covered with a mixture of demolition material, sediments, soil and some other non hazardous mineral materials. Currently, the piles surfaces amount to 49.1 ha (Bleicherode), 56.3 ha (Menteroda), 59.8 ha (Rossleben), 57.5 ha (Sollstedt) and 69.1 ha (Sondershausen).

Field sampling

During several field campaigns, we characterized the current vegetation on the piles and surveyed the physico-chemical conditions of the surface materials. Before starting the field sampling, the potash tailings piles were subdivided into “hydrotopes”. These are areas with consistent hydrological behaviour. Hence, dissimilarities in geographical direction, vegetation, slope, and soil conditions, which likely result in different hydrological functions, served to group the pile areas into hydrotopes. Aerial photos of the piles from 2011 were used for a first estimation of the vegetation patterns and the degree of coverage. The geographical directions and the slope were calculated using LiDAR-Data (Light Detection and Ranging).

We validated all hydrotope positions in the field and assessed each hydrotope's general vegetation characteristics, in detail. These are most dominant plant species, main and secondary usage in addition to their cover ratio, current and maximum growth high and lushness. Moreover, in a subset of hydrotopes we also determined all plant species and degree of vegetation cover, according to Braun-Blanquet (1964) and Pfadenhauer et al. (1986). For the soil survey, we used a stratified simple random sampling design to take about 20 soil samples at each pile and to conduct in-situ measurements of the saturated hydraulic conductivity with an Amoozemeter. The laboratory assessment of the soil samples included pH value, pore volumes, water holding capacity, permanent welting point and oven-dry density.

Simulation of percolation water rates

For modeling the percolation water rate of each hydrotope we used the hydrological model BOWAHALD (Dunger 2002). The model is particularly suited to simulate hydrological processes on piles. Input data for the model consists of climate data, vegetation parameters, maximal root depth and root density (Kutschera 2010, Kutschera & Lichtenegger 2013), minimal cover degree of seven types of hydrotopes, slope, geographical direction, cover category (six classes linked with soil conditions), saturated water content and values of the laboratory assessment. Furthermore, simulations were run for 13 hydrological years (2001-2013) to get an idea about the annual variation of seepage water formation.

We modeled three scenarios of greening:

- Status quo: This contained the current cover and greening (April/May 2015)
- Temporary greening: This version contained the status quo of cover and greening and an additional greening with *Robinia pseudoacacia, Sambucus nigra* and *Urtica dioica* of all anhydrite areas and hillsides without the final coverage (front disposal)
- Complete forest vegetation: The scenario contained the completely coverage (2 meter of cover material) and afforestation with site-adapted and native deciduous tree species

Results

Soil parameters for BOWAHALD calculation

Values of soil water parameters for anhydrite, debris and earthwork are based on exemplary measurements and soil samples. The following values were used for the model: for anhydrite hydrotopes: saturated water content: 70.9 %, field capacity: 15.8 %, permanent welting point: 15.6 %, k_f-value: 8.33×10^{-5} m/s. For debris hydrotopes: 62.3 %, 30.2 %, 21.5 % and 4.98×10^{-5} m/s. For earthwork hydrotopes: 62.4 %, 30.2 %, 21.5 % and 4.98×10^{-5} m/s. The front disposal hydrotopes were split into two parts. Up to one meter soil depth, we used values of final coverage hydrotopes (different for each pile). From one up to two meters soil depth values of anhydrite hydrotopes were used. The measured values on final coverage are very different between each pile. This is a result of variation in the materials used for the coverage. Table 1 shows the pile-specific soil values used for the model.

Table 1 *Mean of saturated water content [Volume-%], field capacity [Volume-%], permanent welting point [Volume-%] and k_f-value [mm/h].*

	Bleicherode	Menteroda	Rossleben	Sollstedt	Sondershausen
Saturated water content	63.4	58.7	57.1	50.1	62.0
field capacity	30.7	32.5	35.1	34.4	34.3
permanent welting point	16.2	17.2	22.8	22.9	20.0
k_f-value	213.7	95.8	97.4	46.4	125.5

Current coverage conditions

Figure 1 shows the different percentage of the pile's coverage conditions. A precise recording of the coverage was necessary to identify the potentials for further greening.

Current vegetation coverage

The current vegetation coverage could be classified into 1) without vegetation, 2) herbal layer, 3) shrub layer and 4) tree layer. Figure 2 shows the distribution for every pile. Trees and shrubs cover today only a small fraction of the potash tailings piles (Bleicherode: 12.1 ha of 49.1 ha, Menteroda: 4.8 ha of 56.4 ha, Rossleben: 2.9 ha of 59.8 ha, Sollstedt: 8.6 ha of 57.4 ha, Sondershausen: 3.4 ha of 69.1 ha.).

Because of a very eutrophic soil, the shrubs layer is dominated by *Sambucus nigra, Rosa spp., Prunus cerasifera, Crategus monogyna* and *Acer campestre*. The herbal layer mainly consists of *Urtica dioica, Galium aparine, Cirsium arvense, Elymus repens* and *Alliaria petiolata*. Additional, halophytes and other salt tolerant plant species were found on anhydrite hillsides and at the pile's basement (e.g. *Aster tripolium, Gypsophila perfoliata, Lotus tenuis*).

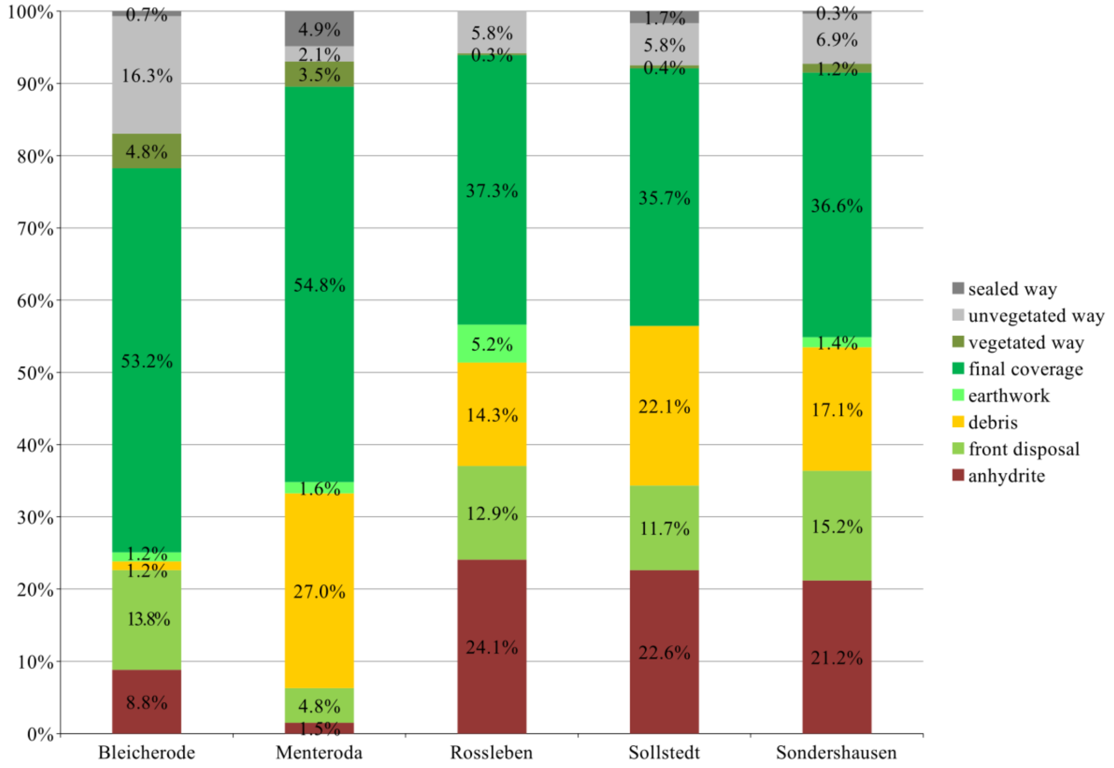

***Figure 1** Percentage of current coverage classes*

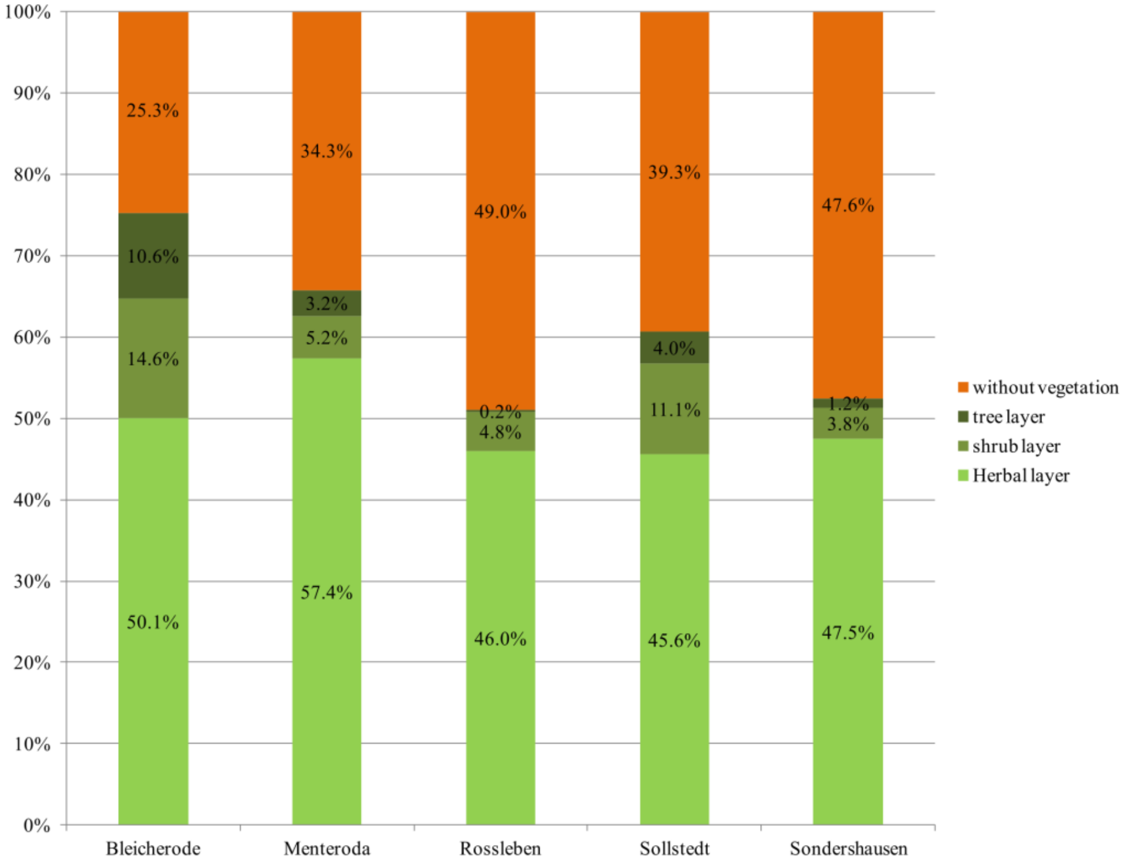

***Figure 2** Percentage of current vegetation cover*

Percolation water rate

In total, the current percolation amount of about 598,000 m³ per year. A temporary greening of anhydrite areas and hillsides with front disposal is able to decrease the percolation water rate by no more than 7 %. In comparison with a final coverage (two meters thickness) and complete forest vegetation a reduction the percolation water volume by 44 % is possible indicating a seepage amount of 335,000 m³ in total per year. Because of the multitude hydrotopes the potential of decreasing can be exactly located upon every pile. Figure 3 shows the median of the percolation share of precipitation for each pile in percentage. Moreover, our dataset allowed mapping the local dispersal of the current and the modeled percolation water rate for every pile. As an example for the maps which were elaborated, figure 4 shows the potash tailings pile Sondershausen.

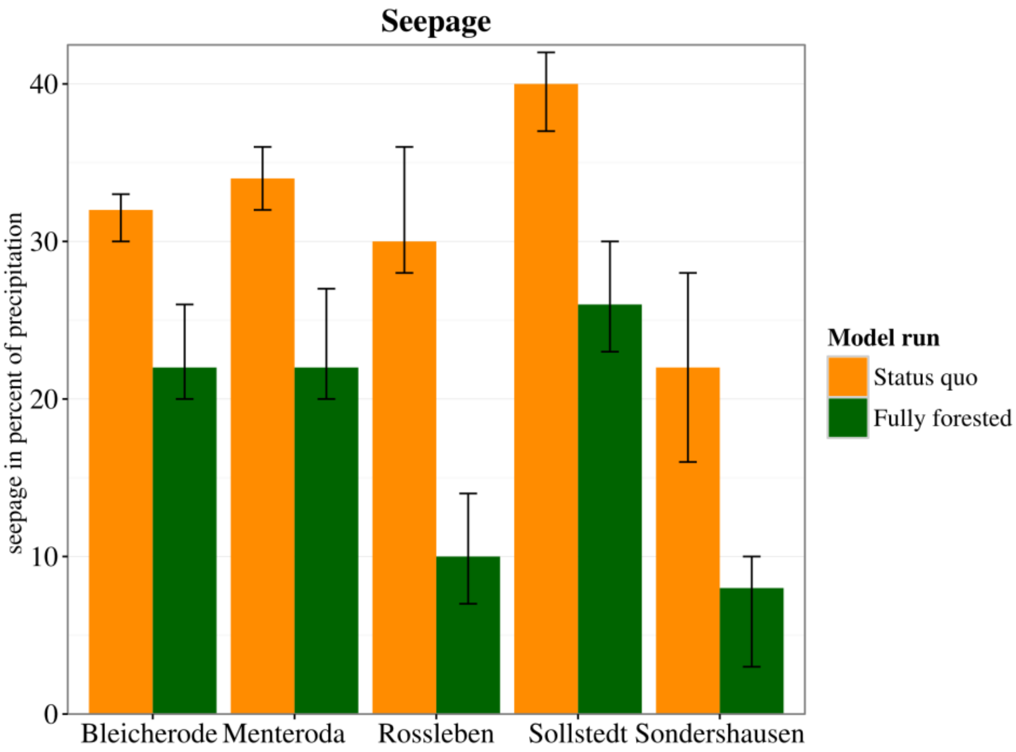

Figure 3 *Current and final seepage in percentage of precipitation, given are the median values. The whiskers represent the range between minimum and maximum.*

Greening recommendation

Out of all single results we derived five greening recommendations. We recommend starting with all final covered areas. The greening ought to start on areas with herbal vegetation, as no preparation is necessary. Secondary, all hydrotops additionally covered by a shrub layer up to 50 % and over 50 %. Within each class of vegetation coverage the calculated decrease of seepage defines the detailed priority list. Finally, trees on all areas with an already existent tree layer will be supplemented. The priority list of areas without the final coverage also depends on the calculated reduction of percolation water amount. Here, the coverage and the greening should begin on hydrotopes with the highest decrease of percolation water.

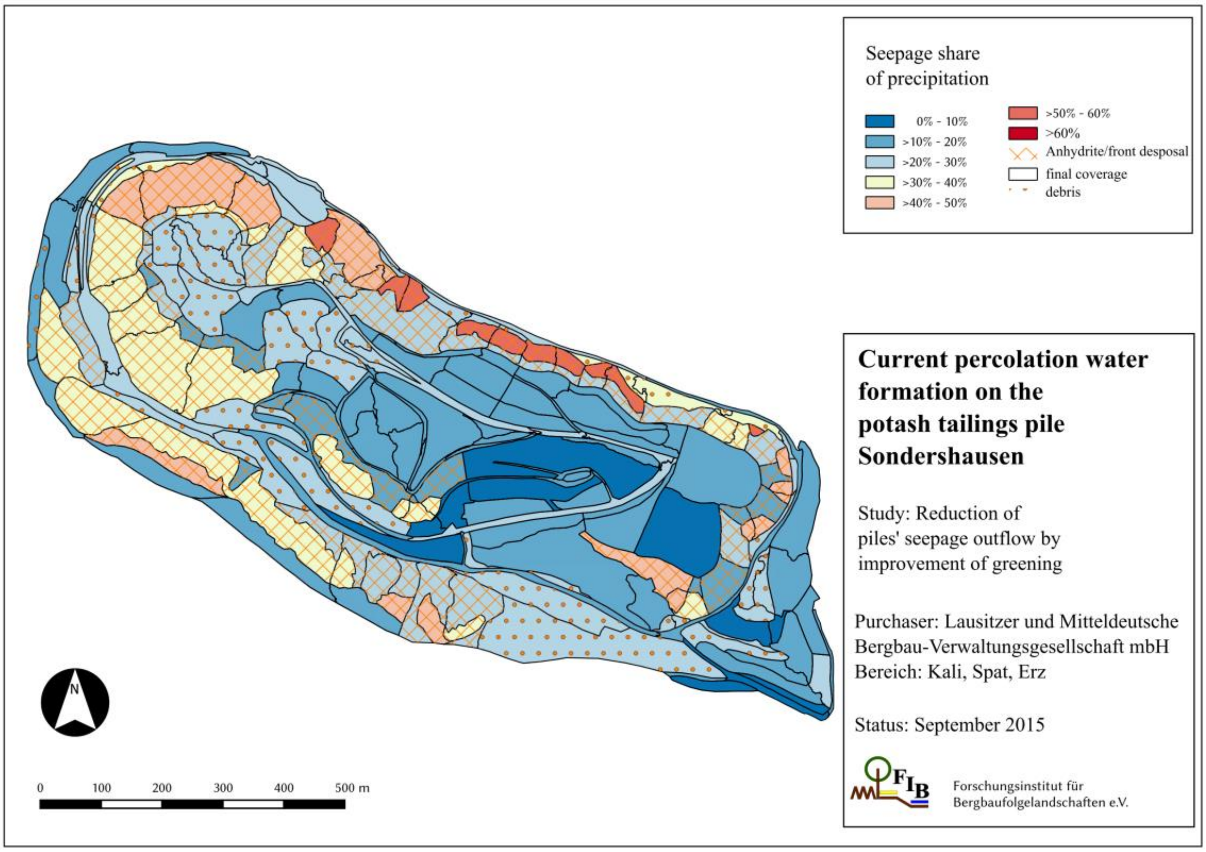

Figure 4 *Seepage in percentage of precipitation (potash tailings pile Sondershausen)*

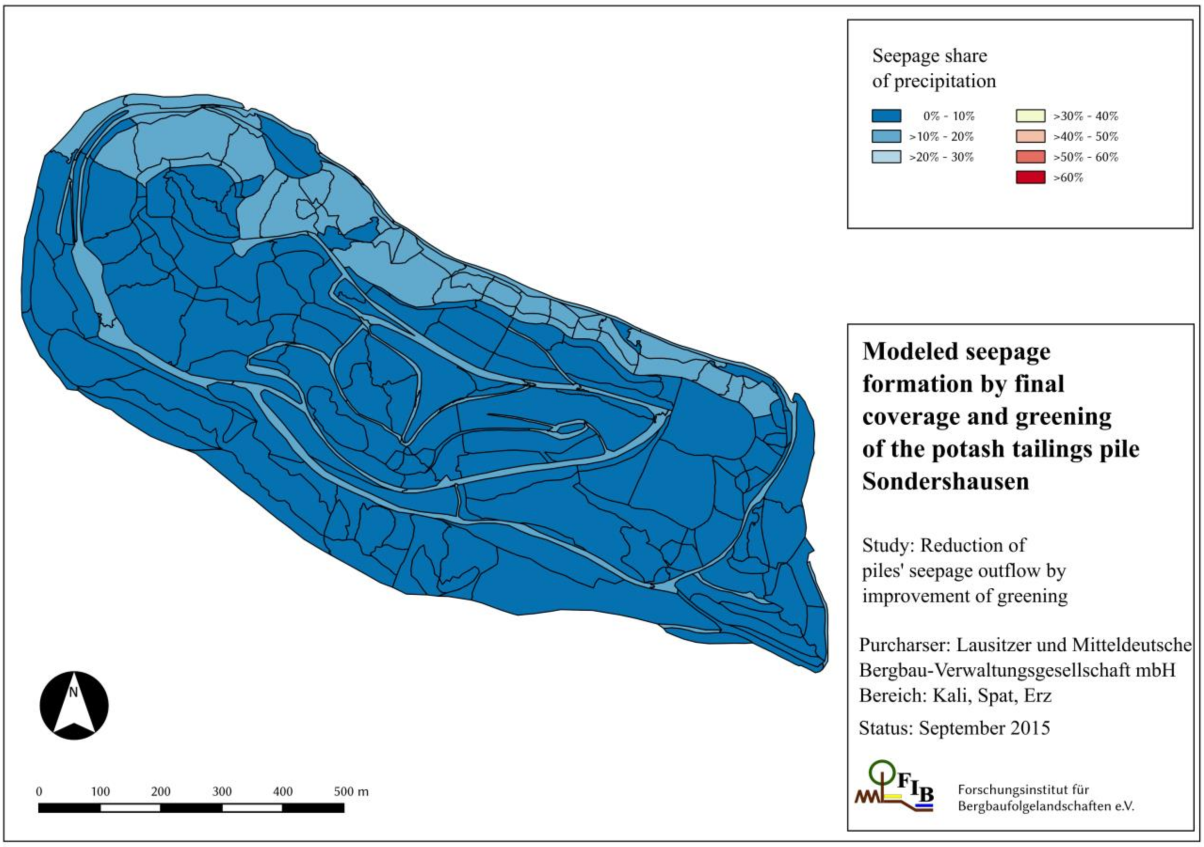

Figure 5 *Final seepage in percentage of precipitation (potash tailings pile Sondershausen).*

Discussion

There are strict regulations for the construction of the coverage system on the potash tailings piles, both for the technical and the soil layer (TLUG 2013). Unfortunately, little is known about the characteristic variables of the soil water storage. Our results about soil characteristics and vegetation conditions provide an indication of water balance conditions of potash tailings piles. Furthermore, we mapped the current stage of coverage and proportion of different vegetation on each of the five piles.

Based on this detailed data, we developed a guiding principle for a protective pile-forest. Compared with the former greening concepts (e.g. Zundel 1991, 1993), high evapotranspiration is the most important target. Further interests like landscape aesthetics or use for recreation are subordinated. Furthermore, the tree composition for the protective pile-forest is adapted to the local soil and climate conditions of each hydrotope.

Seepage water is crucial for the discharge of salts. Earlier research had been undertaken by Stude et al. (2002) with the help of some small lysimeters on the pile Bleicherode. They already modeled the seepage water with the help of BOWAHALD, but the study was restricted to some varying site conditions and vegetation coverage rates. Our study modeled the seepage water for all of the five potash tailings piles, and each of them differentiated into a large number of hydrotopes (altogether 853), based on field data of soil and vegetation.

Our results indicate that 8 to 26 % of precipitation turns into seepage water, even with a complete coverage and a dense protective pile-forest with its closed canopy. There is no guarantee that afforestation indeed reduces the seepage water volume by calculated numbers. The coverage of the piles may locally differ from the intended thickness due to geotechnical restrictions, which cannot be considered. Compared to other landfills, the amount of seepage water appears high. An additional coverage by sealing the surface with plastics here is not applicable, because of ongoing subrosion processes.

A temporary greening results only in a very small reduction of percolation water. Hence, we do not recommend this kind of greening, because of the soil's very low water storage capacity. Heinze & Liebmann (1991) and Schmeisky & Lenz (1998) conducted some early experiments cultivating different plants on only thin coverage or even directly in the anhydrite layer. The growth performance of the plants, selected for high salt tolerance, remained low. Because of the missing soil coverage, this type of greening would not be successful. Our study clearly shows the importance of a water storing soil layer.

Our recommendation focus' on establishing efficient water storing soil layer and target vegetation types with high evapotranspiration.

Conclusions

Our results offer important insights for further recultivation activities. First of all, the regularly prepared soil layers on the top of the mineral covering are suitable for afforestation. The soils are characterized by slightly alkaline conditions and are somewhat cemented. They mainly provide good or sufficient water storage capacity. Based on soil and climate conditions as well as regional presence of tree species, different suitable broad-leaved tree species were selected for an adapted protective pile forest. The hydrological modeling figured out, that a temporary greening has no relevant effect on seepage formation due to the very restricted water storage capacity of anhydrite. We recommend a complete covering and subsequent afforestation with protective pile forests. Depending on local conditions, a reduction of the percolation water down to 31 to 67 % of the current percolation water can be expected. Because all investigated piles are currently lacking any relevant tree or even shrub cover, afforestation with a protective pile forest is the key to maximize evapotranspiration. For direct implementation, we ranked every subarea of the piles relative to its contribution to seepage reduction, both for already covered subareas (where afforestation can immediately start) and for subareas that still need to be covered.

The implementation of our site-specific results in further recultivation are very important for establishing a greening concept, which contains a quickly decrease of percolation water formation from potash tailings piles and salt charge into the nearby catchments.

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Results of field scale phytoremediation experiments on a former Uranium mining site

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Extended Abstract

In the past large heavy metal contaminated sites represented a problem for remediation; especially former mining sites with AMD impact result in a demanding challenge for long-term and sustainable remediation efforts. Since a few years phytoremediation as an alternative remediation method is investigated; the low treatment costs make it feasible even for such sites. Robust phytoremediation plants, which tolerate acidic soils and slight to medium HM concentrations represent one convenient approach for acidic mining areas. Phytoremediation is an emerging, sustainable and very convenient technology for the stabilization and environmental improvement of former mining sites as well as of their ground water quality.

Field scale investigations were applied to an area of the former uranium mining in East Thuringia, Germany. During active mining operations, a low grade uranium leaching dump was situated on this area. After closedown of mining operations, the dump was removed during the remediation process of the site. The remaining underground currently is slightly to moderately contaminated with heavy metals and radionuclides (HM/R) and the actual and future land use of this area is restricted.

In an interdisciplinary research project, concepts for the remediation of HM/R- contaminated sites and for the subsequent utilization of HM/R-loaded plant residues were developed. The application of phytoremediation was investigated in laboratory-, green house– and field experiments by interdisciplinary working groups. One challenge of the experiments was the subsequent utilization of the plants from phytoremediation.

Field experiments were carried out with *Triticale, Helianthus annuus, Brassica juncea* and *Sorghum bicolor* by application of different biological additives (mycorrhiza, HM-resistant streptomyces) and soil amendment strategies (increasing pH and organic matter). As a main result, phytoremediation in combination with the different soil improvement strategies predominantly showed an immobilization of HM/R in the upper topsoil layer (rhizosphere) by sorption and sequestration processes (phytostabilization), as well as a substantial reduction of the seepage water rate.

Different experiments were carried out for the investigation of utilization of the plant material from the field experiments and possible restrictions. A subsequent utilization of the plant biomass as CO2-neutral energy source would represent a convenient solution. The utilization of the HM/R-loaded plant residues after the harvest can contribute to the minimization of wastes, to the winning of energy, and therefore to a reduction of the remediation costs. The processing of the heavy metal loaded plant residues was investigated by different methods. In fermentation experiments with *Solanum tuberosum* and *Secale cereale* good results were achieved compared to industrial standards. Biogas experiments were carried out with *Triticale, Helianthus annuus* and *Brassica juncea*. In the anaerobic biogas process, heavy metals can be precipitated and accumulated in the sludge as a sink. In combustion process, U is immobilized predominantly (80 – 85 %) in the ashes, and finally these remainders (often less than 5-10% of the original plant dry mass) can be deposited .

From the results of the project can be concluded, that phytoremediation is a convenient method for the stabilization and remediation of large sites with slight to medium contaminations, and a further utilization of the plant residues by fermentation, biogas production and thermal utilization, respectively, is feasible.

Key words: Remediation of mining sites, phytoremediation, phytostabilization, uranium, heavy metals

CHAPTER 8

Mine Water Treatment

Developing Sustainable Biotechnologies for Mine Water Treatment in the 21^{ST} Century

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Abstract

Active chemical and passive biological treatments of acidic mine waters both have major detractions, including the need to collect and dispose of large volumes of waste materials (metal-laden sludges or spent composts) in landfill sites, and the fact that resources present in mine waters, such as potentially valuable transition metals, are not recovered and recycled. We have developed modular bioreactors that combine mine water remediation with resource recovery. Two module types have been commissioned, one designed to oxidise ferrous iron and thereby to promote the biomineralisation of pure-grade schwertmannite, and the other to generate hydrogen sulfide via the microbial reduction of either sulfate or elemental sulfur at low pH. These can be configured to treat mine waters of widely different chemical (e.g. pH and metal contents) compositions, and to promote the selective biomineralisation of different transition metals present in mine waters, thereby facilitating the production of defined mineral products that have resale value. Both the schwertmannite-generating and sulfidogenic bioreactors utilise populations of recently-described bacteria that occur naturally in acidic mine waters. More recently, we have also incorporated a third bioreactor which effectively removes soluble manganese from waters of pH 5 and above, into our design protocols. The modules have low construction costs, and the value of the metals recovered often exceeds operational costs. Even discounting the cost of an alternative mine water treatment process that does not facilitate metal recovery, the biomineralisation option would often prove to be highly competive in economic as well as environmental terms. With increasingly strict environmental regulations, diminishing availability of landfill sites, and greater pressure to recycle from waste materials, (bio)technologies that consider mine waters as potential resources as well as environmental pollutants have the potential to be the major growth areas in this sector in the 21st century.

Key words: Biomineralisation, bioreactors, bioremediation, schwertmannite, sulfate reduction

Introduction

Acidic, metal-rich waters generated in, and emanating from, active and abandoned mines and mine waste repositories (rock dumps and tailings deposits) represent a serious global threat to the environment (Blowes et al. 2014; Nordstrom et al. 2015). Various options are available to remediate acid mine drainage (AMD) water, though two approaches - active chemical treatment (aeration and addition of an alkaline material such as lime) and passive biological treatment (use of constructed wetlands and “compost bioreactors”) - have been used most extensively (Johnson and Hallberg 2005). Both of these, however, have major detractions, including the need to collect and dispose of large volumes of the metal-laden sludges or spent composts in landfill sites that, in many cases, need to be designated for storage of hazardous wastes, and secondly that none of the resources present in mine waters, such as potentially valuable transition metals, are recovered and recycled.

Microorganisms play key roles in the genesis of AMD (Blowes et al. 2014), chiefly because of the abilities of some specialised species to oxidise reduced sulfur (to sulfuric acid, thereby acidifying mine waters, sometimes to extremely low pH values) and/or ferrous iron (which generates the powerful oxidant, ferric iron, thereby accelerating the oxidative dissolution of metal-bearing sulfide minerals). However, other microbial species have the potential to facilitate the remediation of AMD by carrying out metabolic activities that either generate net alkalinity, or immobilise metals (biomineralisation), or both. An example of the latter are sulfate-reducing bacteria (SRB). The dissimilatory reduction of sulfate, coupled to the oxidation of an organic carbon substrate can, depending on pH, be either acid-generating, acid-consuming or pH neutral. In moderately to extremely acidic liquors, it is a strongly acid-consuming (alkali-generating) process as the end products are CO_2 and H_2S (as shown in equation [1], where the organic substrate shown is glycerol) rather than, as in high pH waters, HCO_3^- and HS^-:

$$4\ C_3H_8O_3 + 7\ SO_4^{2-} + 14\ H^+ \rightarrow 7\ H_2S + 12\ CO_2 + 16\ H_2O \qquad [1].$$

The hydrogen sulfide generated as a waste product by sulfate-reducing bacteria (SRB) can effectively immobilise many (chalcophilic) transition metals, forming highly insoluble sulfide minerals. Most SRB are obligate anaerobes, however, and are non-active or readily killed on exposure to oxygen. Nascent metal sulfides produced by SRB are also unstable in aerobic environments. SRB have been implicated as important in remediation systems that use constructed wetlands, though substantiated evidence in support of this is often lacking. One reason is that SRB tend, in general, to metabolise readily-degraded, small molecular weight organic substrates such as sugars, alcohols and aliphatic acids rather than more recalcitrant materials (composts, straw etc.) that are used as long-term substrates in constructed wetlands. This problem is readily circumvented when bioreactors containing SRB are used to treat acid mine drainage (AMD). Full-scale systems of this kind (sometimes using hydrogen as substrate and sulfur- rather than sulfate-reducing bacteria) have been developed and operated by the Dutch company *Paques b.v.*, and the Canadian company *BioteQ Environmental Technologies Inc.*.

Sustainable protocols for mine water remediation require capital costs of systems to be minimal, and ideally for net operating costs to be neutral. One way to achieve the latter is to recover some or all of the commercially valuable metals present in AMD in such a way that they have a saleable value, or else convert them into minerals that have useful functions. With this challenge very much in mind, modular bioreactors have been commissioned at Bangor University and tested with a variety of synthetic and actual mine waters. The objectives were to develop empirical but effective units with minimal operating costs, and which could be configured in different ways to meet the requirements of AMD with widely different chemical compositions. These may be used to promote both the selective biomineralisation of metals (and metalloids) present in waters draining metal and coal mines, and to generate alkalinity, thereby ameliorating the pH of net acid AMD waters.

Materials and Methods

The composite systems used involve two main types of bioreactors, one of which catalyses the oxidation of ferrous iron in the first stage of a process for removing iron from AMD, while the other is a low pH biosulfidogenic module that can be used to capture metals both in-line and off-line, and also to partly neutralise the acidity of mine waters. A third bioreactor, which uses undefined microbial populations to oxidise manganese (II) and thereby remove this metal as an insoluble manganese (IV) phase, has also been used occasionally.

Ferrous iron-oxidising bioreactors. These operate as continuous flow systems, where the objective is to use bacteria commonly found in acidic ferruginous mine waters to oxidise ferrous iron to ferric, a reaction that proceeds slowly below pH 3.5 in the absence of microorganisms. Two modular systems have been devised and tested with mine water from the abandoned Mynydd Parys copper mines (Anglesey, north Wales), one of which uses the autotrophic iron-oxidising acidophile "*Ferrovum (Fv.) myxofaciens*" (which is now known to have global distribution in mine waters of pH 2-4; Hedrich and Johnson 2012) and the other the heterotrophic iron-oxidising acidophile *Acidithrix (Ax.) ferrooxidans* (Jones and Johnson 2016). Both of these form the first unit in a composite system for removing iron from AMD, which also includes a second pH-controlled unit, where sodium hydroxide is added to the oxidised AMD to form the mineral, schwertmannite ($Fe_8O_8(OH)_6(SO_4).nH_2O$) and a third, fixed bed bioreactor, which is used to remove residual iron (Fig. 1). Since rates of ferrous iron oxidation far exceed those of ferric iron hydrolysis in the bioreactor unit, only small amounts of ferric iron precipitate in this unit and the accumulation of ferric minerals within it is minimal.

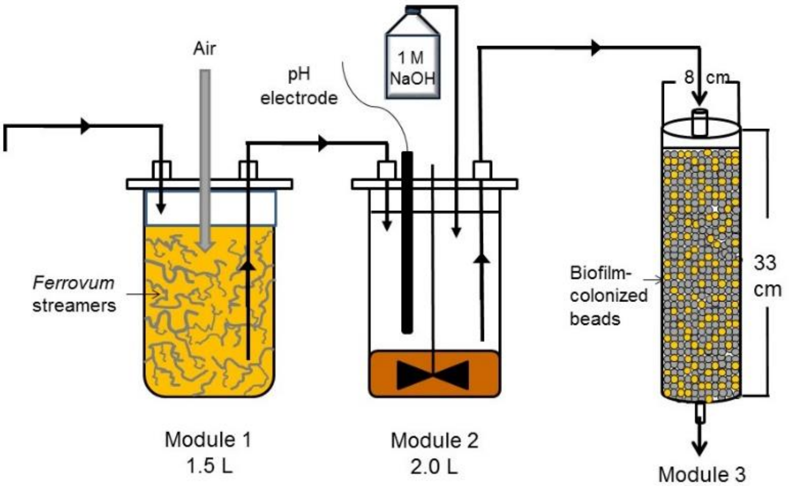

Figure 1 *Schematic of the composite modular system used to selectively remove iron from synthetic mine waters.*

Low pH sulfidogenic bioreactors. Continuous flow biofilm reactors were commissioned to produce hydrogen sulfide via the dissimilatory reduction of sulfate (Fig. 2). These contained novel species of acidophilic and acid-tolerant SRB (aSRB), and other bacteria, immobilised on 1-2 mm diameter porous glass beads. The bioreactors (FerMac 310/60; Electrolab, UK) were operated at between 20° and 45°C (30°C, typically) and at pH values between 2.5 and 5.0. The liquors used as feed solutions for the bioreactors required to be of low pH than that pre-set in the reactor vessel. Proton consumption accompanying sulfate reduction (equation [1]) caused the pH inside the reactor vessel to increase, which triggered automated inflow of the acidic feed. Flow rates (and hydraulic retention times) were therefore dictated primarily by rates of bacterial sulfate reduction. In cases where transition metals precipitated as

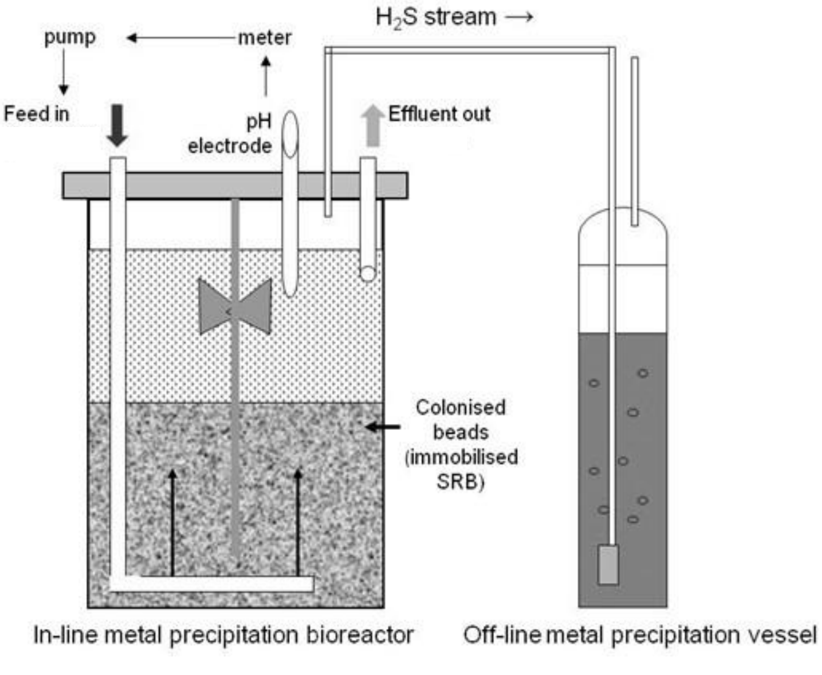

Figure 2 *Schematic of the low pH sulfidogenic bioreactor designed to both precipitate metals in-line (i.e. within the reactor vessel) and off-line (in a separate vessel, using* H_2S *produced in the bioreactor in excess of that required to precipitate metals in situ).*

sulfide minerals or metals (e.g. Al) hydrolysed within the reactor vessel itself, these acid-generating reactions modified the inflow of the acidic feed liquors. Full details of these low pH sulfidogenic bioreactors are given elsewhere (e.g. Ñancucheo and Johnson 2014).

Manganese bioreactors. Empirical continuous flow biofilm reactors (Mariner et al. 2008) were set up to oxidise and precipitate manganese in mine waters that had been treated previously to remove other soluble metals. These comprised Perspex columns, 30 cm by 7 cm (diameter), with working volumes of 1.08 L, that were filled with MnO_2-coated pebbles collected from a stream in the catchment of the Snowdonia mountain range (North Wales). Manganese-containing liquors were pumped into the base and out of the top of the reactors, which were aerated. No other amendment (e.g. addition of organic compounds) was required to facilitate manganese removal.

Results and Discussion

Metals and metalloids commonly found in mine waters, or of particular concern in terms of their toxicities, form sulfides and/or hydroxides that vary in their solubility products. These, and other such data, can be used to predict the most effective method for removing these elements from mine waters via (bio)mineralisation, with the general rule that, where different solid phases can be formed, that the lower solubility product is generally preferable (Table 1).

Table 1 *Solubility products (log K_{sp} at 25ºC) of (a) hydroxide and (b) sulfide phases of metals (and arsenic) of particular concern in mine waters. The highlighted data indicate preferable products of (bio)mineralisation (data from Monhemius 1977).*

	Al	As(III)	Cd	Co	Cu	Fe(II)	Fe(III)	Mn(II)	Ni	Zn
(a)	-32.2	-	-14.3	-14.5	-19.8	-16.3	-38.6	-12.7	-15.3	-16.1
(b)	-	-16.0	-28.9	-22.1	-35.9	-18.8	-	-13.3	-21.0	-24.5

Iron. As shown in Table 1, although ferrous iron forms both sulfide and hydroxide phases, the solubility products of both of these are far greater than that of ferric hydroxide. The most effective way to remove soluble iron from mine waters is therefore to facilitate ferrous iron oxidation (using microorganisms to catalyse this reaction in acidic mine waters) and to precipitate the ferric iron formed as a hydroxy-sulfate mineral, such as schwertmannite in a separate vessel. In the system described by Hedrich and Johnson (2012), co-precipitation of copper and zinc (which were present at 45 and 70 mg/L, respectively, in the mine water tested) with schwertmannite was avoided by maintaining the pH of this unit at between 3.0 and 3.5. Schwertmannite is a useful by-product, as it can be used to adsorb toxic oxy-anions such as arsenate and antimonite, non-toxic anions, such as phosphate, in eutrophic water bodies, or used to synthesise iron pigments (Janneck et al. 2010), though relatively pure grade (not contaminated with arsenic etc.) mineral is required for schwertmannite to have commercial value. Both bacteria used to oxidise ferrous iron in AMD in bioreactors developed at Bangor University ("*Fv. myxofaciens*" and *Ax. ferrooxidans*) have the characteristic of attaching readily to surfaces and forming macroscopic streamer growths in flowing waters. This eliminates the need to fill bioreactors with inert materials that act as supports for bacterial attachment and decrease the volume available for the iron-oxidising bacteria themselves. The advantage of using *Ax. ferrooxidans* when commissioning a new bioreactor is that, as a heterotrophic species, biomass growth and colonisation is much more rapid than when (as has been common practice) autotrophic species are used. Jones and Johnson (2016) showed that *Ax. ferrooxidans* bioreactors oxidised ferrous iron effectively in extremely acidic mine waters (as low as pH 1.37) and that this acidophile was gradually displaced by other (autotrophic) iron-oxidisers when processing non-sterile AMD, with no downturn in bioreactor performance.

Chalcophilic transition metals (Cd, Co, Cu, Ni and Zn). As indicated in Table 1, these five metals can be effectively removed from AMD as sulfide phases. The data also show that there large differences in K_{sp}'s between some of these metal sulfides can be used to segregate their precipitation, e.g. by controlling solution pH. The latter is possible since pH dictates the concentration of soluble S^{2-} (the sulfide species that reacts with the soluble metal, and which decreases in relative abundance to both HS^- and H_2S as solution pH falls). In practical terms, this means that biomineralisation of copper sulfide will occur at pH 2, while all of the other elements listed above (as well as ferrous iron) will remain in solution. By gradually increasing solution pH, it is possible to sequentially precipitate cadmium and then zinc, though the K_{sp}'s of nickel and cobalt sulfides are too similar to segregate them effectively by this means. Using this approach, Ñancucheo and Johnson (2012) were able to selectively recover zinc from AMD containing elevated concentration of zinc and iron, and also copper from a Cu/Fe/Zn-rich AMD.

Arsenic. This metalloid can occur both as As(III) (predominantly as uncharged arsenious acid, H_3AsO_3, in acidic mine waters) and as As(V) ($H_2AsO_4^-$ and $HAsO_4^{2-}$) all three of which are soluble. As indicated in Table 1, As(III) forms a sulfide phase and can be removed from mine waters by this means, as reported by Battaglia-Brunet et al. (2012), though given its K_{sp} it is likely to co-precipitate with other (metal) sulfides. Oxidation of As(III) to As(V) (e.g. by ferric iron) facilitates the removal of this toxic metalloid either as scorodite ($FeAsO_4$, which has a K_{sp} of -20.2) or by adsorption of the negatively-charged arsenic oxyanions onto positively-charged schwertmannite (Janneck et al. 2010). Given the concern about arsenic toxicity, when it is present in significant concentrations in mine waters it is highly desirable to remove it as the first step in a remediation/metal recovery process, as this allows downstream products to be free of this metalloid.

Manganese. Although manganese (II) does form insoluble sulfide and hydroxide phases, their relatively large K_{sp}'s (Table 1) mean that these form at relatively high pH values. Manganese (IV) is far less soluble than Mn(II) and, as is the case with iron, oxidation of the reduced cation, which can be chemically or biologically-mediated, can be used as a method of removing soluble manganese from contaminated waters, though this does not occur in extremely low pH mine waters. The empirical biofilm reactors used in the Bangor laboratories for this purpose show considerable promise for scaled-up tests, with typically 40-80% of soluble manganese removed from moderately acidic (pH 5) test solutions with hydraulic retention times of ~11 hours.

Examples of applications of the modular bioreactor units.

(i) Sequential removal of metals from a synthetic mine water, based on the composition of AMD in a copper mine in Pará state, Brazil. The chemical composition of synthetic mine water according to that draining a copper mine in northern Brazil, prior to and following processing using two of the modular bioreactors described above, is shown in Table 2, and a flow diagram showing the stages involved in the remediation protocol, in Fig. 3. In brief, copper (the major metal in the AMD) was first removed by contacting with H_2S (off-line) generated in an aSRB bioreactor. This caused the pH of the mine water to fall from 5.0 to 2.1, making it suitable as an influent liquor for the sulfidogenic bioreactor. Glycerol was added to the copper-free liquor, and pumped into the reactor, which was maintained at pH 5.0, where cobalt, nickel and zinc (but not manganese) were removed as sulfides. Finally, solutions draining the aSRB reactor were pumped through the Mn biofilm reactor, to remove this metal. This treatment also resulted in significant reductions (~40%) in concentrations of sulfate in the synthetic AMD.

Table 2 *Changes in water chemistry in contaminated water at a copper mine in Brazil, following treatment for combined copper recovery and remediation. All metal and sulfate-S concentrations are mg/L.*

	pH	Cu	Ni	Zn	Co	Mn	SO_4^{2-}-S
Influent	5.0	476	16	1.3	2.4	10.5	660
Effluent	5.0-6.0	<0.5	<0.1	<0.1	<0.1	<0.1	393

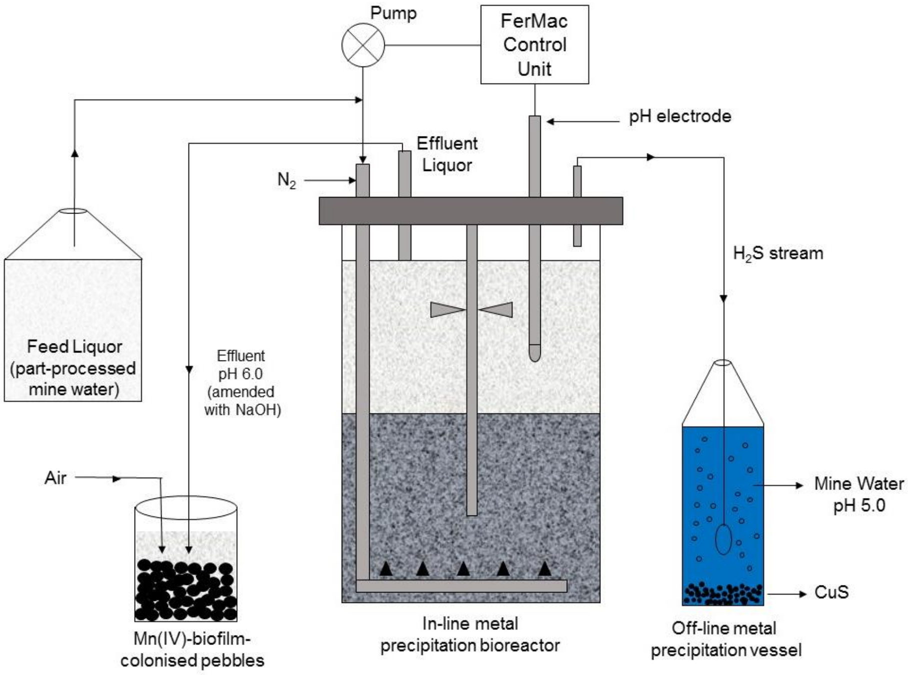

Figure 3 *Schematic representation of the integrated system used to remediate synthetic mine water based on that at a site in Brazil, and to recover copper.*

(ii) Combined remediation of and metal recovery from an extremely acidic (pH 2.3) mine water (Hedrich and Johnson 2014). The chemical composition of AMD at the Maurliden mine (Sweden) and the protocol used to process a synthetic analogue of this water in the Bangor laboratories, are shown in Table 3 and Fig. 4. The first step in the bioremediation process was to remove soluble arsenic from the mine water by allowing it to contact schwertmannite. Next, a bioreactor was used to oxidise ferrous iron in the AMD to ferric, and to produce schwertmannite, 12% of which was used up-front to remove As. Soluble copper and cadmium were removed in the next stage by contacting with biogenic H_2S in an off-line reactor vessel, after which the part-processed mine water was dosed with glycerol and fed into an aSRB reactor. By maintaining the pH of this unit at 4.0, most of the zinc was removed (as ZnS) while co-precipitation of aluminium and manganese was avoided. No further steps were taken to remediate this synthetic mine water, though this could have been achieved by adding a second, higher pH sulfidogenic bioreactor (to remove Al as hydroxysulfate minerals) and a unit to oxidise and precipitate manganese, as described above.

Table 3 *Concentrations of the major components of Maurliden mine water (data obtained from Boliden AB, Sweden).*

Analyte	Concentration (mg/L)	Analyte	Concentration (mg/L)
Zn	464	Cd	1.02
Fe (II)	200	Co	0.4
Fe (III)	203	Ni	0.3
Al	132	Ca	271
Mn	49	Mg	123
Cu	7.72	Na	13.8
As	1.33	K	4.01

Economic considerations. One of the major advantages of the integrated bioreactor protocols developed is that, by recovering metals from AMD, a revenue is generated that can offset, at least in part, operational costs. Some products (e.g. schwertmannite) are difficult to value at present, though increasing use of this mineral in remediation protocols and as a pigment precursor could change this in the near future. Metals such as copper and zinc would be obvious saleable products. Glycerol is used as substrate for biosulfidogenesis in the Bangor reactors since it is not only an innocuous and readily accessed material, but also (as a by-product of bio-diesel production) a relatively cheap organic compound. While relative costs of consumables and products will vary according to metal prices etc., typically \$1 of glycerol consumed would produce ~\$5 (copper) or \$1.25 (zinc) metal value. When costs of alternative remediation treatments (e.g. high density sludge production by chemical treatment) are factored in, the biologically-based systems described in the present report become even more attractive.

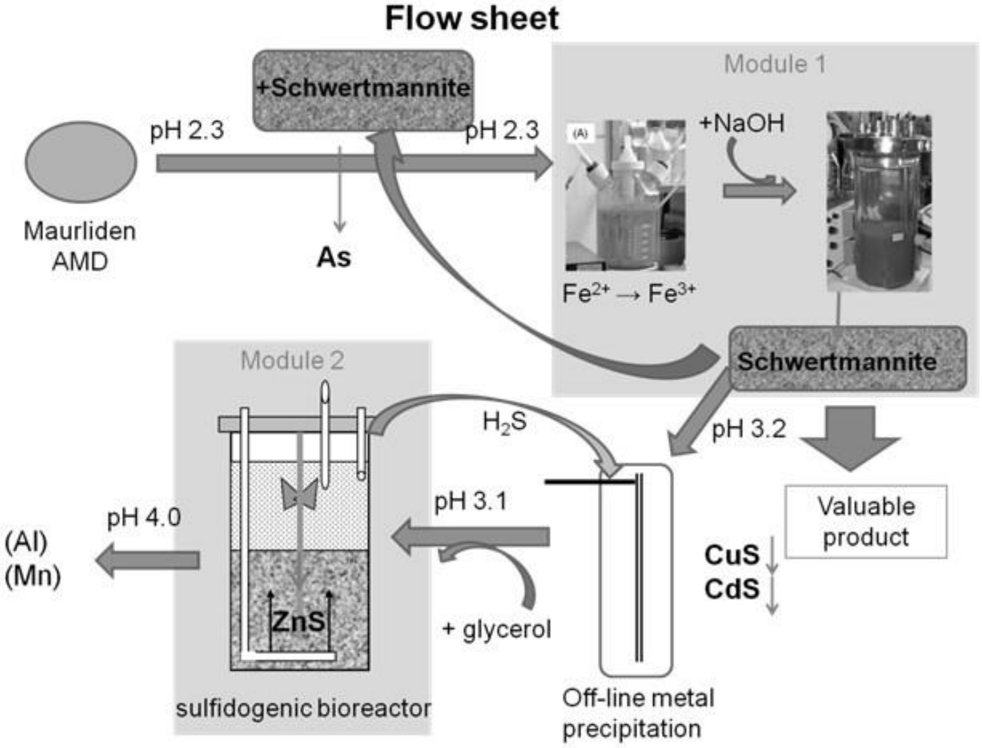

Figure 4 *Schematic representation of the integrated system used to remediate synthetic Maurliden mine water and to recover iron and zinc as mineral products.*

Conclusions

Modular bioreactor units, devised to simultaneously remediate mine waters and recover metals by catalyzing their selective biomineralisation, have been demonstrated to be both effective and economical in laboratory tests. Recovering metals from waste materials, such as AMD, should be viewed as a priority issue as sources of high-grade accessible primary resources become increasingly scarce.

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Passive biochemical treatment of ferriferous mine drainage: Lorraine mine site, Northern Quebec, Canada

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Abstract

The Lorraine mine site is located in the Temiscamingue region of the Quebec's province, Canada. The mine operated only for four years (1964-1968) for the extraction of Au, Ag, Cu, and Ni, but left behind around 600 000 t of tailings, disposed in a pond area of about 15.5 ha. The unsaturated zone of the tailings, located partially below the water table, has been exposed to the atmosphere for about 30 years, entailing sulfides oxidation and the generation of highly contaminated ferriferous (iron-rich) acid mine drainage (AMD).

In 1998 Quebec's Ministry of Energy and Natural Resources initiated a rehabilitation program of the mine site to limit the AMD generation and environmental damages. The restoration plan mainly consisted of prevention measures of the further weathering of tailings using a multi-layer solid cover (cover with capillary barrier effects), as well as four passive treatment units, for the AMD flowing from the underneath of cover, using one limestone and three dolomite drains.

Reclamation strategy proved effective, but the iron-rich AMD in the tailings pores is only progressively leached out over time. Hence, total Fe concentrations decreased from about 11 g/L, before the construction of the preventive cover, to around 2.5 g/L in 2015, while the pH increased from < 3 to 5-6 within only 12 years. However, in 2011 the replacement of one clogged dolomite drain by a three-unit passive biochemical treatment system (train) was necessary. The new train consisted of two biochemical reactors (filled with mixtures of limestone, poultry manure, compost, wood waste, and sand), separated by a wood ash unit. In addition, in 2012 some design changes, entailed by the very slow flow through the three-unit passive treatment system, were required.

Yearly monitoring, during the warm seasons, was implemented and proved the efficiency of passive biochemical treatment system. Results showed that the pH increased from 5 to 6, and Fe and sulfate removal exceeds 70 % and 57% (from average initial concentrations of about 1.85 g/L and 4.7 g/L), respectively. Few more years would still be necessary for the complete leaching out and passive treatment of the ferriferous AMD.

Key words: Iron-rich AMD, dolomite drains, passive biochemical treatment, three-unit system

Introduction

Mine drainage is the most common water-related problem to mining activities worldwide (Nordstrom et al., 2015). Environmental impacts of acid mine drainage (AMD), characterized by low pH ($-3.6 < pH < 6$) and high concentrations of dissolved metals/metalloids and sulfate, are well documented (Neuman et al., 2014). Several active/passive, physicochemical, and biochemical technologies are available for AMD treatment (USEPA, 2014).

Passive treatment is preferred on closed, abandoned or partially rehabilitated mine sites because of the use of low cost natural / residual materials, as well as of the satisfactory performance (Neculita et al., 2007; USEPA, 2014). Research and field experience showed that passive treatment systems give better performance when used as complement to mine drainage prevention measures, and / or with slightly contaminated waters (USEPA, 2014). However, AMD on several mine sites is often highly contaminated with metal/metalloids, such as Fe, Zn, As etc. (Ayora et al., 2013; Genty et al., 2012a, 2012b; Giloteaux et al., 2013). Hence, a combination of two or more units of passive treatment (multi-step systems or trains) has been developed (Ayora et al., 2013; Genty, 2012). To limit coating/passivation (loss of reactivity) and clogging (loss of permeability) caused by secondary minerals (e.g., gypsum, metal oxides-hydroxides) precipitated during the treatment, innovative approach using reactive mixtures, composed of coarse and highly porous material (wood chips), and fine grain size neutralizing agents (e.g., calcite, magnesia), i.e. dispersed alkaline substrate, have also been developed (Macías et al., 2012; Ayora et al., 2013).

Despite the satisfactory performance of the multi-step treatment systems on some mine sites (e.g., Iberian Belt Pyrite, Spain), additional knowledge is required on their long-term efficiency and the stability of metal-rich produced sludge (Macías et al., 2012). Ongoing laboratory and at field-pilot scale research shows promising results on the performance of this last approach for the remediation of iron-rich AMD on several closed and abandoned mine sites in Quebec, Canada and worldwide (Rakotonimaro et al., 2015).

Methods

Study site

The Lorraine mine site is located in the Témiscamingue region of the Quebec's province, Canada (fig. 1). The mine operated only for four years (1964-1968) for the extraction of Au, Ag, Cu, and Ni, but left behind around 600 000 t of tailings, disposed in a pond area of about 15.5 ha. The unsaturated zone of the tailings, located partially below the water table, has been exposed to the atmosphere for about 30 years, entailing sulfides oxidation and the generation of highly contaminated ferriferous/iron-rich AMD.

In 1998 Quebec's Ministry of Energy and Natural Resources initiated a rehabilitation program of the mine site to limit the AMD generation and environmental damages. The restoration plan mainly consisted of prevention measures of the further weathering of tailings using a multi-layer solid cover (cover with capillary barrier effects), as well as four passive treatment units, for the AMD flowing from the underneath of cover, using one limestone and three dolomite drains.

***Figure 1** Lorraine site localisation (Source: St Arnault et al., 2005).*

Reclamation strategy proved effective (Dagenais et al., 2005), but the iron-rich AMD in the tailings pores is only progressively leached out over time. Hence, total Fe concentrations decreased from about 11 g/L, before the construction of the preventive cover, to around 2.5 g/L in 2015, while the pH increased from < 3 to 5-6 within only 12 years (table 1).

The efficiency of one of the three dolomitic drains deteriorated over time due to the built-up of iron precipitates, which clogged the pore spaces, and limited the flow through (Potvin, 2009).

Table 1 *Average composition of iron-rich AMD between 2011 and 2015.*

pH	Alkalinity	Acidity	Al	Ca	Fe	Mg	Mn	Ni	Pb	S_{total}	Zn
	mg/L of $CaCO_3$		mg/L								
5.8	74	2670	0.50	377	1814	30	6.6	0.62	0.19	1583	0.25

Hence, in 2011 the replacement of this clogged dolomite drain by a three-unit passive biochemical treatment system (train) was necessary (Genty, 2012).

Design of the passive biochemical treatment system

The 3-unit treatment system built on Lorraine mine site (figs. 2 and 3) is composed of two sulfate-reducing passive biofilters (SRPB), separated by a wood ash unit. The system was constructed and operated since August of 2011 to treat the iron-rich AMD, for a design flow rate of 5 l/min. The hydraulic retention time within the three treatment units is of 11 days, and the total volume of 120 m^3.

The aim of the first biofilter (SRPB1 - mixture # 4; see table 2 for composition and component proportions) is to decrease the Eh, neutralize free acidity and partially remove metals. The effluent then feeds a wood ash unit to decrease iron concentrations by sorption and precipitation. Finally, the effluent is polished in the second biofilter (SRPB2 - mixture # 1), which also removes the residual metals.

In 2012 some design changes, entailed by the very slow flow through the treatment system, were required. The changes included the mixing of each part of the system, addition of coarse rock between each two units, and removal of the top soil to allow gas evolving (from organic material decomposition).

Table 2 *Components and proportions of reactive mixture composition (Genty, 2012).*

Components (% dry weight)	Mixture # 1	Mixture # 4
Wood chips	36	18
Manure	17	10
Compost	24	12
Sand	21	10
Calcite	2	50

Figure 2 *Passive treatment system on Lorraine mine site, Quebec, Canada.*

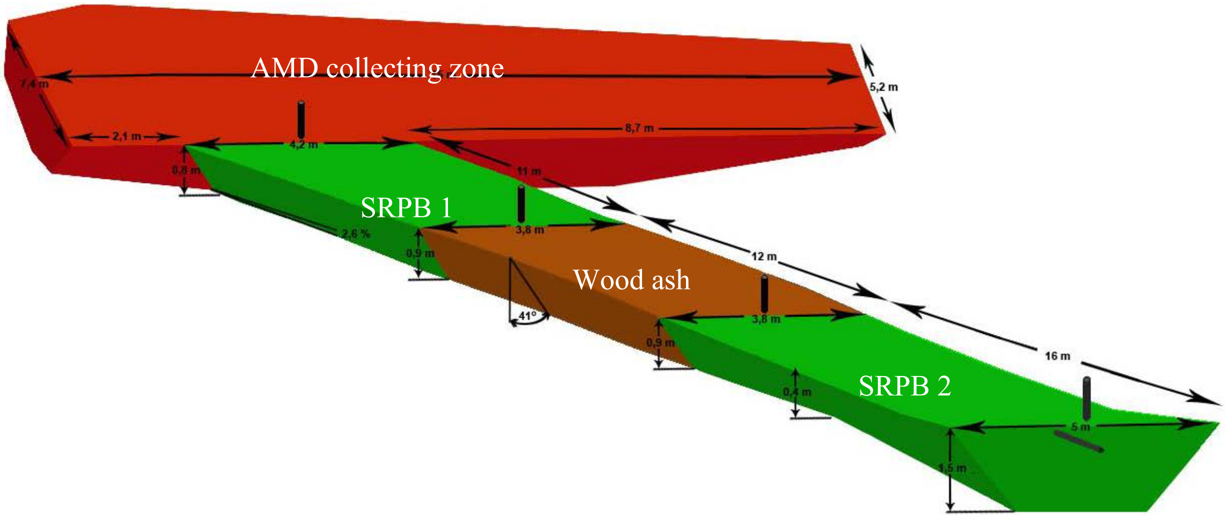

Figure 3 *Model of the passive treatment system constructed on the Lorraine mine site, Quebec, Canada.*

Water sampling and analysis

Water sampling is systematically performed every year, during the warm seasons (usually from May to October). To do so, four piezometers are installed to sample the AMD feed and each treatment unit (fig. 2). Some parameters, such as pH and Eh, are analyzed on site, while preserved samples are transported back to laboratory for other analysis. The pH of sample was determined with an Orion Triode sensor coupled with a Benchtop pH/ISE Meter Orion model 920 (relative precision +/- 0.01 pH) and the Eh (redox potential, values were corrected relative to the standard hydrogen electrode) was measured by a Pt/Ag/AgCl sensor link to a Benchtop pH/ISE Meter Orion 920 (relative precision +/- 0.1 mV). The alkalinity was obtained by titration on non-filtered sample with sulphuric acid 0.02N (relative precision of 1 mg $CaCO_3$/L) and the acidity by titration on non-filtered sample with sodium hydroxide 0.1N (precision of 1 mg $CaCO_3$/L) (APHA, 2012). Filtered samples (with a 0.45 μm filter) used to quantify metal content were acidified with 2% volume with nitric acid (70%) before analysis. The technique used to evaluate metals concentration was the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) using a Perkin Elmer OPTIMA 3100 RL (relative precision of 5%).

Results

Global performance of the passive system

The pH at the exit of the treatment system is in the range 5.8-7 (table 3). However, net acidity (acidity-alkalinity) is high (up to 1010 mg/L of $CaCO_3$) mainly due to the high iron concentration (390 mg/L). Hence, despite a high treatment efficiency (66%) in Fe removal, final concentrations exceed the discharge allowed limits of the Quebec's Directive 019 (table 3). The performance in Mn removal is marginal, with residual concentrations of about 5 mg/L. The presence of high concentrations of iron, which inhibits Mn removal, are partially responsible for this limited efficiency (Neculita et al., 2011). The sulfur concentration is around 610 mg/L (approximately 2070 mg/L of sulfates), which translated in a decrease of 55% of the AMD concentration. In August 2015 the average concentrations of Ni, (<0.004 mg/L), Pb (<0.07 mg/L), and Zn (0.055 mg/L) meet the Directive 019 requirements.

***Table 3** Composition of AMD vs. treated effluent during a 4-year monitoring period (2011-2015).*

Sampling point/others	pH	As	Cu	Fe	Ni	Pb	Zn
				mg/L			
AMD	4.3-6.9	<0.06	<0.003	1799	0.62	0.19	0.26
Treated effluent	5.8-7	<0.01	<0.003	411	0.06	0.03	0.07
Worst values*	5.8	0.18	0.19	1120	0.56	0.094	0.34
Values in August 2015*	6	<0.01	<0.01	389	<0.004	<0.07	0.055
Quebec discharge regulation	6-9	0.2	0.3	3	0.5	0.2	0.5
Compliance with regulation	Yes	Yes	Yes	No	Yes	Yes	Yes

Iron removal in each section of the three-unit passive treatment system

The evolution of iron concentrations over the 4-year monitoring period (2011-2015) shows little variation in the AMD feed, with concentrations toggling yearly between 1 and 3 g/L (fig. 4). This could be seen as an indication of the slow and incomplete flushing-up of the residual contamination of the pore water in the severely weathered tailings (during over 30 years of exposure to water and air) underneath the cover. Once entering the treatment system, iron removal significantly decreased, especially in the SRPB1 and the wood ash unit, sometimes to values as low as below 0.1 mg/L Fe. This high efficiency was recorded prior to 2013. After that, due to the deterioration in the performance of wood ash unit and to some surface overflow, Fe concentrations in the final treated effluent are very high.

Few more years would still be necessary for the complete leaching out and passive treatment of the ferriferous AMD.

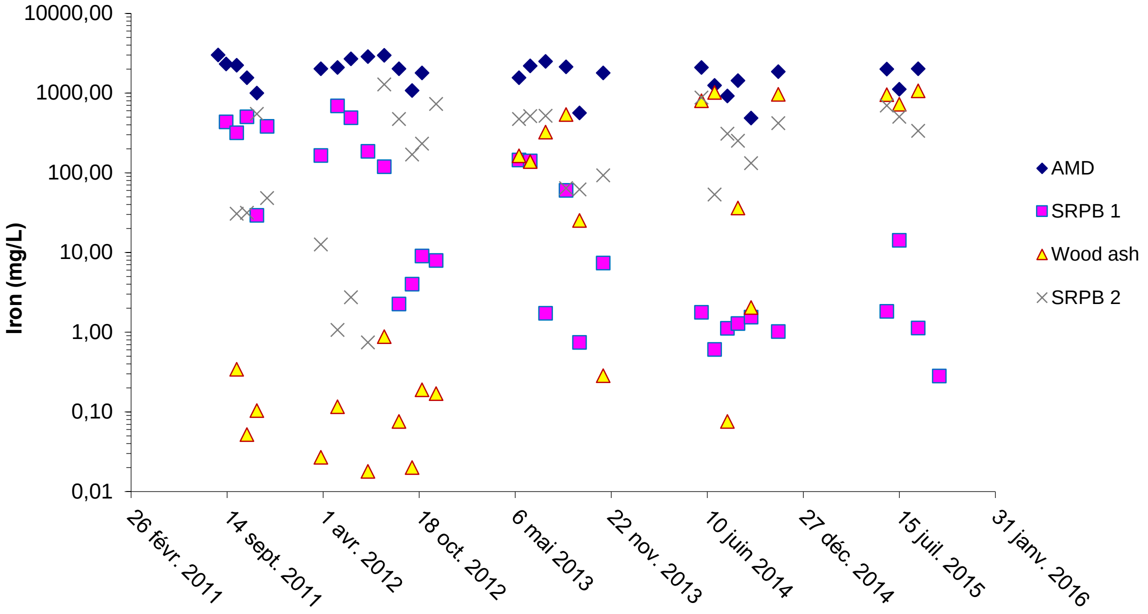

Figure 4 *Iron concentrations in each of the three-unit the passive treatment system constructed on Lorraine mine site, Quebec, Canada.*

Conclusion

The treatment of iron-rich AMD on the Lorraine mine site, Quebec, Canada is performed using a three-unit passive system, installed in 2011. The monitoring of the treatment system performed at various sampling points in the first 48 months of operation shows significant improvement of AMD quality discharged into the environment. The pH and most of the metals meet the discharge regulatory limits of Quebec's Directive 019, with the exception of iron which remains high (despite the decrease from 1800 mg/L to 390 mg/L). Ongoing research work are undertaken at RIME (Research Institute on Mines and Environment)-UQAT (University of Quebec in Abitibi-Temiscamingue) to find viable options to reduce the coating and clogging of the treatment system and improve the overall iron retention performance.

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Microbial communities in passive remediation systems at three abandoned coal mine sites in the United Kingdom

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Abstract

Mining leaves a legacy of potential long-term environmental impact, including ferruginous (and often acidic) waters that are generated within and flow from underground workings, and surface-located waste materials. Passive remediation systems, utilising constructed wetlands, have been widely used in recent years to treat coal mine waters. These utilise the abilities of microorganisms to catalyse redox transformation of iron and sulfur, and to generate alkalinity. The microbial communities in constructed wetlands at three contrasting passive mine water treatment schemes in the United Kingdom were investigated in the present study: (i) a RAPS (Reducing Alkalinity Producing System) to treat net acidic mine water; (ii) a constructed wetland used to treat brackish coal mine drainage; (iii) a passive system used to simultaneously treat coal mine water and secondary treated wastewater effluent. Microorganisms present in water and sediment samples were identified using a combined approach involving cultivation-based and culture-independent methods. While bacteria known to catalyse redox transformations of iron and sulfur were identified in all three sites, the indigenous microbial communities were strongly influenced by the chemistries of the influent mine waters, with bacterial species found in marine waters and those typically found in sewage detected in sites (ii) and (iii), respectively. The diversity of bacteria in mine waters appeared to become increasingly diminished as the water flowed through the passive systems. Archaeal communities in the three sites were dominated by methanogenic species, and some ammonia-oxidizing archaea were also identified. Laboratory experiments demonstrated that the microorganisms present in the sediments were able to remobilise iron (via reductive dissolution of the ferrihydrite-like minerals that accumulated at the water/sediment interface) under conditions of oxygen limitation. This suggested that microbially-catalysed cycling of iron between the ferrous and ferric states is a typical feature of these constructed wetlands, which has implications on their net efficiencies as remediation systems.

Key words: coal mine, passive mine water treatment, bacteria, archaea, molecular biology

Introduction

Waters draining coal and metal mines can have widely different chemical characteristics. One of these, which is often used to delineate many mine waters, is pH. This is a major factor, as it has a high influence on the solubilities of (cationic) metals, rates of (abiotic) oxidation of iron, and on the microflora and macro-organisms that can live in mine waters. At its point of discharge, mine waters frequently contain little or no dissolved oxygen, and the dominant (or even exclusive) form of soluble iron present is ferrous. Oxygenation of mine water streams by diffusion, mass transport and oxygenic photosynthesis creates conditions favourable to the diverse species of bacteria and archaea that can obtain energy from the dissimilatory oxidation of ferrous iron.

Mine waters can be colonized by a wide diversity of microorganisms. Prokaryotic microorganisms (archaea, and particularly bacteria) are found in greater numbers of cells and species (i.e. biodiversity) than eukaryotes, and these have been the focus of a large body of applied and fundamental research.

Microorganisms have a major impact on the behaviour and cycling of metals in the environment. This can be mediated by a variety of opposing mechanisms, including assimilation/adsorption, precipitation/dissolution, oxidation/reduction, and methylation/dealkylation (Johnson 2006). For example, redox changes can result in the production of metal ions that are either more or less soluble under prevailing environmental conditions, leading to their spontaneous precipitation or dissolution. Microbially-catalysed formation of minerals ("biomineralisation") is particularly important in the case of mine water treatment, as this can "lock-up" metals (e.g. iron, manganese and other transition metals) and metalloids (such as arsenic) in forms where they are no longer available to the biosphere, and therefore non-toxic. However, all such biominerals can be subject to dissolution if conditions (e.g. pH, oxygen status) of their local environment changes, for example if anoxic sediments are exposed to air, e.g. as a consequence of lower water levels in constructed wetlands. This means that engineered systems used to immobilise metals and metalloids present in influent mine waters require careful long-term management to avoid the problem or re-release of toxins.

The Coal Authority manages issues related to historic coal mining in the United Kingdom (UK), including pollution caused by mine waters, as well as regulating current mining activities. The Coal Authority operates over 70 mine water treatment schemes (MTWSs) across the UK, the majority of which are passive treatment systems, often using constructed wetlands. Passive systems are perceived as low cost operations although they have limitations (e.g. Johnson and Hallberg 2002). Where mine waters are net acidic, passive MWTSs require an additional source of alkalinity as part of the remediation protocol. This may be derived from microbiologically-catalysed reactions (e.g. sulfate reduction, at pH <7) or, at least in part, from the dissolution of basic minerals. This is the case with SAPS (successive alkalinity-producing systems) and RAPS (reducing and alkalinity producing systems; Younger et al. 2003).

Microbial activity is key to the success of passive mine water treatment. Bacteria and other microorganisms catalyse redox transformations of metals, such as iron and manganese, and of sulfur; these reactions have a major influence on the effectiveness of passive treatment operations. It is pertinent, therefore to understand the composition and dynamics of microbial communities that colonise constructed wetlands used to treat mine waters. However, there have been relatively few reports on the microbial communities that colonise these constructed sites (Johnson et al. 2002). The current study has investigated the microbial communities in water and sediments at three passive MWTSs located at abandoned coal mine sites in England and Wales, and has examined the potential for the cycling of iron in these anthropogenic environments.

Methods

Sampling

Based on data provided by the Coal Authority, three contrasting mine sites in England and Wales were selected for this study: (i) Tan-y-Garn, located adjacent to the Cathan river in Garnswllt (51°46'10.9"N, 3°59'9.42 W; Wales), where the treatment system uses a RAPS (Reducing Alkalinity Producing System) technology; (ii) Horden, located in a coastal area of Co. Durham (54°46'18.02 N, 1°18'36.92 W; England) where the MWTS is used to treat brackish coal mine drainage; (iii) Lamesley, near the Team river in Co. Durham (54°54'18.92 N, 1°35'58.62 W; England), which was the first constructed wetland in the UK to be used for the simultaneous treatment of coal mine water and secondary-treated wastewater effluent. Water samples from the three sites above described were collected in October 2014 at different locations within the passive MWTSs, as described below.

Water samples were taken at Tan-y-Garn MWTS at the (i) inflow (water flowing into the RAPS system); (ii) mid-flow (water draining the RAPS); (iii) outflow (water draining the final reed-bed), (fig.1). In addition, two solid samples were removed (for laboratory analysis and experimental work) from the RAPS system itself (fig.1). These were: (i) ochreous material (ferric iron-rich), which had accumulated on the surface of the RAPS, and (ii) residual black organic compost material, taken from about 15 cm depth within the RAPS. A similar sampling regime was adopted at Horden MWTS to that used at Tan-y-Garn (3 water samples taken from similar points, plus two solid (ochre and compost) samples from the primary wetland (fig. 1). Sampling at the Lamesley co-treatment site differed from the approach used at the other two sites. Unfortunately, the site had suffered a serious act of vandalism the previous night, resulting in the temporary cessation of mine water pumping. On the day of sampling only secondary treated wastewater (sewage water) was being discharged into the site. It was therefore deemed to be inappropriate to use the same sampling protocol to that used at Tan-y-Garn and at Horden; only a single water sample was taken (that draining the final reed-bed; fig.1). However, ochre and compost samples were removed from the first reed-bed as before, as these were considered not be have been significantly impacted by the temporary cessation of mine water input.

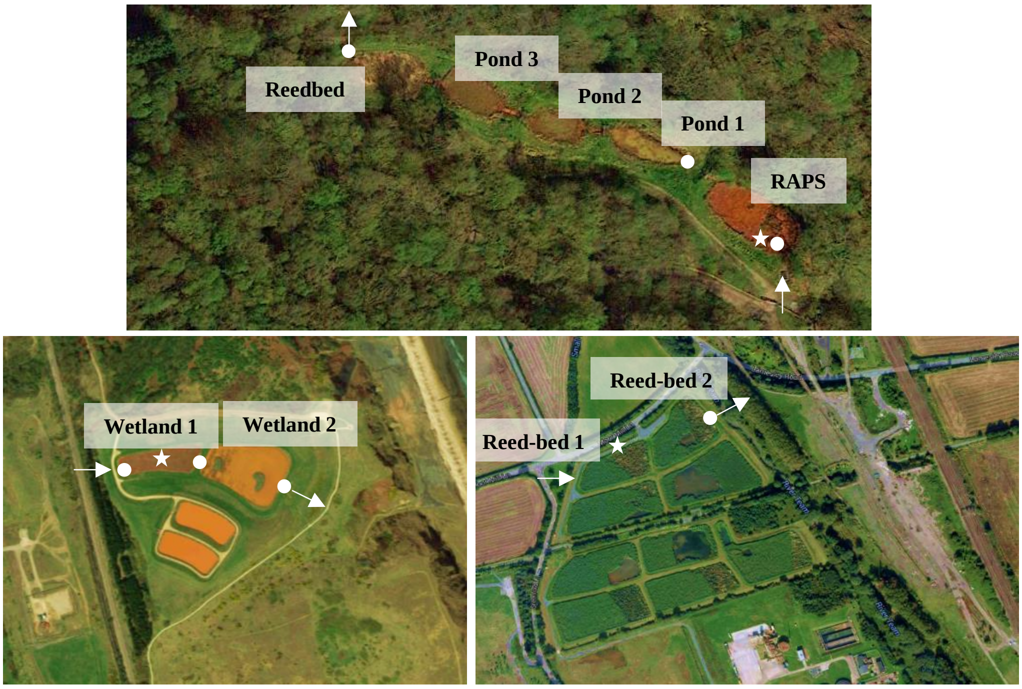

Figure 1. *Aerial view of sampling at water (circles) and sediment (stars) samples were taken at the Tan-y-Garn (top), Horden (bottom left) and Lamesley (bottom right) sites. Arrows indicate water flow. Aerial photographs taken from Google Earth.*

Physico-chemical analysis

Temperature (T), redox potential (ORP), pH value, conductivity (SC) and concentration of dissolved oxygen (DO) in all water samples were measured in situ using a Multi-parameter System (YSI 556 MPS). Laboratory analyses of sulfate, iron, dissolved organic carbon (DOC), and transition metals were carried out 2-4 days after sampling on cold-stored acidified, filtered mine waters. Sulfate was measured using a Dionex IC25 ion chromatograph with an Ion Pac AS-11 column equipped with a conductivity detector. Ferrous iron and total iron concentrations in water samples were determined using the Ferrozine method (Stookey 1970). Transition metals were measured with a Dionex-320 ion chromatograph fitted with an IonPAC® CS5A column and an AD absorbance detector. Concentrations of DOC were measured using a LABTOC DOC analyzer (Pollution and Process Monitoring, UK).

Microbiological analysis

Cultivation-based microbiological analysis of water and sediment samples was restricted to looking for the presence of acidophilic bacteria that catalyse redox transformations of iron. Water samples (50 µL) and sediment samples from the three mine sites were spread onto a variety of solid overlay media designed to promote the growth of different physiological groups of acidophilic microorganisms (Johnson and Hallberg 2007). The inoculated plates were incubated aerobically at 30°C for up to 4 weeks. Colonies were identified as iron-oxidizers (ferric iron-encrusted) or potential iron-reducers, and their identities confirmed by amplifying and sequencing their 16S rRNA genes.

Biomolecular analysis of indigenous microbial populations

In order to avoid problems endemic to cultivation-based analysis of microbial populations, a biomolecular approach was used based on the amplification of a target gene (the 16S rRNA gene) using the DNA present in microbial biomass collected on membranes by filtering water samples, or present in ochre and compost samples taken from the RAPS, wetland 1 or reed-bed 1 in each of the test sites (Tan-y-Garn, Horden and Lamesley, respectively). This involved two separate but complimentary analyses:

(i) community profiles, using T-RFLP (terminal restriction enzyme fragment length polymorphism); (ii) construction and analysis of clone libraries using amplified 16S rRNA genes.

DNA was extracted from the mine water filtrates and sediment samples using MoBio “ultraclean soil DNA isolation kits”, following the manufacturer’s instructions. Terminal restriction enzyme fragment length polymorphism (T-RFLP) analysis of amplified genes was carried out to assess the microbial diversity of samples as described by Kay et al. (2013), and the T-RFs (terminal restriction fragments) identified by comparing them with those in the databank maintained at Bangor University.

Clone libraries were constructed to identify bacterial and archaeal composition of one sample from each mine site. The most diverse sample at each sites, as determined by the complexities of their T-RFLP profiles, were selected for library construction. For bacterial clone libraries these were: (i) Tan-y-Garn, mid-flow (for both bacterial and archaeal clone libraries); (ii) Horden, mid-flow (bacterial) and inflow (archaeal); (iii) Lamesley, outflow (bacterial and archaeal). The protocols followed during the construction of the clone libraries are described in Falagán et al. (2014).

Mesocosms set up

Samples of ochre and compost were suspended, separately, in pH 7 basal salts solution to produce homogeneous slurries, 1 mL of which were dispensed into sterile foam-bunged 20 mL universal bottles (i.e. each bottle received 1 mL of ochre slurry and 1 mL of compost slurry from a particular wetland site). Different volumes of glucose were added, equivalent to 0, or 10, 100 or 1000 mg dissolved organic carbon (DOC)/L, and the volumes in each bottle were made up to 10 mL with sterile pH 7 basal salts solution. Each test was carried out in duplicate (24 bottles in total). Samples were removed for analysis of ferrous iron (using the Ferrozine assay; Stookey 1970) and then the bottles were placed in jars within which anaerobic environments were generated using the AnaeroGen system (Oxoid, UK). The jars were incubated for 2 weeks at 30°C, after which they were opened, visually examined and photographed, and samples removed again to determine concentrations of soluble ferrous iron.

Results

Physico-chemical analysis of mine water samples

Data obtained in the field and in the laboratory on the chemical analysis of mine waters in different locations in the three sites are shown in table (tab. 1).

Table 1 *Physico-chemical data from the three sites sampled. Units: E_H (mV), T (°C), SC (mS/cm), DO (%), DOC, metals and sulfate (mg/L). I, inflow; M, mid-flow; O, outflow; <, below detection limit; n.a., not analysed.*

	pH	E_H	T	SC	DO	DOC	Fe^{2+}	Fe^{3+}	Fe_{total}	SO_4^{2-}-S	Mn	Zn	Co
Tan-y-Garn													
I	5.14	327	11.0	0.397	21	3.24	37.4	2.8	40.2	72	2.7	0.3	2.3
M	6.46	256	11.1	0.470	45	2.00	11.2	<	11.2	45	1.4	0.4	0.3
O	5.80	394	10.9	0.367	68	2.34	<	<	<	47	<	<	<
Horden													
I	6.45	282	14.1	35.29	88	1.11	21.2	16.2	37.4	1020	2.9	0.3	1.0
M	6.99	203	14.1	31.10	88	0.24	6.1	3.9	10.1	917	2.7	0.1	0.2
O	7.48	238	13.5	34.98	90	0.23	1.7	6.7	8.4	949	2.8	0.1	<
Lamesley													
I	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<	0.9	0.9	n.a.	n.a.	n.a.	n.a.
M	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
O	7.15	336	12.9	1.27	68	6.87	<	0.8	0.8	22	0.3	<	<

Microbial community compositions

Few isolates were obtained from the water and sediment samples. Only two acidophilic bacteria were obtained, a strain of the recently-described species “*Acidibacillus ferrooxidans*”, which catalyzes both the oxidation and reduction of iron (isolated from the compost collected at Horden), and strains of the iron-reducing heterotrophic acidophile *Acidiphilium* sp. which were isolated from all the mine sites.

Other bacterial isolates obtained from Tan-y-Garn and Lamesley sites were either known pathogens (e.g. *Rhanella aqualitis*) or closely related to pathogenic bacteria.

Tan-y-Garn MWTS

The T-RFLP profiles obtained from amplified bacterial 16S rRNA (fig. 2) showed that the bacterial community in the mine water that flowed into the site was highly heterogeneous, but became increasingly less diverse as the water flowed through the passive system. Over 40% of the total T-RFs in water draining the site was accounted for by a single T-RF (and therefore possibly a single bacterial species; 226 ± 2 nt; HaeIII digests) and three other T-RFs of 10-15% relative abundance each, were also present. Bacteria closely related to species known to catalyze the dissimilatory reduction of ferric iron (*Geobacter psychrophilus*), oxidation of sulfur and reduction of nitrate (*Sulfuricella denitrificans*), methylotrophs (methane/methanol-oxidizers) and anaerobic aromatic compound-degraders (*Syntrophorhabdus* sp.) were detected. Over 50% of the T-RFs for archaea in the mine water samples were accounted for by a single T-RF (213 ± 2 nt; HaeIII digests) although analysis of the sequences of clones obtained of archaea indicated a more heterogeneous archaeal community. Species closely related to those identified as ammonium-oxidizers (*Nitrosopumilus maritimus*) and methanogens (e.g. *Methanomassiliicoccus luminyensis*) were detected, and corresponded to dominant T-RFs in T-RFLP profiles.

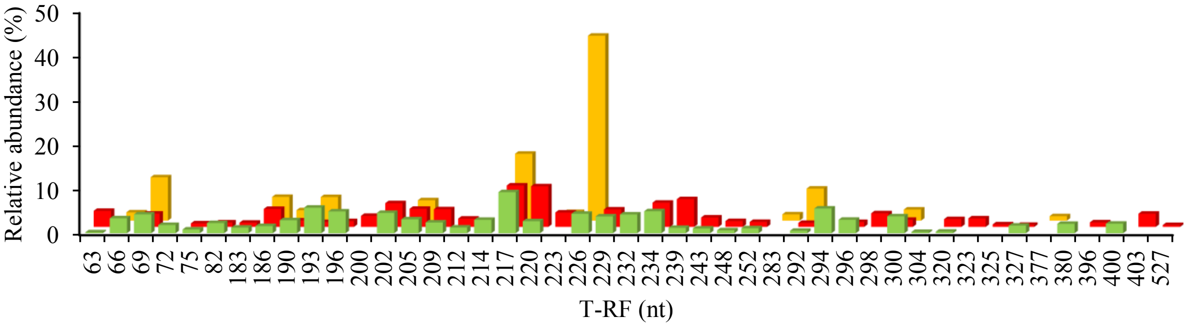

Figure 2 *T-RFLP profiles of HaeIII-digested bacterial 16S rRNA genes obtained from DNA extracted from harvested biomass from water flowing into the RAPS (green bars), water flowing out the RAPS (red bars) and water flowing out the final reed-bed (yellow), at the Tan-y-Garn MWTS.*

Horden MWTS

As with Tan-y-Garn, the bacterial community became increasingly less diverse as the water flowed through the wetland, though in this case this was due to the increasing dominance of a single T-RF of 192 ± 2 nt (HaeIII digests) which accounted for 65% of the total in the water discharged from the site. Analysis of the sequences of clones obtained, showed that most of the clones were related to bacterial species found in marine environments (e.g. *Desulfuromusa ferrireducens*). The bacterial communities at the Horden site were shown to be the most metabolically diverse of those in the three sites investigated. Bacteria identified included those closely related to species known to catalyze the dissimilatory reduction of ferric iron and of manganese (IV) (*Geobacter bemidjiensis*), oxidation of sulfur (*Pelobacter carbinolicus*), ammonium oxidation (*Nitrosomonas europaea*), sulfate reduction (*Desulfuromonas machiganensis*) and nitrate reduction (*Tistrella bauzanensis*). However, in contrast to the bacterial communities, analysis of the sequences of archaeal clones obtained from samples from the Horden site showed that most were closely related to isolates known to be methanogenic (e.g. *Methanomassiliicoccus luminyensis, Methanothermococcus okinawensis, Methanobacterium aarhusense*), and only one related to an ammonium-oxidizer (*Nitrosopumilus maritimus*).

Lamesley MWTS

In contrast to waters sampled at similar points at Tan-y-Garn and Horden, where species diversity appeared to be relatively limited, the T-RFLP profile from Lamesley treated water discharge implied a highly heterogeneous bacterial community, though T-RFs of 192 ± 2 nt and possibly 226 ± 2 nt (the dominant peaks in Horden and Tan-y-Garn, respectively) were also present, albeit in small relative percentages. Analysis of the sequences of clones showed the presence of pathogenic bacteria (*Legionella* spp.) and nitrate reducers (*Aquabacterium commune*), as well as others. Archaea closely related to species known to be methanogens (e.g. *Methanomassiliicoccus hollandica, Methanosarcina* spp.), ammonium-oxidizers (*Nitrososphaera viennensis*), thermophilic (*Ignisphaera aggregans*), and sulfur-reducers (*Hyperthermus butylicus*) were detected.

Mesocosm experiments

The concentration of ferrous iron in the Tan-y-Garn mesocosms prior to being incubated under anaerobic conditions was 0.02 mM (~1 mg/L). However, concentrations increased by over two orders of magnitude in all of the incubated mesocosms, whether or not they were amended with glucose. Final concentrations of ferrous iron were quite similar in non-amended Tan-y-Garn mesocosms and in those containing 10 or 100 mg DOC-glucose/L, though these were significantly higher in both mesocosms that had been amended with 1000 mg DOC-glucose/L (fig. 2). The concentration of ferrous iron in the Horden mesocosms prior to being incubated under anaerobic conditions was 0.009 mM (~ 0.5 mg/L). As with the Tan-y-Garn samples, concentrations of ferrous iron increased in all of the Horden mesocosms, though final concentrations were far lower than with the Tan-y-Garn samples. Also in contrast to Tan-y-Garn, the addition of glucose did not appear to have a major impact on final ferrous iron concentrations, and the smallest of these were found in mesocosms that had been amended with the largest concentration (1000 mg DOC-glucose/L) used (fig. 2). The concentration of ferrous iron in the Lamesley mesocosms prior to being incubated under anaerobic conditions was the lowest of the three MWTSs (0.004 mM; ~0.2 mg/L). Concentrations of ferrous iron increased as a consequence of being incubated under anaerobic conditions with final concentrations being intermediate between those found in Horden and Tan-y-Garn mesocosms. As with the Horden mesocosms and in contrast to Tan-y-Garn, the addition of glucose did not appear to have a major impact on final ferrous iron concentrations (fig. 2), and the smallest of these were found in mesocosms that had been amended with 100 mg DOC-glucose/L.

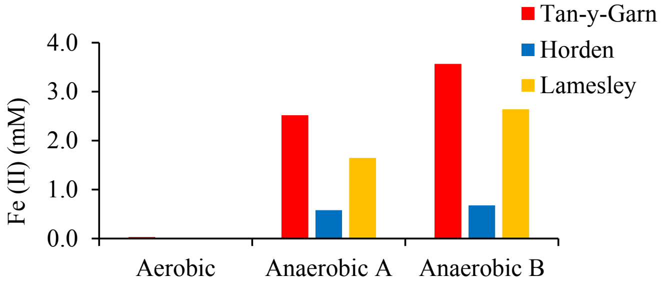

Figure 2 *Comparison of the amounts of ferrous iron generated in mesocosms prepared using compost and ochre from the three MWTS (no glucose was added). Concentrations of soluble ferrous iron present in replicate mesocosms generated after two weeks incubation under anaerobic conditions are shown in comparison to those at the start of the experiment ("aerobic")*

In contrast to iron reduction, evidence for microbially-catalyzed dissimilatory reduction of sulfate was only observed in mesocosms amended with glucose. Visual examination of mescosms following anaerobic incubation showed that in virtually all cases where glucose had been added, the color of the sediment had changed from brown to jet black, a clear indication that amorphous FeS/hydrotroilite ($FeS.nH_2O$) had formed, presumably via bacterial reduction of sulfate in the water to hydrogen sulfide which reacts with ferrous iron at circum-neutral pH ($Fe^{2+} + HS^- \rightarrow FeS + H^+$). Confirmation of biomineralization of iron sulfide came from addition of acid to the blackened sediments, which resulted in a rapid evolution of H_2S.

Discussion

Given the circum-neutral pH of the mine waters being treated at the three sites investigated in the present study, the possibility of detecting acidophilic microorganisms might be expected to be remote. However, given the heterogeneous nature of ochres and composts samples and the known abilities of many species of acidophilic bacteria and archaea to catalyze redox transformations of iron and sulfur, trying to detect some of these microorganisms in the three MWTSs was considered to be a worthwhile exercise. Two representative species of acidophilic bacteria, both known to reduce ferric iron and one know to oxidize ferrous iron, were isolated from the sites. These bacteria did not show up in T-RFLP profiles, which suggests that their numbers were small relative to other bacteria.

Microbial communities within the three MWTS sites were strongly influenced by the chemistry of the water entering the treatment systems. Tan-y-Garn was dominated by bacteria known to be involved in the iron and sulfur cycles. Horden microbial communities were dominated by bacterial species related to those found in marine environments. Lamesley was dominated by bacteria typically found in sewage. Archaeal communities in the three sites were dominated by methanogenic species and archaea involved in the nitrogen cycle (ammonium oxidation, nitrate reduction). Significantly, bacterial diversity in mine waters at both Tan-y-Garn and Horden appeared to become increasingly restricted as the water flowed through the treatment systems.

Large amounts of iron were remobilized by incubating mixtures of composts and ochres under oxygen-free atmospheres. Addition of glucose had little impact on net iron reduction. One of the interesting observations was that, although large amounts of ferrous iron were remobilized (presumably via microbially-catalyzed reductive dissolution of ferrihydrite and other ferric iron minerals present in the accumulation of ochreous materials as the wetlands aged), this varied significantly between samples from the three wetland sites. The reason for this may be due to differences in the nature of the compost materials or the ochres (or both). The former is considered to be more likely, implying that the residual compost at Tan-y-Garn is far less recalcitrant than that at Horden, and that the Lamesley compost falls between the two, where wastewater effluent provides a second source of carbon. Differences in ochre mineralogy cannot be ruled out however, as the susceptibility of ferric iron minerals to reductive dissolution is known to vary with their degrees of crystallinity, with amorphous ferric iron hydroxide being more readily reduced than ferrihydrite, which is in turn more susceptible to reductive dissolution than is goethite etc., (Bridge and Johnson 2000).

The observation that oxygen limitation can result in rapid remobilisation of iron in constructed wetlands used to remediate ferruginous mine waters has important implications in terms of the net efficiencies of these as remediation systems. Anoxic conditions are likely to prevail at the compost layer and during the summer months due to the higher temperatures and growth of wetland plants. The interface of the compost and ochre layers is therefore likely to be an intense zone of redox transformations and cycling of iron between the ferrous and ferric states. This necessarily cuts down the efficiency of the constructed wetlands as sites for iron precipitation, though the fact that concentrations of ferrous iron in waters draining all three sites were still relatively small (though the data for Lamesley were compromised by the site problems on the day of sampling) implies that the sites were working effectively overall. It is conceivable, however, that by eliminating or greatly lowering the potential for biological remobilization of iron, the footprints of the sites could be greatly reduced while at the same time maintaining their net effectiveness. The fact that bacteria known to catalyse the reductive dissolution of ferric iron minerals (*Geobacter* and *Acidiphilium*) as well as others that catalyse the oxidation of ferrous iron (e.g. *Acidibacillus*) provides further evidence that iron cycling is a dynamic process in these environments. The presence of wetland plants is likely to promote iron reduction and remobilization, due to oxygen uptake by plant roots and their additional input of organic carbon (readily metabolizable exudates and lysates, as well as more recalcitrant dead plant matter).

Ferrous iron generated by microorganisms could itself be biomineralized (as FeS) as a consequence of bacterial sulfate reduction, which also requires anoxic conditions. However, data in table (tab. 1) show that concentration of sulfate in waters flowing into and out of the MWTS sites are very similar, indicating that the reduction of sulfate to sulfide is at best a minor process in these environments. It is interesting in this respect that bacterial sulfate reduction was only observed in those mesocosms to which glucose had been added, suggesting that, although sulfate-reducing bacteria were present, most of the DOC present in the wetlands could not be metabolized by these microorganisms.

Conclusions

The microbial communities in the three MWTS examined were determined primarily by their water chemistries; Tan-y-Garn was dominated by bacteria implicated in the iron- and sulfur-cycles; brackish waters at Horden were dominated by salt-tolerant bacteria, the organic carbon-rich waters at Lamesley had large numbers of copiotrophic bacteria (and pathogens). Archaeal community seems less influenced by the water chemistries; methanogens and other archaea involved in the nitrogen cycle were present in the three mine sites.

Iron-metabolising bacteria were identified in relatively small numbers at the three sites. Iron-oxidising bacteria are likely to have only minor impact on net removal of Fe in these circum-neutral pH waters, though they may be important at the micro-aerobic interface between the compost and ochre layers in the wetlands. Bacteria that catalyse the reduction of iron appear to be more abundant and presumably more active. The organic carbon required by these bacteria may come from (i) the compost itself; (ii) exudates from the roots of *Phragmites* and other wetland plants (iii) wastewater effluent in Lamesley MWTS, and (iv) surrounding vegetation. Inputs of organic matter from will tend to promote the reductive dissolution of ferric iron minerals, which may have a negative impact on the net efficiency of iron removal. Effective management of organic carbon sources could improve the efficiency of iron removal in passive mine water treatment. For example, this could imply separating treatment system elements based on non-biological oxidation and precipitation of iron from constructed wetlands used downstream for polishing the mine waters.

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Performance review of an operational Reducing Alkalinity Producing System (RAPS) treating coal mine waters at Tan-y-Garn, Wales

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Abstract

The Coal Authority’s passive coal mine water treatment scheme (MWTS) at Tan-y-Garn in Wales incorporates a Reducing Alkalinity Producing System (RAPS). A long-term performance review has been undertaken after 10 years of continuous operation without any major maintenance. Over the life of the MWTS, raw mine water quality has gradually improved due to flushing. Tan-y-Garn RAPS continues to generate alkalinity and raise mine water pH but the alkalinity generation efficiency has declined over time. Alkalinity generation within the RAPS is predominantly due to limestone dissolution. Sulfate-reducing bacteria are present in the RAPS but net redox transformations of sulfur are interpreted to be of minor significance to the current mine water treatment process. The RAPS removes a significant proportion of iron from the mine water. Short-term variations in iron removal efficiency reflect variations in flow rate and iron loading. Longer-term decline in iron removal efficiency is also occurring despite decreasing iron concentrations in the raw mine water. The performance of the Tan-y-Garn RAPS has declined over the past decade but the system continues to achieve the desired treatment goals. RAPS technology is considered a viable option for the long-term passive treatment of coal mine waters.

Key words: mine water, passive treatment, coal, alkalinity, iron

Introduction

The Coal Authority’s coal mine water treatment scheme (MWTS) at Tan-y-Garn in Wales, commissioned in 2006, incorporates a Reducing Alkalinity Producing System (RAPS). A performance review of the long-term water treatment efficiency of the Tan-y-Garn RAPS has been undertaken after 10 years of continuous operation.

Construction and Operation of Tan-y-Garn RAPS

Tan-y-Garn Colliery was a small drift mine at Garnswllt, Ammanford, Carmarthenshire, Wales, UK. The colliery worked the Ynysarwed seam, part of the Westphalian Upper Coal Measures of the South Wales coalfield. The mine was worked from 1876, abandoned in 1990 and allowed to flood to surface. This resulted in pollution of the nearby watercourse, Afon Cathan. A passive MWTS was constructed by the Coal Authority at Tan-y-Garn to remediate the mine water pollution in the river. The MWTS, commissioned in January 2006, comprises primary RAPS treatment, followed by three small settlement lagoons and a small constructed wetland. The overall size of the MWTS was constrained by the availability of suitable land. The treated water is discharged to the nearby watercourse.

The RAPS has a surface area of around 280 m^2 and is oval in plan view (approximately 30 m by 10 m). The RAPS is designed to produce alkalinity through the dissolution of limestone and by sulfate reduction within the organic materials (Hedin et al. 1994). Anaerobic conditions created by microbial activity in the compost in the RAPS help prevent blinding of the limestone surface by iron precipitation.

The RAPS at Tan-y-Garn MWTS comprises:

- Up to 300 mm maximum depth of supernatant water, with depth controlled by overflow pipes;
- 100 mm thick basal layer of limestone gravel;

- 600 mm thick layer of mixed compost and limestone gravel (mixed 50:50 by volume);
- 100 mm cover layer of compost;
- 225 mm thick underdrainage system, comprising pipes surrounded by silica gravel.

The compost used in the RAPS system met the requirements of the Specification for Composted Materials BSI PAS100:2005. The compost was provided by Swansea City Waste and was classified as a Civic Amenity Green waste. The compost was specified to have a minimum pH of 6 and not to be derived from peat. The limestone was local calcitic Carboniferous Limestone with a maximum clast size of 40 mm. Although the mass of material installed in the RAPS was not accurately recorded, it is estimated that around 180 tonnes of limestone were installed. The compost-limestone mix was designed, building on previous research by Amos & Younger (2003) and Bowden et al. (2005) to optimise the residence time within the RAPS for alkalinity generation and to maintain sufficient hydraulic conductivity to maintain throughflow. No slurry or similar materials were used in order to limit early performance spikes from enhanced sulfate reduction, and also to limit the chance of elevated DOC or nitrogenous concentrations affecting the receiving watercourse. Silica gravel was used in the underdrainage system to help retain structure and hydraulic conductivity, unlike the sacrificial limestone gravel within the reactive media.

Water monitoring has been undertaken at Tan-y-Garn since prior to MWTS commissioning. Water quality monitoring was undertaken ~twice monthly for the first 5 years and then ~monthly thereafter. In situ measurements have been undertaken using calibrated field instruments. Laboratory analysis has been undertaken in accordance with procedures approved by the UK Accreditation Service.

Minimal maintenance activities have been undertaken at Tan-y-Garn MWTS since construction. Near-surface hydrous ferric oxide (HFO) sludge has been removed occasionally but the RAPS compost has not been replaced. Self-seeded vegetation is now growing on top of the RAPS (Fig. 1).

Figure 1 *Photograph of Tan-y-Garn RAPS; note accumulation of HFO at the surface and vegetation growth*

There is not continuous flow monitoring at Tan-y-Garn MWTS but spot readings of flow rates have been obtained between 2006 and 2015 using thin-plate weirs. Mine water flow rates at Tan-y-Garn vary seasonally and in response to significant rainfall events; typical flow rates are in the range 1-2 L/s with peak flows up to 6 L/s recorded. During high flow events, a proportion of the mine water flow bypasses the RAPS with the overflow re-entering the treatment scheme further downstream in the treatment system, where it mixes with the water that has flowed through the RAPS.

Tracer testing at Tan-y-Garn MWTS by Watson et al. (2009) allowed estimation of a 4.4 hour residence time in the reactive media of the RAPS, dropping to less than 2.2 hours residence time during peak flow conditions. These residence times are considerably lower than the minimum residence time of 15 hours within the limestone layer recommended by Watzlaf et al. (2004). However, work by others has also confirmed that alkalinity can be generated more rapidly than suggested by original design guidance; e.g. Trumm et al. (2008) reported that an 8-hour residence time was adequate for a pilot RAPS. Taylor et al. (2016) reported that residence times at Tan-y-Garn RAPS decrease proportionally to increasing flows. The hydraulic conductivity of the Tan-y-Garn RAPS is interpreted to have reduced over time due to compaction and biogeochemical activity (Watson et al. 2009).

Changes in Raw Mine Water Quality at Tan-y-Garn

Raw mine water quality at Tan-y-Garn is gradually improving due to flushing of the shallow mine workings by rainfall. Net acidity has declined over time and the mine water is now only marginally net acidic. The annual average (and minimum) pH of the raw mine water has increased from 5.9 (5.5) in 2006 to 6.5 (6) in 2015. Since MWTS construction, annual average concentrations of total iron have decreased from 47 to 36 mg/L. Similarly, total concentrations of manganese, nickel and zinc have gradually decreased in the raw mine water since 2006. The long-term performance of the Tan-y-Garn RAPS needs to be considered in the context of improving raw mine water quality.

Alkalinity Production within Tan-y-Garn RAPS

Within the RAPS, there is a net gain in alkalinity and mine water pH increases to around 7. The magnitudes of the pH rise and net gain in alkalinity within the RAPS have gradually declined over time (Fig. 2). Despite the decline in RAPS alkalinity generation efficiency over the past decade, the RAPS performance remains sufficient to neutralise the net acidity of the raw mine waters.

Alkalinity generation within the Tan-y-Garn RAPS is predominantly due to limestone dissolution. Alkalinity production due to limestone dissolution is assumed to be proportionally related to the measured increase in calcium concentrations; a 1 mg/L increase in calcium concentrations is assumed to be equivalent to 2.497 mg/L of alkalinity as $CaCO_3$ (Watzlaf et al. 2000). Calcium concentrations increase within the RAPS by around 70 mg/L, equivalent to around 175 mg/L of alkalinity as $CaCO_3$ (Fig. 3). Dissolution of the limestone is interpreted to be occurring at around 7842 kg/annum, based on the average flow rate of 1.42 L/s. The limestone within the RAPS is thus predicted to last around 23 years (e.g. for another 13 years), which is broadly in line with the 25-year design life of the MWTS.

Alkalinity can also be generated within RAPS by microbial sulfate reduction. The microbial community present at Tan-y-Garn MWTS includes bacteria and archaea involved in iron and sulfate cycling, including sulfate-reducing bacteria (Falagan et al. 2016). Sulfate concentrations have decreased within the RAPS on average by 6%, suggesting that some sulfate reduction is occurring. A 1 mg/L decrease in sulfate concentrations is assumed to be equivalent to 1.042 mg/L alkalinity as $CaCO_3$ (Watzlaf et al. 2000). Equivalent alkalinity generation due to sulfate reduction within Tan-y-Garn RAPS has gradually declined over time (Fig. 4). Net redox transformations of sulfur are interpreted to be of minor significance to the current mine water treatment process.

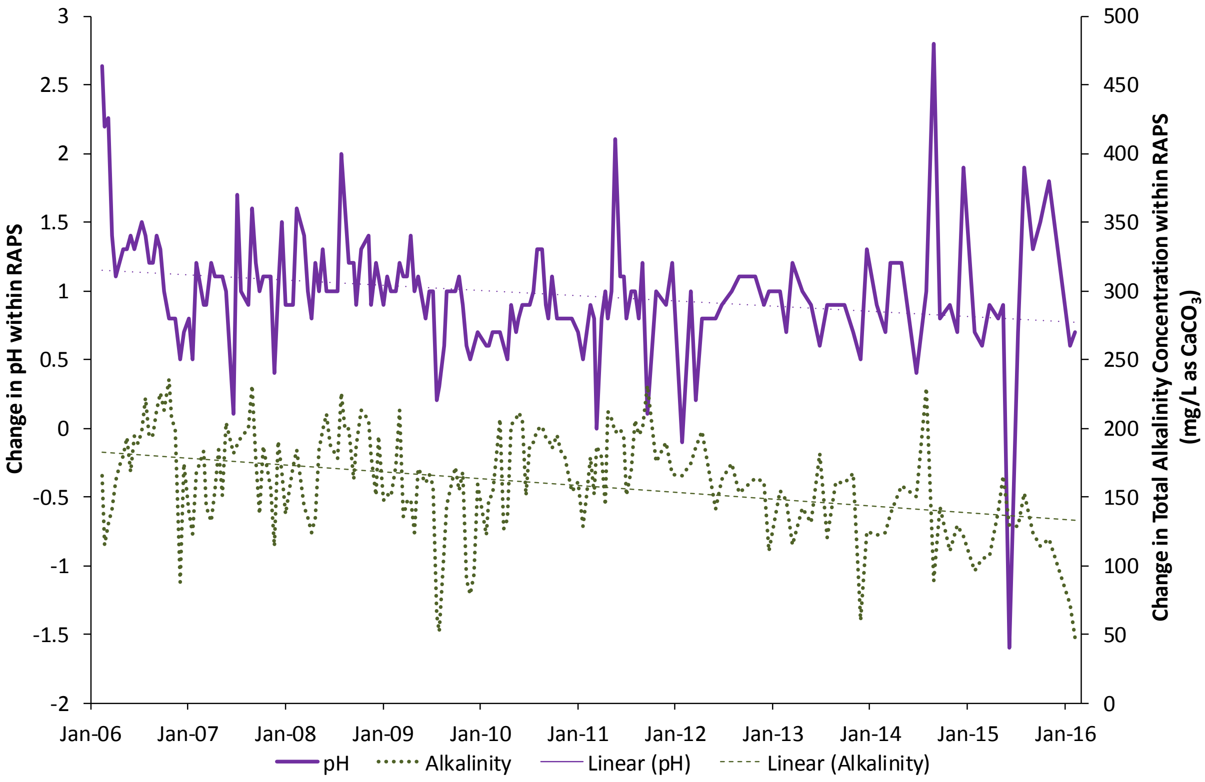

Figure 2 *long-term variations in RAPS performance in relation to pH and total alkalinity (as $CaCO_3$)*

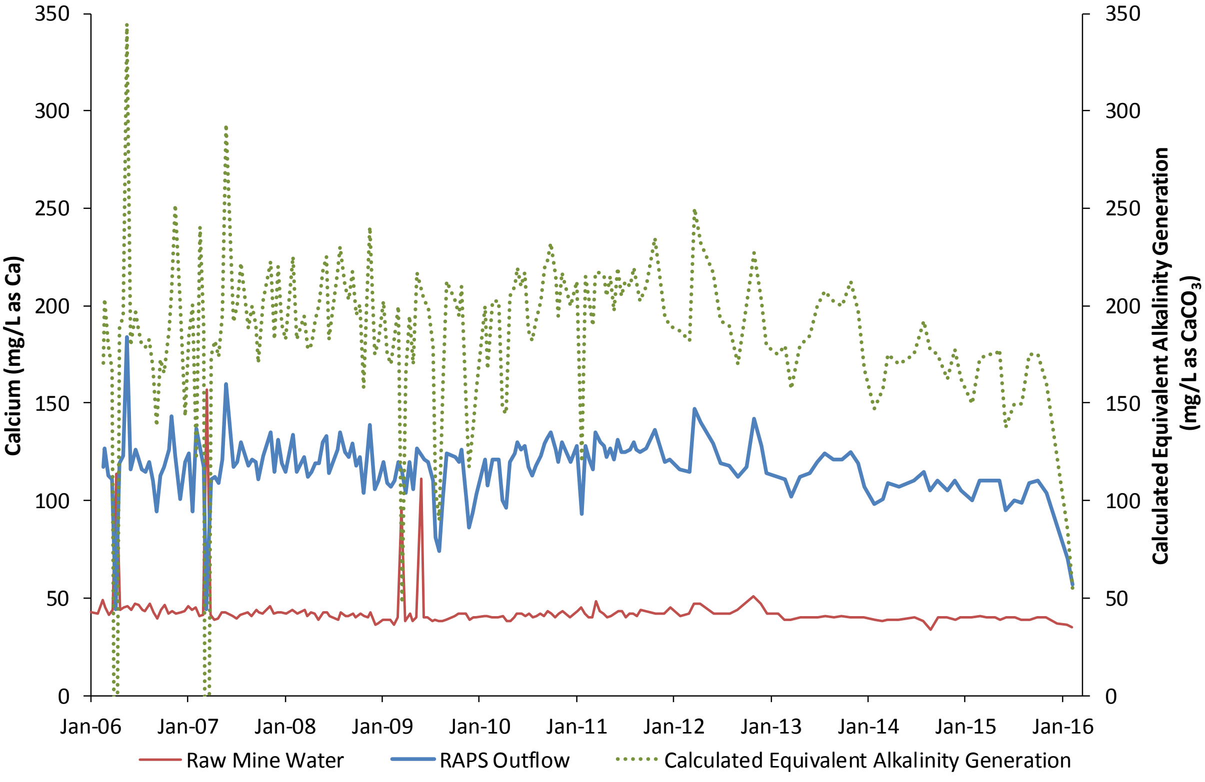

Figure 3 *Calculated equivalent alkalinity generation due to limestone dissolution based on change in calcium concentrations within the RAPS*

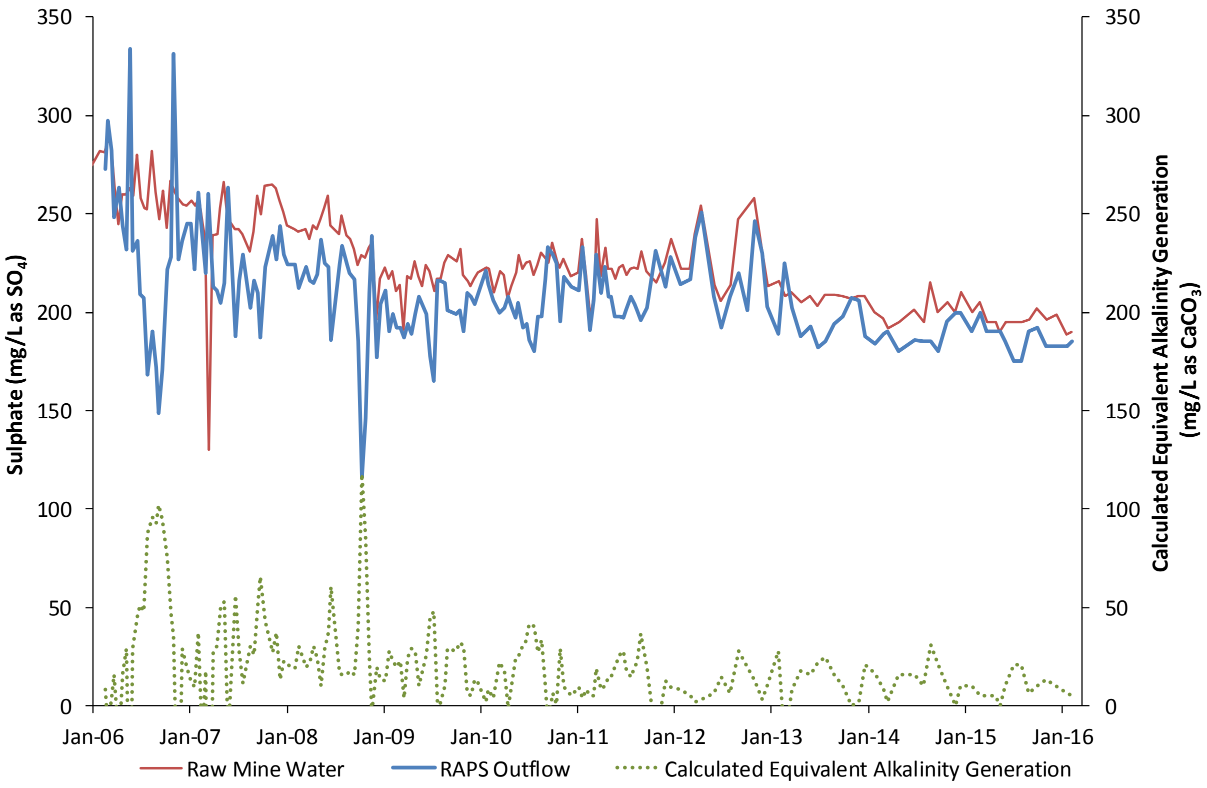

Figure 4 *Calculated equivalent alkalinity generation due to microbial sulfate reduction based on change in sulfate concentrations within the RAPS*

Alkalinity generation patterns observed at Tan-y-Garn MWTS are consistent with those reported by Watzlaf et al. (2000), with alkalinity production due to sulfate reduction declining as the RAPS ages whereas alkalinity production due to limestone dissolution continues. The decrease in hydraulic efficiency previously reported by Watson et al. (2009) is interpreted to explain the observed gradual decline in overall alkalinity generation efficiency.

Mesocosm experiments by Bangor University for the Coal Authority (Falagan et al. 2016) showed that providing an additional bioavailable source of organic carbon (glucose) stimulated bacterial sulfate reduction in incubating compost and HFO samples from Tan-y-Garn RAPS under anaerobic conditions. Therefore, if RAPS performance were to require boosting in future, providing an additional source of bioavailable carbon could stimulate additional alkalinity generation by microbial sulfate reduction. However, the longevity of such stimulus would need to be assessed and the cost-benefits of potential multiple stimuli compared with regeneration of compost/limestone media.

Metal Removal within Tan-y-Garn RAPS

Although RAPS are designed primarily to generate alkalinity and raise pH, the Tan-y-Garn RAPS also removes a significant proportion of the total iron from the mine water (Fig. 5). Iron remains predominantly (93%) in the ferrous state at the RAPS outlet, confirming that reducing conditions are maintained inside the RAPS. Mesocosm experiments by Falagan et al. (2016) showed that ferrous iron concentrations in Tan-y-Garn compost samples increased on incubation under anaerobic conditions, whether or not additional carbon (glucose) was provided.

Iron removal efficiency within the RAPS is temporally variable. Short-term variations in iron removal efficiency correlate with fluctuations in flow rates and thus iron loading (Fig. 6). Longer-term decline in iron removal efficiency has also been observed. Despite the decline in influent concentrations, total iron concentrations at the outlet of the RAPS have gradually increased (Fig. 5). This longer-term trend of declining iron removal efficiency is interpreted to reflect the decline in microbial sulfate reduction as well as decreasing availability of sorption capacity.

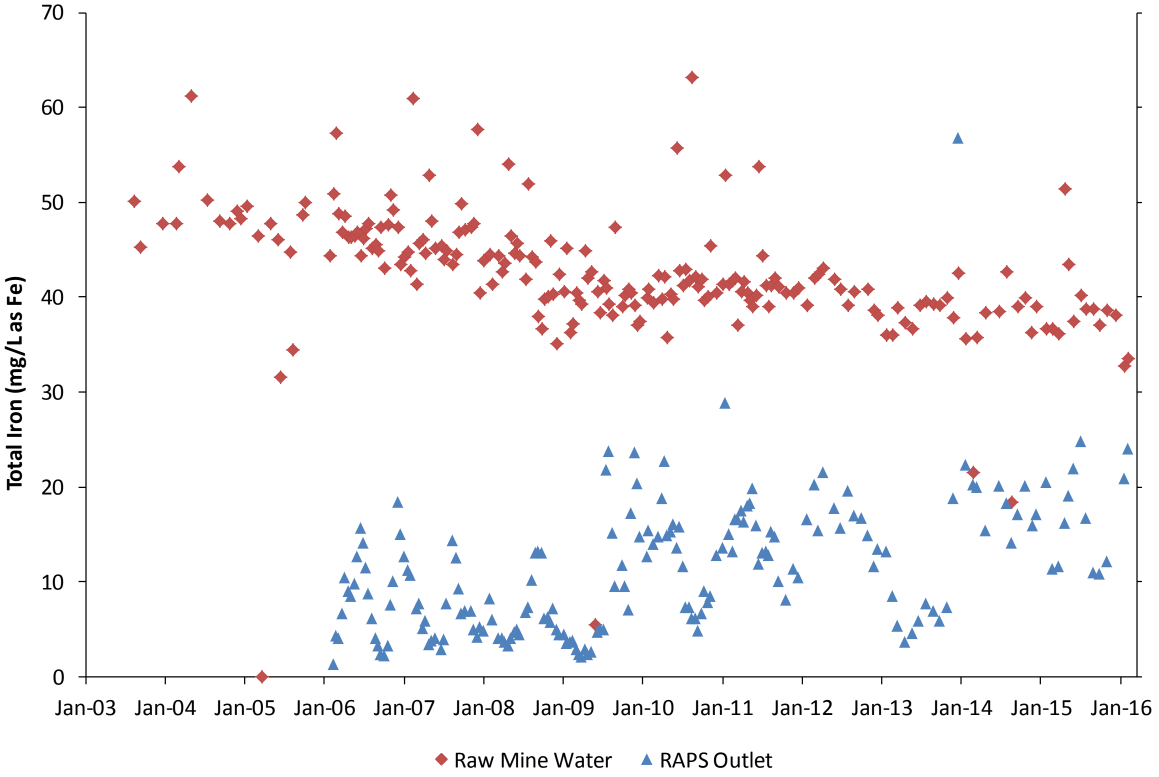

Figure 5*: Long-term variation in total iron concentrations at Tan-y-Garn MWTS*

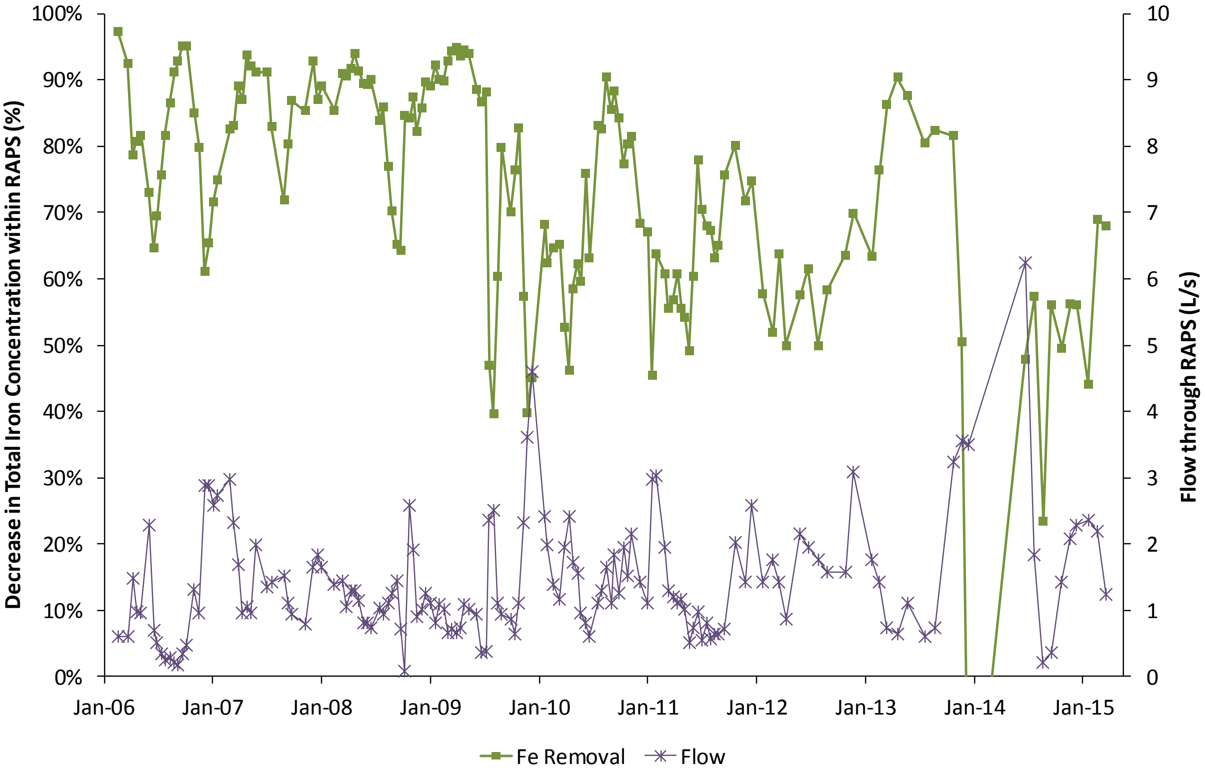

Figure 6*: Variations in iron removal rates and flow rates at Tan-y-Garn MWTS RAPS*

Iron oxidation is occurring near the surface of the RAPS lagoon. HFO build up on the surface of the RAPS has an adverse influence on lagoon hydraulics (Watson et al. 2009). Similar issues have been reported at other RAPS (e.g. Skousen & Ziemkiewicz 2005). Incorporating a settlement lagoon before the RAPS, as was suggested by Watzlaf et al. (2000), might have reduced HFO build up on the top of the RAPS. This might have benefited the long-term hydraulic performance of the RAPS. Incorporating a pre-RAPS settlement lagoon may also help manage short-duration fluctuations in flows following rainfall events, potentially decreasing the proportion of flows bypassing the RAPS.

In addition to removing iron from the mine water, the RAPS also reduces concentrations of other metals. A significant proportion of the aluminium is removed within the RAPS. The average total aluminium concentration at the RAPS outflow is 0.03 mg/L compared with 0.12 mg/L in the raw mine water. Manganese concentrations at the RAPS outflow are 7% lower on average than in the raw mine water. As was observed for total iron, total manganese concentrations at the RAPS outflow exhibit greater variability than is observed in the raw mine waters. RAPS are not usually expected to be effective in removing manganese (Kepler & M^{c}Cleary 1994). Zinc and nickel concentrations are also lower (typically below the reporting limits of the analytical method used, <0.01 mg/L) at the RAPS outflow than in the raw mine water, where average concentrations of zinc and nickel are 0.02 mg/L and 0.03 mg/L respectively. It is considered likely that manganese, nickel and zinc are predominantly removed through sorption or co-precipitation with iron, although zinc and nickel may also precipitate as sulfides within the RAPS.

Conclusions

The RAPS system at Tan-y-Garn MWTS has been operating for 10 years with relatively little maintenance. The RAPS remains functional although performance has gradually declined over time. Alkalinity generation within the RAPS is primarily due to limestone dissolution. Sulfate reduction is currently of negligible importance. The RAPS also removes a significant proportion of iron and other metals. Due to the gradual improvement in raw mine water quality due to flushing, it is possible that it will not be necessary to replace the current RAPS once it has reached the end of its operational life. Traditional passive treatment using settlement lagoons and constructed wetlands may ultimately be sufficient. RAPS technology has been demonstrated to be a viable option for the long-term passive treatment of coal mine waters. The Coal Authority will continue to consider new RAPS as a passive alternative to chemical dosing.

Acknowledgements

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Baffle Curtain Installation to Enhance Treatment Efficiency for Operational Coal Mine Water Treatment Schemes

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Abstract

Passive coal mine water treatment schemes in the United Kingdom typically incorporate settlement lagoons to precipitate iron and collect HFO (hydrous ferric oxide). Laminar flow in the lagoons enables HFO particles to settle out under gravity. Preferential flow paths through the lagoon can have a detrimental effect on treatment efficiency due to short circuiting. A field trial was undertaken at the operational Clough Foot mine water treatment scheme, Yorkshire, to assess the impact of incorporating baffles within an existing operational lagoon. Baffle curtain installation was predicted to improve lagoon hydraulics and enhance treatment performance by creating flow paths to reduce short circuiting of mine water within the lagoon.

The field trial confirmed that baffle curtains can be retrofitted into operational settlement lagoons to improve treatment performance. Concentrations of iron and aluminium at the outlet of the baffled lagoon were lower than at the outlet of the control lagoon. Baffle curtains could be used to enhance treatment scheme performance where a lagoon may be undersized or struggling to treat the mine water to the required metals concentration. Baffle curtains could also be incorporated into the design of new treatment schemes where lagoon size is constrained by the availability of suitable land. Creating vertical flow paths by changing the orientation of the open areas within each baffle curtain might yield higher removal efficiencies but may be more affected by the accumulation of HFO at the base of the lagoons. Incorporating baffle curtains into settlement lagoons offers an effective method of improving the operational efficiency of traditional passive coal mine water treatment schemes.

Key words: mine water, treatment efficiency, baffle curtains

Introduction

The Coal Authority has been treating polluted water from abandoned coal mines in the United Kingdom for the past 20 years by refining methods developed by Hedin et al. (1994) and Tarutis et al. (1999). The Coal Authority operates over 70 mine water treatment schemes and uses both passive and active treatment technologies. Typical treatment schemes use passive technologies, which allow HFO (hydrous ferric oxide) to precipitate and settle out under gravity. Passive mine water treatment schemes generally comprise of an aeration cascade, two settlement lagoons and a polishing aerobic wetland, as recommended by the PIRAMID guidelines (2003).

Land availability proves to be an ongoing problem for the Coal Authority. Passive treatment requires a substantial area of flat land for treatment to be effective. Maximising the efficiency of treatment systems is essential to achieve sufficient discharge water quality with limited land availability (Sapsford and Watson 2011).

HFO deposition is controlled by two rate-limiting steps; oxidation and settlement (Sutton et al. 2015). In conventional schemes oxidation of the mine water is achieved by passing the mine water over a cascade, aiding aeration and degassing. Precipitation commences within circumneutral pH mine waters as soon as oxidation is underway; HFO can be observed to be deposited within the cascade and the pipework. The majority of iron removal, however, occurs within settlement lagoons.

This trial proposed to optimise HFO settlement within lagoons by installing baffle curtains to determine whether improved hydraulics within a lagoon can increase the overall treatment performance of a conventional passive coal mine water treatment scheme. Baffle curtains are designed to optimise flow paths within lagoons, thereby, enhancing the lagoon hydraulics, improving the efficiency of HFO settlement.

The objectives of the study comprise:

- To assess the iron removal performance of the treatment technology;
- To assess the reliability of the technology;
- To identify and assess any constraints on implementation.

Method

Trial Site

Trialling of the baffle curtains was undertaken at the existing Clough Foot mine water treatment scheme (MWTS) in Yorkshire, UK. Clough Foot MWTS commenced treatment in 2012 and treats between 5 and 20 L/s of mine water, utilising typical passive mine water treatment techniques.

Treatment comprises a single large cascade that splits into two short open channels, where peroxide dosing can be conducted, if required. These channels are designed to create turbulence and facilitate mixing around the dosing point after which, the flow is split into two identically sized settlement lagoons, which are operated in a parallel arrangement. After the lagoons, open channels transport the mine water into a constructed wetland for polishing before discharging through a v-notch weir into the adjacent Midgelden Brook.

Clough Foot MWTS was selected for this trial as the parallel arrangement of the settlement lagoons was identified as being ideal for enabling a comparison between the trial system and the control system. An assessment of the baseline monitoring data for the two settlement lagoons was undertaken prior to the commencement of the trail, which confirmed that there was no significant difference in performance between the two lagoons.

Baffle Design & Installation

Three baffle curtains were installed into one treatment lagoon to enhance the lagoon hydraulics and to prevent any short circuiting of the lagoon system. Installation of the plastic baffle curtains took three days to complete. These were retrofitted into the lagoon, whilst it remained fully operational.

The baffle curtains selected by the Coal Authority for this trial were designed to create defined flow paths within the settlement lagoon using a horizontal flow pathway, where the mine water zig zags through the lagoon (Figure 1). An alternative option is a vertical ‘duck and dive’ pathway design, which is likely to be more efficient as it encourages mixing on a vertical scale and eliminates potential ‘dead’ areas within the lagoon. However, the horizontal flow approach was undertaken during the trial as HFO sludge was known to be present at the bottom of the lagoon. Using a vertical flow curtain arrangement could have led to the bottom curtain openings being clogged with sludge and creating a barrier to the mine water flow. A vertical pathway design could also lead to the re-suspension of settled HFO sludge from the base of the lagoon.

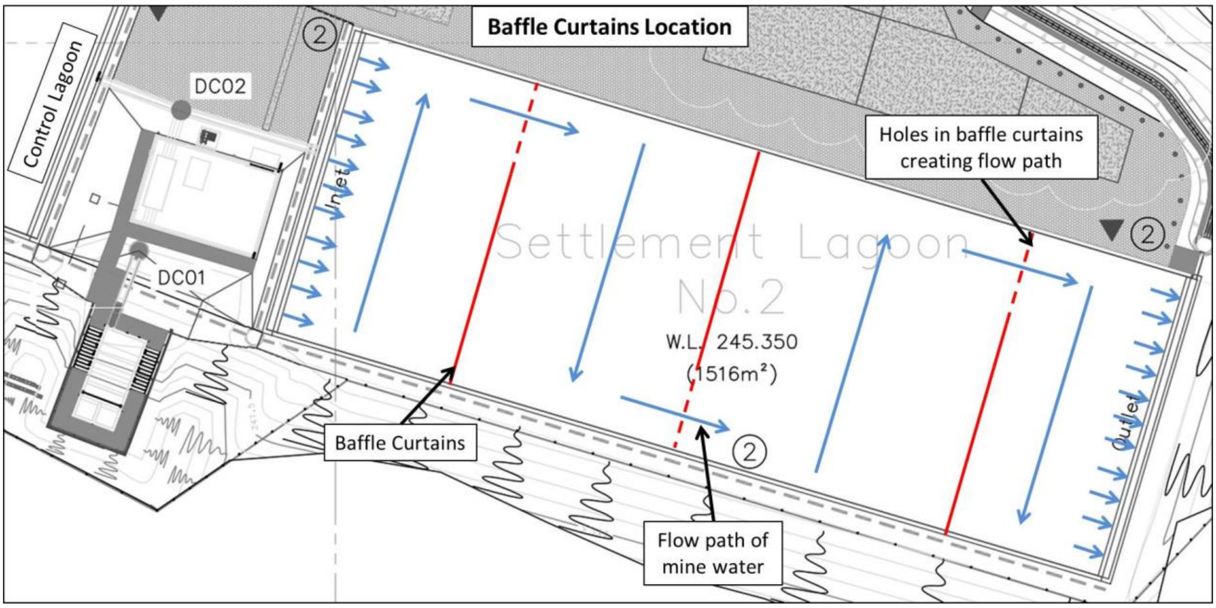

***Figure 1** – Baffle curtain locations, orientations and the resultant mine water flow path through the lagoons*

Power Plastics Ltd. designed, manufactured and installed the baffle curtains (Figure 2). Chains are attached to the curtains that sink down through the previously accumulated HFO sludge at the base of the lagoon, weighing the plastic baffle curtains down and keeping them in place. During installation, this chain is dragged across the base of the lagoon, which temporarily disturbs the settled HFO sludge. There was a hiatus of three weeks following the installation of the baffle curtains prior to monitoring commencing, to allow the HFO sludge, disturbed by the installation process, to re-settle within the lagoon.

Open areas of the baffle curtains comprised laser-cut circles. This circular shape, combined with the use of a stronger material around the edges of these sections, is designed to make the open areas less prone to damage during installation and maintenance than if they were square or rectangular, which could potentially lead to weak points that might tear more readily.

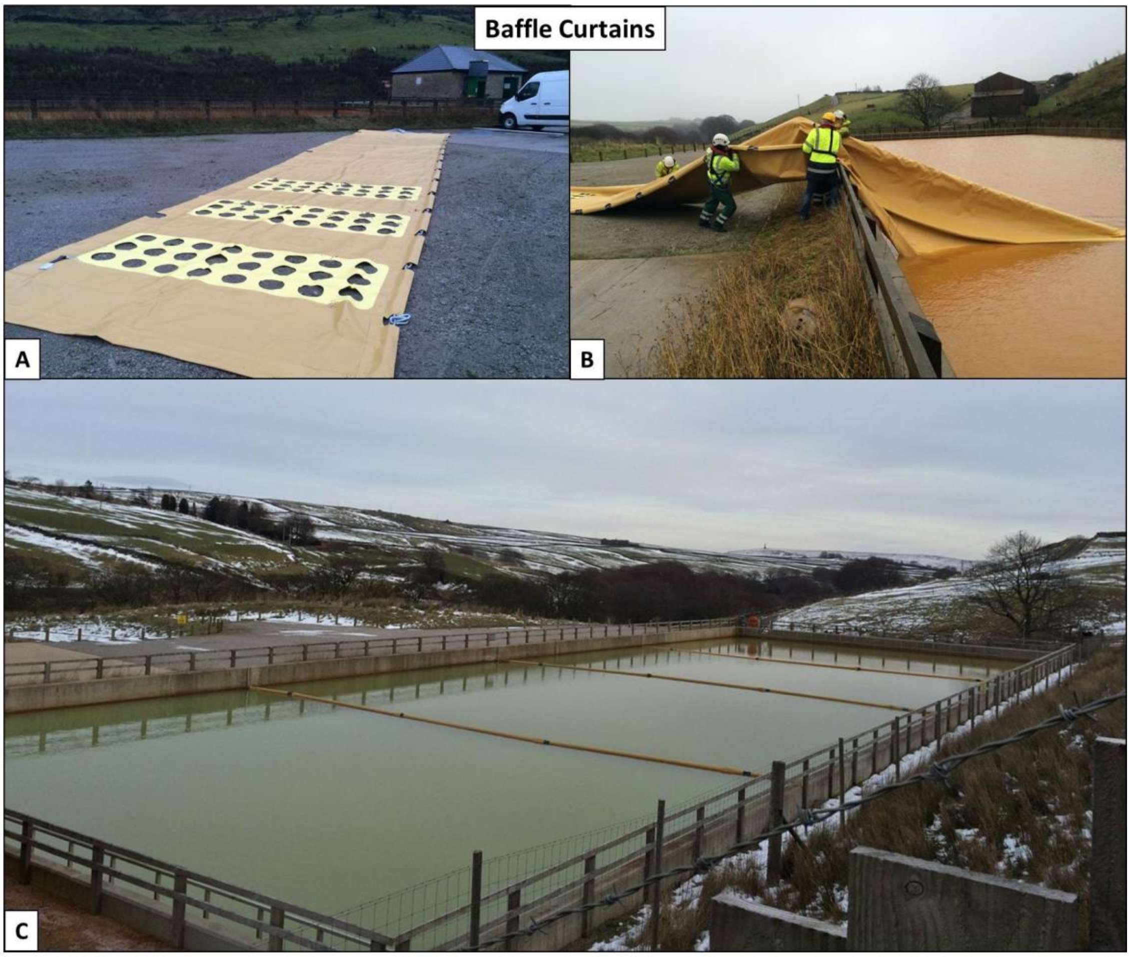

Figure 2 – *Baffle Curtains; A) Baffle curtain prior to installation B) Retrofitting of the baffle curtains C) Baffle curtains after installation*

Monitoring

Field monitoring was undertaken at multiple points throughout the MWTS for the duration of the trial, which was complemented by laboratory analysis of mine water samples. Key parameters analysed were pH, in conjunction with total and dissolved metals. Ideally, both hot and cold acidity would be measured in the field; however, hot acidity measurements were not undertaken during this trial due to health and safety concerns. There is currently no way to measure flow to the inlets and outlets of the lagoons, therefore flow has been assumed to have an equal split between the lagoons. This is considered a reasonable assumption based on the configuration of the lagoon inlets. The laboratory analysis was undertaken in an independent commercial laboratory using UKAS accredited procedures. Intense monitoring of three days per week was undertaken for eight weeks. After this intense monitoring period, routine operational monitoring resumed at the MWTS.

Results

Baffle curtain installation had a positive influence on iron and aluminium removal efficiency in the lagoon. During the main monitoring period for the trial, the baffled test lagoon removed on average 41% more iron (Figure 3) and 34% more aluminium (Figure 4) compared to the control lagoon. During the trial a natural acid flush event occurred. This was due to high volumes of water entering the mine workings, which flooded and scavenged minerals from previously unflooded fire clay workings. This flooding caused the mine water to have a higher than normal mineral acidity, which hindered the performance of the settlement lagoons during this time.

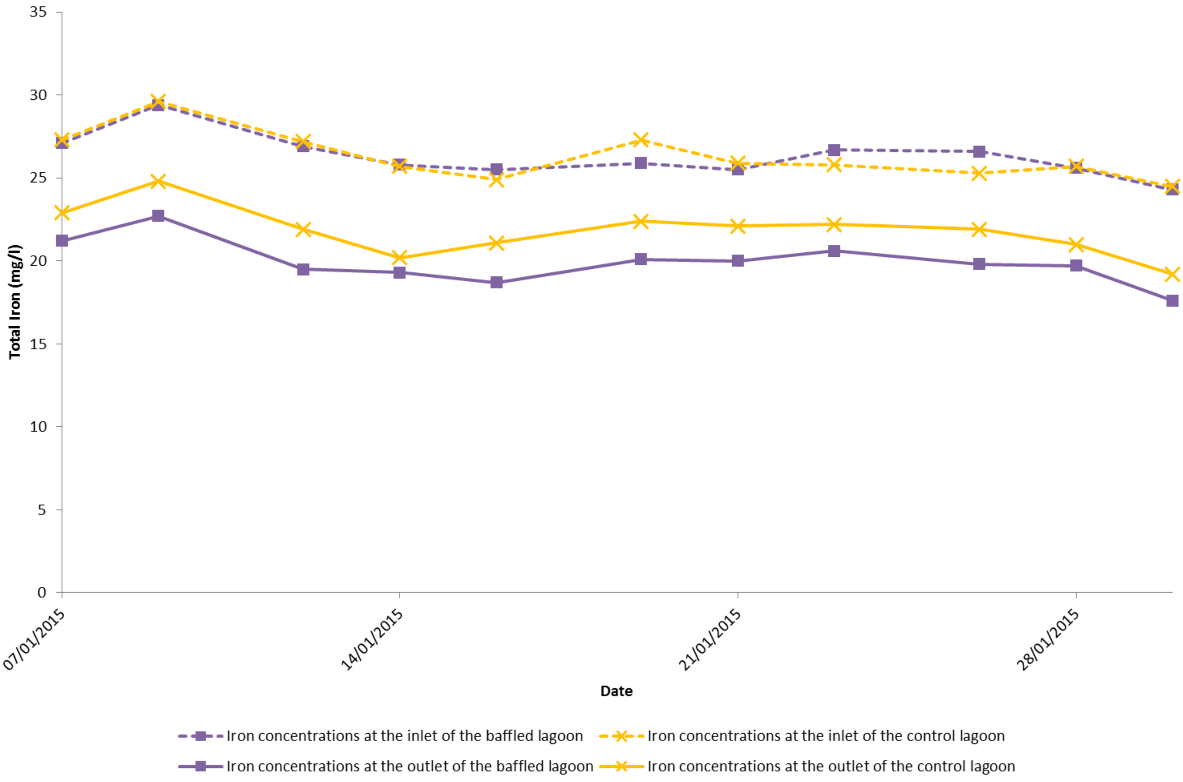

***Figure 3** – Influence of baffle curtains on total iron concentrations*

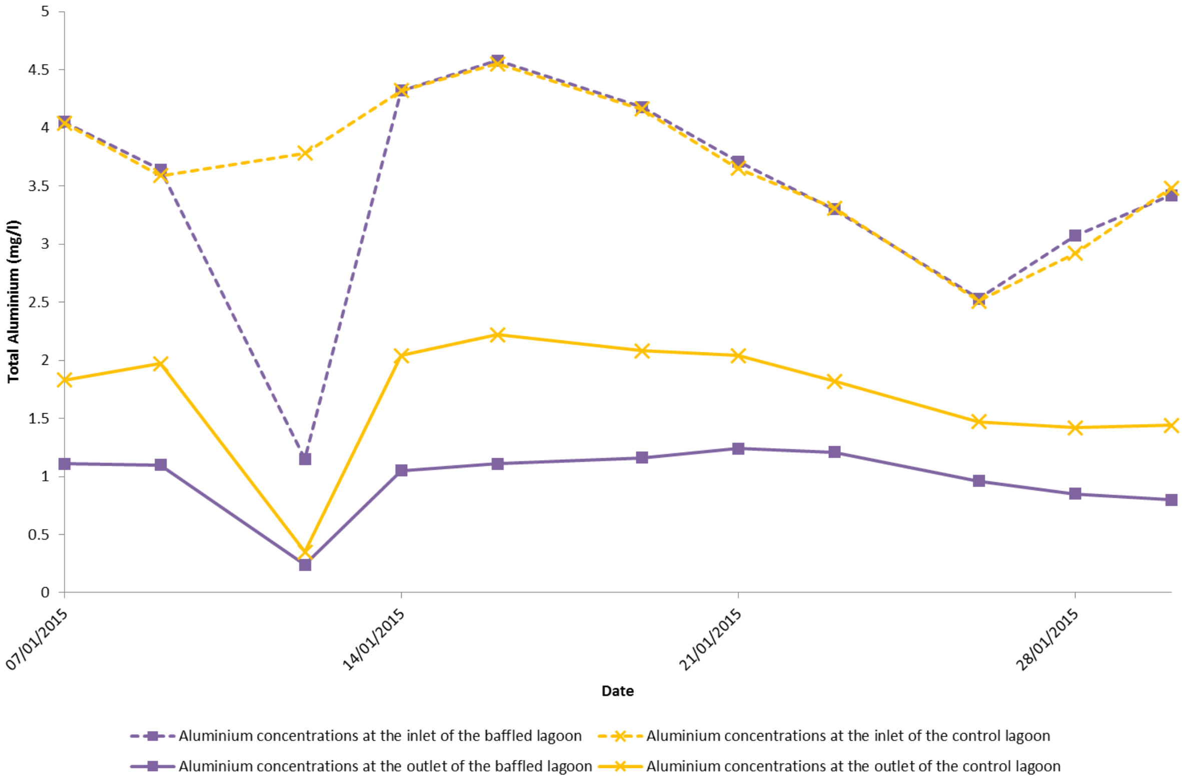

***Figure 4** – Influence of baffle curtains on total aluminium concentrations*

Routine monitoring data was compiled from May 2015 onwards. During this period the mine water returned to normal net-alkaline conditions. During the period May 2015 to October 2015, the test lagoon was on average 10% more efficient than the control lagoon for iron removal (Figure 5). Post-trial data indicates that the baffle curtains are continuing to enhance metal removal efficiency over the longer term, albeit by a lower amount than that observed during the main trial.

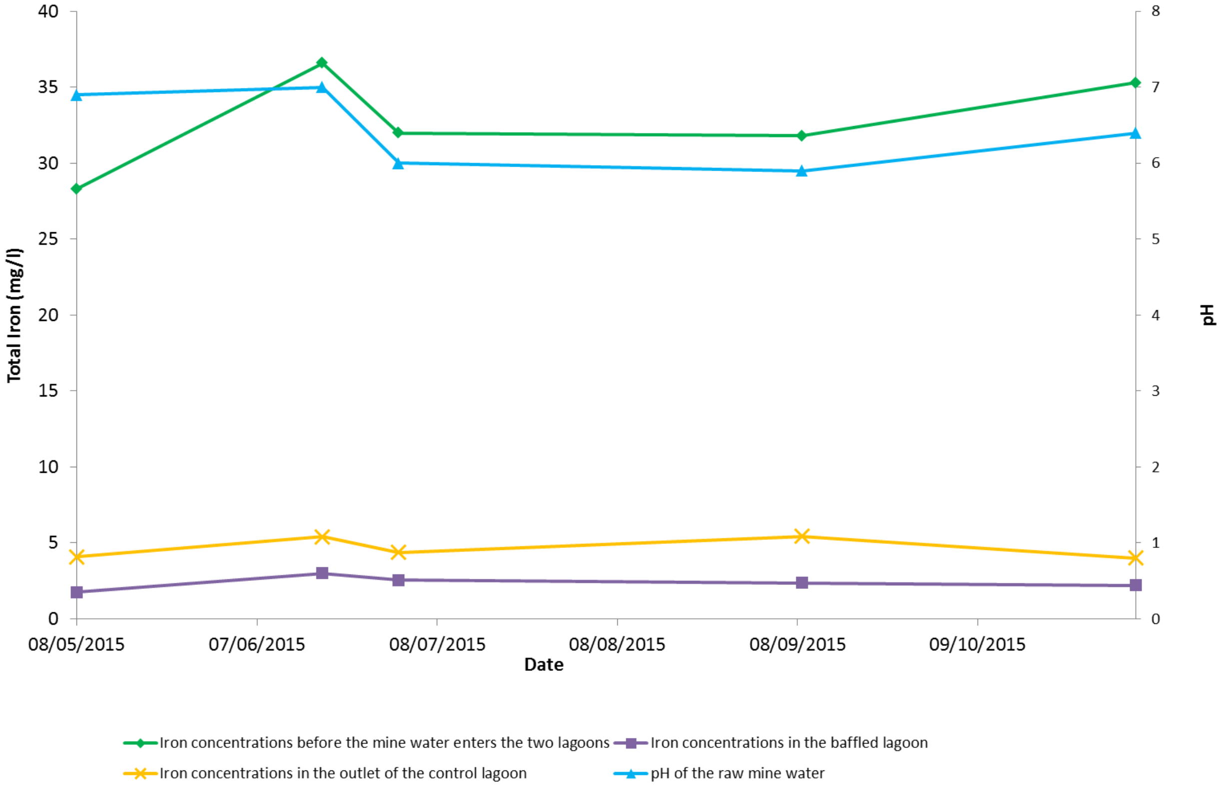

***Figure 5** – Influence of baffle curtains over time*

Manganese removal efficiency was not affected by the installation of the baffle curtains, however, this was expected as the settlement lagoons are not designed to remove manganese (PIRAMID 2003). Nor was there any significant difference in the concentrations of zinc or nickel observed between the test and control lagoons. An improvement in the metal removal efficiency is interpreted to relate to improved lagoon hydraulics aiding settlement of HFO particles (Kusin 2013).

Conclusions

Baffle curtains have had a positive effect on both metal (iron and aluminum) removal and improving lagoon hydraulics. However, even though the residence time and hydraulic efficiency is almost tripled, only 10% betterment is observed when it comes to the removal of metals.

Benefits of improving lagoon hydraulics, in terms of treatment performance, may be constrained by oxidation rates. Column testing undertaken at Clough Foot MWTS using the methodology described in Sutton’s paper (2015), indicated that oxidation rates were the rate limiting factor affecting this particular site. This explains why increasing the residence time at Clough Foot MWTS only achieved relatively minor improvements in metal removal efficiency.

Column testing has been undertaken at numerous Coal Authority sites by Cardiff University (Sutton et al. 2015). Where settlement rate is determined to be the rate limiting factor, increasing residence time within the lagoon and improving the lagoons hydraulic efficiency by adding baffle curtains is expected to result in a greater improvement in metal removal efficiency than was observed during the trial at Clough Foot MWTS.

To increase the hydraulic efficiency of the lagoons, more baffle curtains should be installed. Increasing the number of flow paths will help to decrease ‘dead’ zones within the lagoons. Adding baffle curtains might improve the hydraulic efficiency, however, from a cost perspective, it is better to minimize the number of curtains required to achieve the optimal treatment for the site.

Creating a vertical flow pattern using the baffles may be more efficient as it encourages mixing on a vertical scale, decreasing dead spots, that may be missed using horizontal flow paths. However, the effectiveness of vertical flow pattern baffles may be more influenced by the build-up of HFO sludge at the base of the lagoon. Vertical flow paths are likely to disrupt the build-up of HFO, which can lead to re-suspension of the sludge. Overall, this could lead to a decrease in baffle curtain performance.

Land availability is a key issue for the construction of MWTS’s and often settlement lagoons are undersized for the concentrations of metals that are needed to be removed. Installing baffle curtains at MWTS that are currently undersized and/or that are not performing adequately may provide benefit. Future mine water treatment schemes in areas without sufficient land availability for traditional lagoons may become feasible as smaller lagoons with baffle curtains may be sufficient to achieve the required level of treatment. However, this would need to be reviewed on a case by case basis.

Capturing HFO within settlement lagoons is advantageous when considering whole life costs for mine water treatment. HFO that has been captured within settlement lagoons is likely to be more suitable for re-use or metal recovery than HFO that is captured within an aerobic wetland, which can contain a significant amount of organic matter. Baffle curtains could be used to encourage HFO precipitation in settlement lagoons where there is less potential for contamination, allowing the HFO to be more easily developed into salable products. Aerobic wetland refurbishment is a complex and costly process; once an aerobic wetland has reached its operational capacity it often requires replacing. Reducing the metal loadings reaching the constructed wetlands used for polishing is also considered to be beneficial; by reducing maintenance requirements and extending the operational life before an aerobic wetland desludging is necessary.

Recommendations

Tracer testing should be conducted on the site to confirm that the lagoon hydraulics in the baffled lagoon have an increased hydraulic efficiency. When prioritizing sites for retrofitting curtains, Cardiff University’s column testing methodology (Sutton et al. 2015) should be used and baffles should be installed where HFO settlement is the rate limiting factor. Column testing at Clough Foot MWTS indicated that oxidation was the rate limiting factor; installing baffle curtains into a system where settlement is the rate limiting factor should improve the iron removal rates significantly. For future MWTS designs, the ability to measure flow at both the inlets and outlets of the lagoons should be incorporated.

Acknowledgements

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Passive water purification of pit lakes – a case study from the closed Hammaslahti Cu-Zn-Au mine

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Abstract

The Hammaslahti pit lake study introduces passive water treatment technologies applied in two flooded open pits. Materials consist of physical measurements of the water beds, physical, microbiological and chemical analysis of water samples from selected levels, and microbiological analysis of bottom sediments. Originally the N pit was the pilot site for biological sulphate reduction and it was presumed that sulphate reducing pockets within organic substrate would spread via an adit to the Z pit. Notable differences in geochemistry and the microbial content of waters and bottom sediment of the two pits suggest there is not a hydraulic connection via an adit between the N and Z pit. Water remediation in the N pit is mainly driven by metal sulphide formation, but in the Z pit, the formation of Fe oxyhydroxides and their adsorption capacity facilitate metals retention. The results showed that both oxidizing and reducing bacteria can maintain reactions that retain sulphate and metals via accumulation of stable secondary precipitates at the bottom of the pit. Furthermore, the pit lakes revealed to be challenging sites for biologic sulphate reduction based on-site pit treatment. One reason for inadequate activity of the SRB could be the cold temperature of the pit water, especially at the bottom of the pit. This suggests the need for further study of the behaviour of cold-tolerant microorganisms and their impact on water remediation.

Key words: passive treatment technology, sulphate reducing, pit lake waters, pH, redox

Introduction

The closed Hammaslahti Cu-Zn-Au mine is located in Joensuu, eastern Finland. The open pit mining was started in 1973, followed by underground mining from 1976 to 1986. The Cu-Zn-Au ore is hosted by Proterozoic metaturbidites (arenites, ergillites) subjected to intense silicification and chloritization. In deeper parts of the mine, the black schist is host to remobilized sulphides. The ore body in the N pit mainly consisted of chalcopyrite and the Z ore body in the Z pit of pyrite-pyrrhotite and sphalerite ores with minor chalcopyrite. (Loukola-Ruskeeniemi et al. 1993)

This study presents passive water treatment technologies applied in two flooded open pits (called N and Z pit) of the Hammaslahti mine. The open pits filled with water after mine closure at the beginning of the 1990's. To promote biologic sulphate reduction, pig manure (sludge) as source of bacteria and nutrients, was added several times in the first (N) pit (in 1998, in 2000 and 2004) and followed by additions of slowly decaying wood bark chips (in 2002) and ethanol (in 2005) as carbon and energy source for the bacteria. Originally, it was presumed that sulphate reducing pockets within the organic substrate would spread via an adit from the first (N) to the second pit (Z).

The aims of this study are to examine the physical, chemical and biological quality of the pit waters, microbiology of the bottom sediments, water remediation mechanisms and the subsequent precipitation of metal sulphides (see also Räisänen et al. 2015). Overall, it is of interest to evaluate the applicability of bacteria addition in form of pig manure to activate sulphate reduction.

Methods

Materials for the N and Z pit study consist of physical measurements of whole pit water columns (measurements taken at depth intervals of every 1 to 2 meters), physical, microbiological and chemical analysis of water samples from selected levels, and microbial analysis of bottom sediments (Räisänen et al. 2015). On-site filtered pit water samples and bottom pit sediment samples from both pits were taken in March and in September in 2014. Sampling methods and the pretreatment of water and sediment samples were described detailed in the web publication by Räisänen et al. (2015).

Alkalinity of the pit water samples was measured on-site using a Hach digital titrator with 0.1600 N or 1.600 N H_2SO_4 to an end point of 4.5. Temperature, pH, redox potential, electrical conductivity (EC), oxygen concentration and oxygen saturation of waters at each sampling site were measured on-site with a multiparameter field meter (Räisänen et al. 2015).

Concentrations of Br, F, Cl, NO_3 and SO_4 in the water samples were determined with ion chromatography and concentrations of 34 elements were analyzed using ICP-OES or MS-ICP. Concentrations of dissolved organic carbon and total carbon were measured with a C analyzer. The content of solids was determined by gravimetric method (SFS-EN 872:2005). Concentrations of Fe^{2+} were measured with a spectrophotometer. All the laboratory analyses were carried out at the FINAS-accredited testing laboratory of Labtium Ltd.

The microbiology was assessed from the water and sediment samples collected in March 2014. For the characterization of microbial communities, microbial DNA was isolated from the samples using the NucleoSpin Soil DNA extraction kit from two replicates of each sample. First, the microbial biomass was collected on 0.2 µm pore-size cellulose acetate filters (Corning) by vacuum suction, where after the filters were cut out from the funnels using sterile scalpels and forceps, put in to sterile 50-mL plastic screw cap tubes (Corning) and stored at -80°C until DNA extraction. The 1L watery sediment samples were left stationary for several hours until the sediment had set on the bottom of the bottles. The water was carefully decanted and the sediment collected in 50-mL sterile plastic screw cap tubes (Corning). Excess water was separated from the sediment by centrifugation and DNA was extracted from 0.5 g samples. In the DNA extraction, one replicate sample was extracted with buffer SL1 and the other with SL2. Enhancer solution was used in all extractions and the DNA was eluted in 100 µL elution buffer.

The total concentration of bacteria in the pit water was estimated by a DNA based qPCR method, where the number of bacterial taxonomical marker genes for the ribosomal small subunit (ssu) was calculated (as described in Tsitko et al. 2014). The bacterial community composition was determined by characterizing the whole community profile of the bacterial ribosomal ssu genes using high throughput amplicon sequencing on the Iontorrent platform. Bacterial ribosomal ssu genes were amplified with primers S-D-Bact-0341-b-S-17 and S-D-Bact-0785-a-A-21 (Klindworth et. al., 2012), targeting the variable region V3-V4 of the ssu gene. PCR amplification was performed in parallel 25 µl reactions for every sample containing 1x MyTaq^{TM} Red Mix (Bioline, London, UK), 20 pmol of each primer, up to 25 µL molecular-biology-grade water (Sigma) and 2 µL of DNA. The PCR program consisted of an initial denaturation step at 95°C for 3 min, 35 cycles of 15 s at 95°C, 15s at 50°C, and 15 s at 72°C, and a final elongation step of 30 s was performed at 72°C. The PCR products were verified with agarose gel electrophoresis. Amplicons were sent to Ion Torrent sequencing with PGM equipment (Bioser, Oulu, Finland) and amplicons were purified before sequencing at Bioser. The sequence data was analyzed with the QIIME pipeline (Caporaso et al. 2010) using the Greengenes database (DeSantis et al. 2006) for identification of sequence reads.

Results and discussion

Water quality and acid generation in the N and Z pits

The number of bacteria in the N pit water varied between 4.6×10^7 ribosomal ssu gene copies in the oxygenated water and 9.6×10^5 in the anoxic water at 40 m depth in March 2014. In the Z pit water, the number of bacteria varied between 5.1×10^6 - 4.3×10^7, with the lowest number of bacteria at 45 m depth. The bacterial communities in the N and Z pits were very diverse and distinct from each other (figs. 1 and 2). The bacterial community in the N pit was dominated by putative sulphur oxidizing and iron reducing Burkholderiales in the surface water (fig. 1, Farkas et al. 2013). Members of the uncultured and uncharacterized group Sbla14 betaproteobacteria were common at 22 m depth in the N pit water, but their ecological role is not clear. At 40 m depth 8-22% of the bacterial community consisted of epsilonproteobacterial Campylobacterales bacteria, which oxidize sulphides and other oxidized sulphur compounds, and fix carbon from CO_2 (Handley et al. 2014). These bacteria may also be able to oxidize Fe^{2+} (Chan et al. 2013). The water at 40 m depth contained between 6 and 8% SRB (sulphate reducing bacteria) belonging mainly to the Desulfobacterales clade. The bacterial community in the sediment of the N pit belonged almost exclusively (86-93%) to the fermenting Clostridiales bacteria. This group is responsible for the degradation of organic materials, producing acetic and lactic acids, ethanol, and also CO_2 and H_2 gases, which function as carbon and energy sources for the microorganisms.

Burkholderiales bacteria were a major group (14-16%) in the oxygenated water of the Z pit (fig. 2). Gallionellales bacteria were abundant in the water column at the transition zone between oxygenated and oxygen depleted water (fig. 1b). These bacteria are common iron oxidizers that precipitate iron as iron oxyhydroxide (Hallbeck et al. 1993). SRB belonging to deltaproteobacterial clades (Desulfuromonadales and Desulfobacterales) were present only at depths of 35 m and below, and were only below 1% of the total bacterial community. However, their abundance increased slightly in the sediment, where deltaproteobacterial SRB formed 1-2% of the bacterial community. The Bacteroidetes were prominent in the sediment of the Z pit. These bacteria degrade organic matter and thus provide simple organic molecules for the benefit of the whole bacterial community.

In both pits the physical and chemical quality of the surface water above 5 m was better than that of the mid and deep waters (Räisänen et al. 2015). An oxygen deficit occurred below the depth of 20 m in the N pit and below the depth of 30 m in the Z pit (tab. 1). The interface between oxic and anoxic water was about a meter higher in autumn than in spring. The pit water data showed no evidence of spring overturn of pit waters, but partial mixing of surface waters with mid waters occurred in the N pit (Räisänen et al. 2015). The acidification of oxygenated surface waters and especially water at the interface depths of 20 to 22 m, above the anoxic water, indicates the mixing of oxygen rich melt water downwards with relatively reduced waters in spring. Furthermore, the decrease in the pH results in dissolution and hydrolysis of Al at pH<5. The enhanced acidity was followed by oxygen consumption in the water column that can be linked to the oxidation of soluble Fe^{2+} to Fe^{3+} coupled with the release of protons (Nordstrom & Alpers 1999, Bachman et al. 2001).

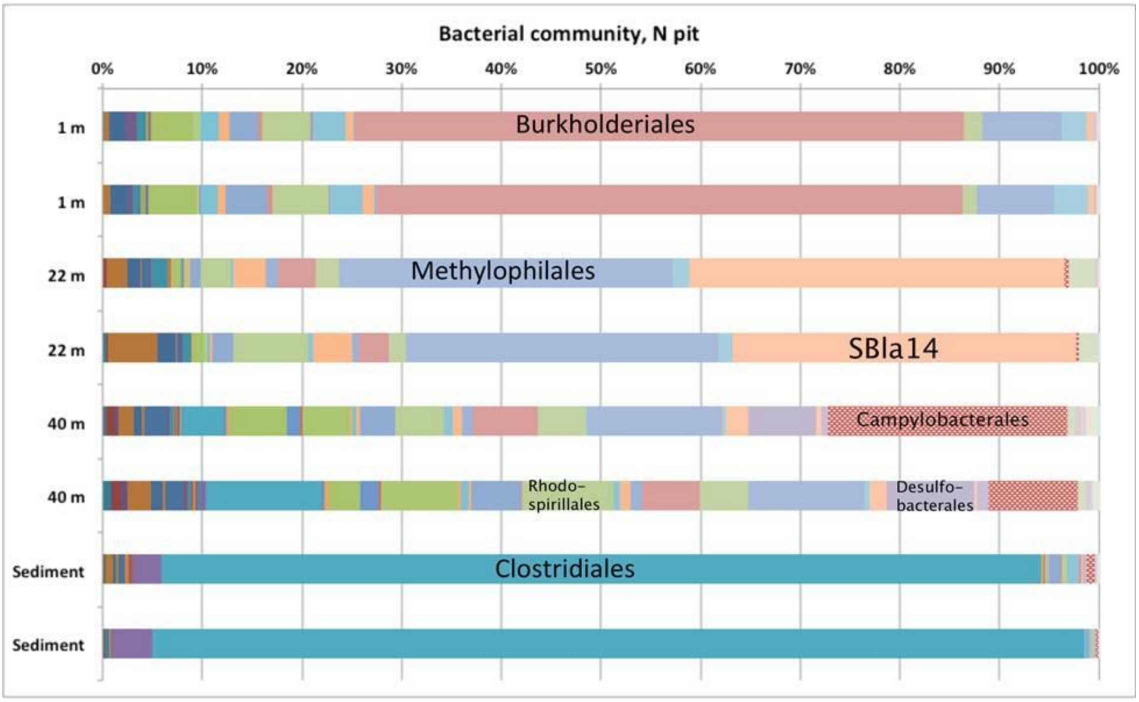

Figure 1 *The bacterial community of the N pit water and sediment resolved by high throughput amplicon sequencing. The bars indicate relative abundance of bacterial clades. Each sampled depth is presented with two replicate samples.*

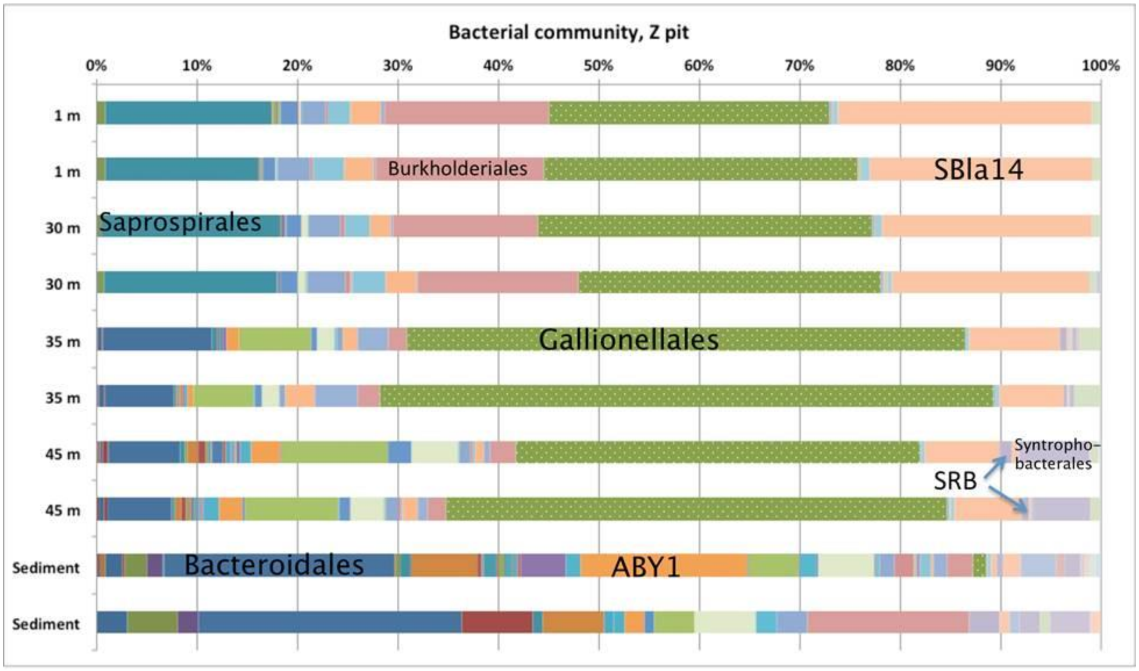

Figure 2 *The bacterial community of the Z pit water and sediment resolved by high throughput amplicon sequencing. The bars indicate relative abundance of bacterial clades. Each sampled depth is presented with two replicate samples.*

The relatively high abundance of methylotrophic bacteria in the water column of the N pit, especially at 22 m indicates high organic matter degradation with the production of methylated compounds and methanol. Methanol is produced by the degradation of, for example pectin, which is abundant in plant cell tissue, such as coniferous tree bark, added to the N pit in 2002. Other sources of methanol and methylated compounds may include the pig manure additions (1998, 2000, 2004), hydrolysis of added absolute ethanol (2005) (Vestola & Mroueh, 2008), or recalcitrant carbon compounds trapped in the black shale of the rock. The high abundance of Clostridiales bacteria fermenting organic matter in the bottom sediments probably reflects the addition of high amounts of organic matter in the N pit. The fermentation process supports putative methanogenesis in the anoxic parts of the N pit.

In the Z pit, the pH of surface and mid waters stayed pretty constant, near 6, and the pH of deep waters varied a little from spring to autumn (Räisänen et al. 2015). On the basis of alkalinity, waters throughout the Z pit had excellent buffering capacity (tab. 1). Presumably, pit waters have been acidified, or are acidifying actively by Fe sulphide oxidation on pit walls. However, potentially because there was only a single sampling site in each pit, the results did not reveal active sulphide oxidation. Additionally, results do not show that acidic water from the N pit is flowing into the Z pit. The interpretation of active acid generation is based on the marked increase in alkalinity, especially in the deep waters of the Z pit.

The predominance of ferrous Fe in the total soluble Fe content of the surface and acidified waters somewhat contradicted the above interpretation of the water acidification mechanism at the N pit (tab. 2). Furthermore, the predominance of bacterial groups that degrade organic matter and potentially reduce Fe oxyhydroxides (consuming, not producing acid) suggest an alternate acidity source, such as the desulphurization of decaying organic material (e.g. chips) via photosynthetic oxidation in oxygenated waters (Sánches-España et al. 2008, NCSU 2015).This mechanism is supported by the discrepancy in total soluble sulphur and sulphate-sulphur results (tab.2), which indicate the occurrence of reduced soluble sulphides potentially in both oxygenated and reduced water layers.

Table 1 *Physical property of the waters at the depths sampled in the N and Z pits, the closed Hammaslahti mine area, eastern Finland. Keys: < below the lowest detection limit, n.d. = no data.*

	Depth m	Temp °C	pH	Redox mV	Oxygen mg/l	EC mS/m	Alkalinity$^{1)}$ mmol/l	Solids mg/l
N pit								
March 24th	1	1.6	4.9	276	12.4	10.4	n.d.	<10
Sept 8th	1	15.2	5.6	216	8.86	10.5	0.04	< 2
March 24th	22	4.5	3.9	463	1.29	32.5	n.d.	<10
Sept 8th	20	4.6	4.0	516	3.33	22.3	n.d.	< 2
March 24th	40	5.5	5.6	-58	-0.05	49.9	0.21	128
Sept 8th	37	5.5	5.7	-3.8	0.12	34.6	0.28	4.7
Z pit								
March 25th	2	3.5	6.3	143	5.29	85.9	0.50	<10
Sept 9th	2	15.2	7.2	147	9.05	81.2	1.00	< 2
March 25th	30	3.4	6.3	135	4.99	85.8	0.50	<10
Sept 9th	30	5.0	6.4	120	1.30	61.6	1.04	< 2
March 25th	35	4.9	6.2	-4.6	-0.01	188	2.36	28
Sept 9th	35	4.7	6.4	-58	0.12	137	3.66	68
March 25th	45	5.2	6.2	-31	-0.06	219	0.53	<10$^{2)}$
Sept 9th	45	5.1	6.5	-82	0.10	155	5.43	34$^{2)}$

$^{1)}$no = non measurable alkalinity (pH ≤ 4.5)

$^{2)}$The duplicate sample from the depth of 45 m had solids 110 mg/l in March and 120 mg/l in September.

Table 2 *Concentrations of organic carbon, and soluble main and trace elements in water samples taken from the N and Z pit, the closed Hammaslahti mine area, eastern Finland. Keys: < below the lowest detection limit, n.d. = no data, Duplic. =duplicate sample.*

N pit	Depth m	TOC mg/l	DOC mg/l	S-SO$_4$$^{1)}$ mg/l	S mg/l	Ca mg/l	Al mg/l	Fe mg/l	Fe^{2+} mg/l	Mn mg/l	Zn µg/l	Cu µg/l
March 24th	1	12	11	21.4	26.5	18.8	0.97	0.45	0.51	0.24	327	41.9
Sept 8th	1	8.6	7.9	23.7	24.1	19.2	0.32	0.16	0.16	0.19	226	41.5
March 24th	22	1.4	0.93	76.8	87.1	49.5	4.28	0.75	0.66	1.32	1810	42.8
Sept 8th	20	1.7	1.3	76.8	75.9	47.7	3.77	0.46	0.07	1.29	1750	60.3
March 24th	40	3.7	1.4	130	152	79.4	1.25	38.2	41.2	1.83	20.4	<0.1
Sept 8th	37	2.0	1.3	129	132	77.3	1.02	36.6	37.4	1.81	21.9	0.28
Z pit												
March 25th	2	1.7	0.81	267	322	287	0.003	1.11	1.25	2.83	91.7	0.15
Sept 9th	2	1.9	1.5	264	268	278	0.17	0.05	<0.02	1.10	46.4	<0.1
March 25th	30	1.6	1.3	270	321	291	0.005	1.15	1.26	2.84	89.8	0.23
Sept 9th	30	1.8	1.5	260	265	276	0.17	0.05	<0.02	2.76	84.0	<0.1
March 25th	35	6.9	4.0	634	786	547	0.004	259	n.d.	12.4	44.8	<0.1
Sept 9th	35	5.3	3.9	624	620	503	0.17	179	181	10.1	44.3	<0.1
	45	2.1	1.2	267	334	298	0.003	5.12	6.00	3.01	88.0	<0.1
March 25th	Duplic.	6.2	5.1	701	927	549	0.003	411	n.d.	15.5	18.3	<0.1
	45	7.5	5.6	731	724	508	0.17	302	324	13.7	22.4	<0.1
Sept 9th	Duplic.	6.4	5.4	721	708	494	0.17	294	n.d.	13.6	24.2	<0.1

$^{1)}$calculated by dividing SO$_4$ concentration with 2.996

The profile of the bacterial community in the N pit water supports the reduction of Fe^{3+} in the water at least in the uppermost, oxygenated water layer where the Burkholderiales iron-reducing and sulphur-oxidizing bacteria dominated. This feature may also be present at 22 m depth, but the role of the betaproteobacterial SBla14 cluster is not yet clear. At greater depths Fe^{2+} is probably oxidized by epsilonproteobacteria. In addition, these epsilonproteobacteria detected in the N pit at 40 m depth are sulphur oxidizers, which could affect the acidification of water as well as prohibit the formation of Fe sulphides. SRB clades were generally detected only at relatively low abundances in the most diverse bacterial population at 40 m depth, and these bacteria coincided with the sulphur oxidizing epsilonproteobacteria. Thus, the results indicate that an active sulphur cycle is present at this depth. Chemical investigations indicated that sulphate reduction occurs in the anoxic parts of the pit. While the bacterial community reveals only low abundances of SRB in these parts of the N pit, it is, however, possible that a small but efficient population of SRB is responsible for the formation of Fe sulphides (Räisänen et al. 2015).

The high abundance of the iron oxidizing Gallionellales bacteria in the Z pit water strongly supports a biological iron oxidation process where iron is precipitated as Fe oxyhydroxides. In the oxygenated water from 1 to 30 m depth resultant Fe^{3+} may be reduced to Fe^{2+} by Burkholderiales bacteria, thus maintaining an iron reduction/oxidation cycle. The high diversity of bacterial groups present in the Z pit sediment indicates that the pit has not been influenced by anthropogenic organic carbon additions, as there is not a predominance of fermenting bacteria.

Water remediation mechanisms in the N and Z pits

Boundary conditions for biological sulphate reduction in the bottom water layer of the mine pit are characterized by anoxic water conditions, organic substrate, and SO_4^{2-} (Lu 2004, Vestola & Mroueh 2008). Other recommended parameters are pH >5.5, Eh (redox) potential <-100 mV (García et al. 2001), and temperature >6 °C (Vestola and Mroueh 2008). When observing the Hammaslahti N pit (which has been the project site for biologic sulphate reduction) the bottom water was clearly anoxic in March, and almost completely anoxic in September, indicating suitable conditions for SRB. However, the observed redox-potentials were rather high for biologic sulphate reduction. SRB have the ability to generate negative potentials (Sheoran et al. 2010), but this has not happened during the 15 years of treatment in the N pit. However, SRB can also perform successfully under positive Eh conditions when anoxic, reducing "pockets" in organic substrate exist (Sheoran et al. 2010). It is very possible that these pockets are found in the deepest water, just above the bottom sediments, although microbiological sampling found only minimal SRB in the sediments (Räisänen et al. 2015).

In the N pit, the redox potential ranged from -58 mV to 0 mV when measured with Ag/AgCl electrode, equivalent to values between +140 mV and 200 mV (SHE). According to Glasby & Schultz (1999) FeS_2 tends to dissociate to Fe^{2+} and SO_4 under these conditions. Furthermore, SRB groups coincided with sulphur oxidizing epsilonproteobacteria that resulted in an active sulphur cycle and moderately high solubility of sulphate in deep waters. These findings suggest that FeS_2 may be unstable, especially during the summer when overturn can increase redox potential. On the other hand, the low water temperature (<+6 °C) and slightly unfavourable redox potential (>-100 mV) are obvious reasons for a great decrease in SRB activity. Nevertheless, biologic sulphate reduction seems to be more active than the dissolution of FeS_2, as concentrations of SO_4 and Fe have clearly decreased during the treatment (Räisänen et al. 2015). Improvements to the N pit biological treatment can most likely be achieved by the addition of organic substrate in the future to promote the development of the sulphate reducing bacterial community. One possibility would also be to introduce more cold-tolerant bacteria to the pit.

In the Z pit, the source for excellent buffering capacity (i.e. alkalinity) is obviously carbonate weathering followed by sulphide oxidation of pit walls (Räisänen et al. 2015). That explains additional release of soluble Ca in deep waters (See tab. 2). However, crystalline gypsum ($CaSO_4 \times 2H_2O$) was identified from the bottom sediments (Räisänen et al. 2015). The precipitation of gypsum is one of the main neutralizers of acidity. According to Räisänen et al. (2015), the bottom sediments were rich in Fe oxyhydroxides but no Fe sulphides was identified. This suggests that sulphate is first fixed with Fe oxyhydroxides, forming schwertmannite and/or ferrihydrite, which then transforms into crystalline goethite in deep waters and/or bottom sediments (Bigham et al. 1992, Kumpulainen et al. 2007, Sánchez-España et al. 2011). The transformation includes dissolution of sulphate and it can contribute to pH-buffering (Nordstrom & Alpers 1999). According to Bigham et al. (1992), the precipitation of Fe oxyhydroxides controls the formation of Fe sulphides. The above findings can explain the excess sulphur in relation to Ca and Fe in deeper waters. Furthermore, the abundance of soluble Mn may have restricted Fe sulphide formation in slightly acidic and reducing waters (Bigham et al. 1992, Kerrick & Horner 1998).

Conclusions

This study revealed marked differences in physical, chemical and biological contents of the waters in two open pits (N, Z) in the closed Hammaslahti Cu-Zn-Au mine. Bacterial communities in the N and Z pits were very diverse and distinct from each other. These findings indicate that there is no adit connection between the N and Z pits.

The physical and chemical quality of the surface water above 5 m in both pits was better than that of the mid and deep waters. An oxygen deficit occurred below 20 m in the N pit and below 30 m in the Z pit in spring as well as in autumn. Deep waters and bottom sediments of both pits were characterized by year-round slightly reducing and $pH \geq 5.5$ conditions.

In the oxygenated waters of both pits, the sulphur reducing and iron oxidizing Burkholderiales bacteria were common, whereas the deep water and bottom sediments contain a small but efficient population of sulphate reducing bacteria (SRB). Overall, it can be concluded that the sulphate reducing bacteria addition together with organic carbon feed (pig mature, wood chips) has promoted Fe sulphide formation in the Hammaslahti mine N pit. In contrast to waters of the Z pit, the oxygenated water of the N pit showed acidification, most perceptibly, as a result of spring overturns. Unfortunately, the pH of the system has not increased to neutral, possibly due to insufficient activity or abundance of SRB. Indeed, very low amounts of SRB were detected from the sediments and waters during sampling. This is most likely due to the low temperature of the N pit waters. Furthermore, the rocks in the N pit, in contrast to the Z pit, do not bear carbonate minerals and such silicates that can increase buffering capacity via weathering. One possibility to improve the N pit biological treatment would be to introduce more cold-tolerant sulphate reducing bacteria to the pit.

In the Z pit, Fe and SO_4 were mostly precipitated as Fe oxyhydroxides, and the mineralogy of the bottom sediments did not reveal the occurrence of Fe sulphides, despite the fact that the S results revealed some soluble sulphide in waters. However, it is expected that crystalline goethite and other ferrihydroxides adsorbed trace metals, and therefore the retention rate for Zn and other metals was quite good. However, the formation of Fe oxyhydroxides, as well as the buffering reactions resulting from carbonate weathering, increases the solubility of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and sulphate. Therefore the discharge from the Z pit is characterized by elements that increase the water salinity but not the content of trace metals downstream.

Acknowledgements

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Field trial of an ion exchange based metal removal technology in the treatment of mine waters

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Abstract

A pilot scale field trial for a novel metal removal technology in the treatment of mine waters was performed using mine water from White Tip, part of the former Snailbeach lead mine in Shropshire, United Kingdom (UK). The water is circum-neutral pH and contains elevated zinc (Zn), cadmium (Cd) and lead (Pb). The novel treatment process is based on ion exchange (IE) using a bespoke mesh in a rotating disc reactor. Effects of process parameters such as regeneration of IE mesh, residence time (RT) and rotation speed (RS) of the discs were investigated.

Treatment performance of the system was consistent for the removal of Zn and Pb whereas for Cd it was more variable. The order of removal efficiencies was Pb (75.04%) > Zn (64.18%) > Cd (22.37%). Accordingly, 4.15 kg of Zn, 5.22 g of Pb and 5.55 g Cd were removed from 131.46 m^3 of mine water in 170 days. Removals of metals / metalloids such as iron (Fe), aluminium (Al), manganese (Mn), copper (Cu), barium (Ba), arsenic (As), nickel (Ni), boron (B), chromium (Cr) and small amounts of sodium (Na), potassium (K) and strontium (Sr) and non-metallic water quality parameters such as acidity, suspended solids (SS), alkalinity and small amounts of nitrate (NO_3-N) and total anions were also observed. The system generated a small amount of ammoniacal nitrogen (NH_3-N), sulfate (SO_4-S) and hardness. An average rise of pH by ~0.5unit in treated water was observed. Performance of the treatment system was not significantly affected by the regeneration of the mesh and RS of the discs. The treatment process was not affected by the temperature variations in the range of 0.7°C to 20°C. Maximum removals of metals were observed when $RT \geq 1.33$ hours.

Key words: mine water, metals, regeneration, removal efficiency, ion exchange

Introduction

Water is undoubtedly the single greatest pathway and receptor for mining-related contamination. Oxidative dissolution of rock or waste soil and rock heaps when exposed to water and oxygen results in the generation of contaminated mine water (Brown et al. 2002, Mayes et al. 2009). Mine drainages continue to be a significant environmental problem for decades after cessation of mining (Younger et al. 2002). Mine water can contain elevated concentrations of toxic contaminants such as Zn, Cd and Pb. Although some of the metals, e.g. Zn, in the mine water are essential trace elements for plants and mammals (Förstner & Wittman 1981), they can be toxic to aquatic ecosystems even at relatively low concentrations, which is reflected in the Water Framework Directive (2000/60/EC) and in the European Union (EU) environmental quality standards (EQS). For example, the maximum acceptable concentration of Zn for salmonid fish is 8-125 ppb in the hardness (as ppm $CaCO_3$) dependent EQS. Thus, treatment of mine waters is an important aspect of managing the environmental impacts associated with mining (Sengupta 1993).

Literature shows a wide range of active and passive remedial options available for the treatment of mine waters contaminated with metals such as Zn, Cd and Pb. Selection of appropriate treatment methods not only depends on mine water chemistry but also on economic factors. Active and passive treatment systems are established for acidic mine waters enriched with Zn, Cd and Pb where these metals are prevalent as Zn^{2+}, Cd^{2+} and Pb^{2+}. However, in circum-neutral mine waters, which occur in many metal mine discharges in the UK (Jarvis et al. 2007), Zn is present predominantly as carbonate (CO_3^{2-}) complex (⟦ZnCO⟧_3^°), which will not readily react to form non-carbonate solids. In such cases, aerobic passive treatment systems have not always been successful. Conventional alkali dosing active treatment systems could be used but are often not cost effective.

Ion Exchange (IE) is a well-established water treatment process. Dissolved salts and metals can be extracted from wastewater by passing through beds of IE resins. Traditional IE uses resins in the form of small (0.5-1mm) diameter beads to achieve a high surface area. These beads can be very susceptible to fouling by particulate matter (e.g. soil or Fe precipitates), which need to be removed prior to treatment. Therefore, this study investigated an innovative technology in the treatment of mine waters heavily contaminated with Zn, Cd and Pb. This technology removes metals using IE fibrous mesh supported on rotating discs in a novel patented reactor.

The mesh contains a mixture of cationic, anionic and chelating IE sites supported by a cross-linked polymer matrix. Cation exchange (CE) sites on the mesh are predominantly weak carboxylic (-COOH) acid groups, and chelating oxime (-NOH) groups. The precise CE capacity of the -COOH groups depends on the pH of the influent water. Below pH 6 the majority of the -COOH groups are un-ionised and do not pick up cations very well. However, the chelating -NOH groups are unaffected and are very selective for complexing with heavy metal cations. The mesh also contains amine ($-NH_2$) groups, which protonate below pH 6 and act as anion exchangers removing sulfate and CO_3^{2-} groups.

This technology has been trialled in the UK at pilot scale to investigate its effectiveness in the treatment of mine waters. The mine water used in this trial was drainage water infiltrating through the White Tip site, part of the former Snailbeach lead mine at Minsterley, Shropshire, UK. The mine water has a circum-neutral pH containing a mixture of metal cations (mainly Zn- ~ 50 ppm, Cd- ~ 0.14 ppm and Pb- ~ 0.06 ppm). Removal of these metals was investigated in this trial. Ratios of Zn-total to Zn-dissolved (Zn-T/Zn-D=1.05), Cd-total to Cd-dissolved (Cd-T/Cd-D=1.09) and Pb-total to Pb-dissolved (Pb-T/Pb-D=4.75) suggest that Zn and Cd are mostly present in dissolved form whereas ~80% of Pb is present in an insoluble form. This trial aimed to assess reactor performance in the field, in particular considering the effect of regeneration of the mesh, RT, and the RS of the discs.

Methods

Treatment set up

Figure 1 shows a schematic diagram of pilot scale set up for the treatment of mine water. A 60 litre (L) reactor housed thirty discs covered with 11 kg of IE mesh. The discs were fixed onto a shaft connected to a motor (90 W), equipped with an inverter enabling the RS to be varied, via a timing belt. A dosing pump was connected to a 5 m^3 influent storage tank and to the inlet side of the reactor. The outlet of the reactor was connected to a collection pump station comprising a tank (300 L) and a submersible pump with a float switch. The inlet sampling tap was located between reactor influent and the dosing pump whereas the effluent sampling tap was located between reactor outlet and the collection pump station. Data loggers comprising pH and temperature probes were positioned inside the reactor at both inlet and outlet ends and readings were taken every two minutes.

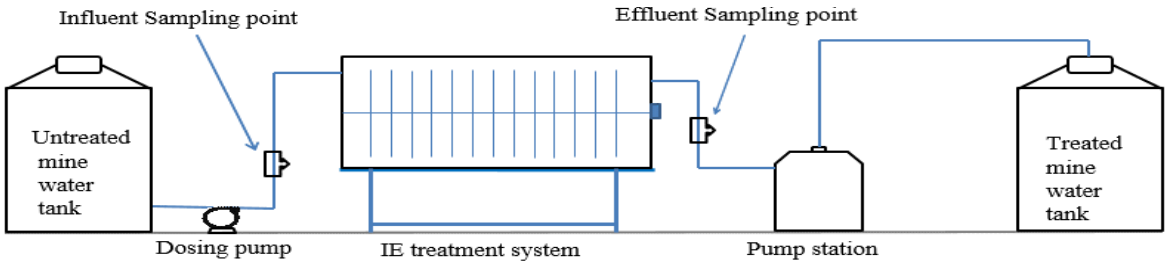

***Figure 1** Schematic diagram showing mine water treatment set up*

Mine water was tankered ~weekly from Minsterley and was stored in the influent storage tank. Mine water was pumped by the dosing pump into the reactor, where the rotating discs ensured effective mixing and contact with the novel IE mesh with a desired typical RT of approximately 2 hours. The flow rate was determined by measuring the volume exiting the reactor per unit time. The effect of RT on metal removal efficiency was investigated. Treated effluent was fed by gravity from the reactor outlet into the pump station which was pumped into an effluent storage tank for disposal.

This trial was commissioned on 5th November 2014 and terminated on 17th August 2015. During this trial, the treatment process was stopped twice due to logistical and access constraints: for two weeks from Day 44 and for fourteen weeks from Day 125. Therefore, this trial was run for a total of 170 days. Regeneration of the mesh was performed on Day 79. Accordingly, the system was run for a total of 79 and 91 days before and after the regeneration process respectively.

Sampling, sample handling and analyses

Un-acidified influent and effluent samples were collected five days per week for internal analysis at De Montfort University (DMU). Samples were stored and transported in cool dark conditions. Samples were allowed to settle and the supernatants of the samples were taken for analysis. Double distilled water was used in all analyses when dilution was required. AAnalyst™ 200 Flame Atomic Absorption Spectrophotometer (F-AAS) (Perkin Elmer Instruments, LLC) was used to analyse the water samples and was calibrated using AA standard solutions supplied by Fisher Scientific. Weekly influent and effluent samples were collected for independent analysis by an UK Accreditation Service (UKAS) accredited external commercial laboratory.

Regeneration of the mesh

The regeneration of the IE mesh was performed on Day 79 using hydrochloric acid (HCl) and sodium hydroxide (NaOH). Desorption of metals and other contaminants was performed in three batches. In each batch, the reactor was filled with 50 L of 5% HCl and left to react with the mesh for approximately 30 minutes. After acid wash, the mesh was normalized to pH 8.5 with NaOH solution, ensuring the pH never exceeded 12.5. A total of 205 moles of HCl and 19 moles of NaOH were used during the regeneration process.

Results

Removal of water quality parameters

A very important aspect of this treatment technology in terms of longevity is the regeneration of the IE mesh. Regenerated process was trialled on Day 79 (note annotation on Figure 2). Thus, the performance of the system is presented in three forms; overall, before and after the regeneration process. Table 1 presents a detailed breakdown of system performance before and after the regeneration process.

***Table 1** Summary of the pilot scale trial of mine water based on internal analyses.*

Parameters	Overall	Before Regeneration	After Regeneration
Treatment duration (days)	170	79	91
Average flow rate (L/hr)	32.22	28.18	35.60
Volume of treated mine water (m^3)	131.46	53.43	77.75
Average influent/effluent Zn concentration (ppm)	49.14/17.23	53.43/15.51	45.36/18.73
Average Zn removal efficiency (%)	64.18	70.40	58.78
Amount of Zn exposed/removed (kg)	6.46/4.15	2.85/2.01	3.53/2.07
Average influent/effluent Cd concentration (ppb)	188.8/146.2	248.5/192.3	137.1/106.2
Average Cd removal efficiency (%)	22.37	21.54	23.08
Amount of Cd exposed/removed (g)	24.82/5.55	13.28/2.86	10.66/2.46
Average influent/effluent Pb concentration (ppb)	53.00/14.00	42.30/8.70	62.00/18.50
Average Pb removal efficiency (%)	75.04	77.73	72.75
Amount of Pb exposed/removed (g)	6.95/5.22	2.26/1.76	4.82/3.51

The treatment system consistently removed Zn and Pb from the mine water. Removal of Cd was more variable. Figure 2 shows the internal results for influent and effluent concentrations of Zn, Cd and Pb

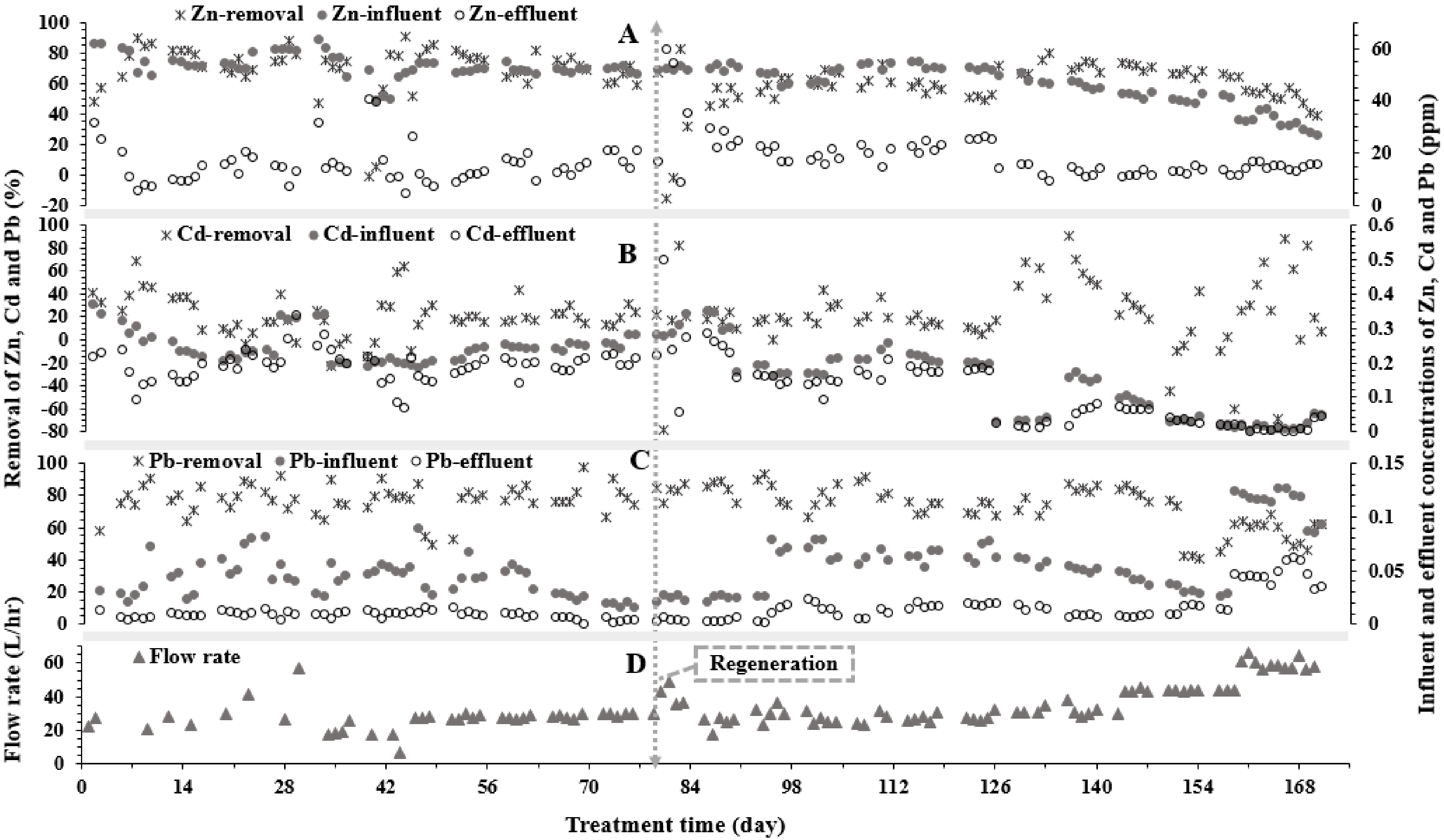

***Figure 2** Influent and effluent concentrations and removal efficiencies of a) Zn, b) Cd and c) Pb with respect to the corresponding flow rates (d).*

and their removal efficiencies with respect to the corresponding flow rates. Average removal efficiencies for Zn, Cd and Pb achieved during this trial were 64.18% (max-90.58%), 22.37% (max-90.16%) and 75.04% (max-97.28%) respectively. Accordingly, 4.15 kg of Zn, 5.55 g of Cd and 5.22 g of Pb were removed from 131.46 m^3 of mine water.

Figure 3 shows the external results for average removal efficiencies of water quality parameters. In addition to Zn, Cd and Pb, the treatment system also removed a wide range of metals; in particular Fe, Al, Cu, Mn, Ba and Ni. The system also removed non-metallic parameters such as acidity, SS, alkalinity, NO_3-N and total anions but contributed to the NH_3-N, SO_4-S, hardness and total cations. Conductivity was also reduced by the system.

Leaching of NH_3-N from the mesh occurred for the first four weeks but subsequently decreased, with most of the outlet concentrations for the remainder of the trial within the range of 0.2-0.3 ppm. This initial flush of ammonia could be mitigated by pre-washing of mesh at the manufacturing stage.

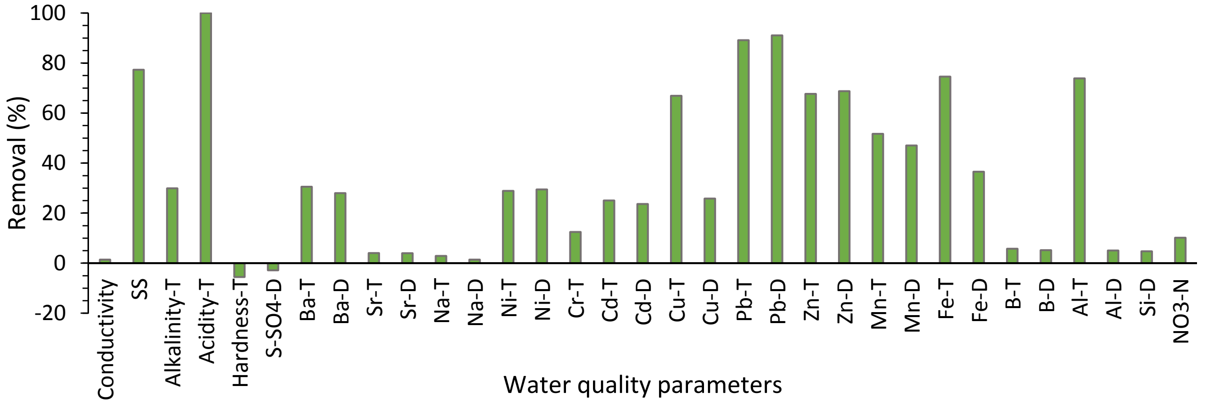

Figure 3 *Average removal efficiencies of water quality parameters analysed by UKAS accredited lab (D = dissolved, T = total).*

Effluent pH increased by ~0.5 pH unit with respect to degassing of carbon dioxide (CO_2). Continuous stirring of mine water without mesh performed in the lab showed a similar rise in pH. Degassing of dissolved CO_2 from the mine water is believed to have shifted the equilibrium from bicarbonate towards carbonic acid resulting in the consumption of hydrogen ions, thereby increasing pH.

Effect of regeneration of mesh on removal of metals

Regeneration of the mesh should be performed after breakthrough in the performance of the system. In this study, regeneration of the mesh was performed before reaching breakthrough of the system due to time constraints. Regeneration of the mesh was performed on Day 79 of the trial. Figure 2a shows that after the regeneration process, the removal efficiency of Zn gradually increased for a week and reached to the same extent (70%) as before the regeneration process. However, the average removal efficiency of Zn after the regeneration process dropped to 59% thereby bringing the overall treatment efficiency to 64%. This decrease is linked with the higher flow rates towards the end of the trial. Figure 2b and 2c show removal efficiencies for Cd and Pb were not affected by the regeneration process.

Mesh samples were taken from the first and the last discs in the reactor and digested in conc. HCl (37%) for two hours at 148°C to determine metal content; 98% of Zn, 81% of Cd and 91% of Pb (based on Pb-T) removed by the system before the regeneration process were desorbed off the mesh.

Effect of residence time (RT) on removal of metals

Flow rate determines both RT and mass transfer in the reactor. Lower flow rates decrease the pollutant load and increase the RT and vice versa. Lower flow rate are considered to increase removal efficiency by ensuring effective mass transfer between the solution and the rotating discs. This effect was investigated (from Day 126 to Day170) by increasing the flow rate from 30 L/hr to 45 L/hr and 60 L/hr respectively. Flow rates of 30 L/hr, 45 L/hr and 60 L/hr correspond to RTs of 2 hrs, 1.33 hrs and 1 hr respectively. Flow rate was increased from 30 L/hr to 45 L/hr on Day 143 and further increased to 60 L/hr on Day 159. The effect of flow rates on the removal of metals can be seen in Figure 2.

There was no significant drop in removal efficiency of Zn when the flow rate was increased by 1.5 fold (30 L/hr to 45 L/hr). Meanwhile, a 21% reduction in the removal efficiency of Zn was observed when the flow rate was doubled (30 L/hr to 60 L/hr). Removal efficiency of Pb dropped by 18% when the flow rate increased by 1.5 fold. However, further increase in flow rate did not result in a significant decrease in removal efficiency; removal of Pb decreased to 21% when the flow rate doubled. As most of the Pb was present in insoluble form, the minimal decrease in the removal efficiency of lead could be attributed to filtration by mesh. Meanwhile, the removal efficiency for Cd did not follow a particular trend. Overall, these results suggest that a minimum RT of 1.33 hrs should be used for the IE to liquor ratio and contamination levels reported in the present study. In full-scale treatment schemes, this will vary depending on the flow rate, reactor size, mine water quality and amount of IE mesh in the reactor.

Effect of rotation speed (RS) of the discs on metal ions removal

Disc RS was expected to potentially affect the removal efficiency by influencing the mixing and contact time. This was investigated by varying the RS of the discs. The field trial commenced with an initial disc RS of ten revolutions per minute (rpm), which was lowered to 2.5 rpm on Day 118. Lowering the rotation speed by a factor of four did not have significant effect on the removal of Zn, Cd and Pb.

Removal mechanism

Continuous removal of metals after exhaustion of IE capacity of the mesh suggests the existence of another removal mechanism, which is likely to be sorption and/or co-precipitation. To enable an estimation of metal removal arising from precipitation in comparison to IE, the solid residue was removed from the mesh samples taken at the end of the trial by gently squeezing and tapping. The mesh and the residues were each digested separately in conc. HCl (37%) for two hours at 148°C to determine metal content. Analysis of the residues suggested that at least 77% of Zn, 47% of Cd and 63% of Pb were removed by means of precipitation onto the surface of IE mesh. Amounts of Zn, Cd and Pb desorbed off the mesh were equivalent to the corresponding amounts removed after the regeneration process. X-Ray Diffraction (XRD) analysis of the solid residue on the mesh confirmed the presence of some variant of hydrozincite, a basic $ZnCO_3$, with general formula $Zn_4(CO_3)(OH_6).H_2O$. Diffraction peaks were extremely broad, consistent with very small particle size in the powdered specimen. Both lines of evidence indicate that precipitation occurred on the surface of IE mesh and not at the base of the reactor.

It is suggested that the metal removal mechanism first begins with ion-exchange, which seeds the mesh to favour co-precipitation and sorption. Results of the control experiments performed in the laboratory using raw mesh (before chemical conversion into an IE mesh) and IE mesh support this hypothesis. Removal of Zn by IE mesh was 72% whereas that of raw mesh limited to 24%. This mechanism was aided by persistent rise in pH due to degassing of dissolved CO_2. Degassing of CO_2 and precipitation of CO_3^{2-} resulted in a decrease in alkalinity. This is supported by an average decrease of 29.3% in alkalinity in the effluent.

Predominant Zn species in the mine water change as pH rises. Nuttall and Younger (2000) found that, on raising the pH from 6 to 8.5, zinc carbonate ($ZnCO_3$) and zinc hydroxide ($Zn(OH)_2$) species increase at the expense of free Zn ions and $ZnSO_4$. According to Hem (1972), stable $ZnCO_3$ (smithsonite) can be formed over a narrow pH range of 7.5-8.0 in natural waters.

Clever et al. (1992) documented that solubility of $ZnCO_3$ increases with partial pressure of CO_2 and temperature and decreases rapidly as pH rises around circum-neutral. A study by Paulson et al. (1989) found that, with 2 mM/L total dissolved CO_2 and at pH below 8.2, crystalline hydrozincite forms, whereas above pH 8.2 poorly crystalline hydrozincite forms and eventually at high pH zinc oxide (ZnO) forms. This is further backed up by Alwan and Williams (1979), who explained the anomalous stability of hydrozincite in nature based on the calculated solubility product constant of hydrozincite in natural waters as $\log K_{sp} = -14.9$. Stumm and Morgan (1970) suggest that below pH 7.5 $ZnCO_3$ is the most insoluble species and as pH increases, as is the case in this study, a basic $ZnCO_3$, hydrozincite, becomes controlling. These previous studies are consistent with the XRD analysis of the white precipitate on the mesh.

According to Miller et al. (2011), cation removal by sorption to an amphoteric surface is dependent on pH and is best at the pH which correlates with the point zero charge. The extent of Zn removal depends on a complex interplay between the nature of the aqueous medium and the speciation of the surface. As pH increases CO_3^{2-} sorbs onto the surface of the substrate to form $ZnCO_3$. As pH increases further, Zn sorption increases forming $Zn(OH)_2$. There is competition between aqueous and substrate phases for Zn complexation. As pH and alkalinity increase, the increased concentration of CO_3^{2-} in the aqueous phase outcompetes the substrate bound CO_3^{2-} stripping Zn from the surface of the substrate resulting in increased concentration of $ZnCO_3$ in solution. When surface sites are in abundance, the pH dependent removal dominates and alkalinity effects are minimal. When surface sites are restricted then a more complex behaviour is exhibited dependent on pH, alkalinity and number of sites.

The IE mesh used in this trial is a complex material comprising both anion exchanging $-NH_2^+$, cation exchanging -COOH and complexometric -NOH sites. At pH of around circum-neutral the $-NH_2^+$ sites are likely to be partially protonated, -COOH sites completely deprotonated and -NOH sites unchanged. Thus, the mesh provides excellent sites to support both IE and sorption of Zn cations and CO_3^{2-} / hydroxide etc. ions.

Miller et al. (2011) showed that the presence of alkalinity and dissolved Fe in the drainage water helps remove almost all dissolved Zn by precipitation or sorption onto precipitated Fe-oxy, hydroxyl species. However, on moving to continuous flow field trials where RT on the limestone drain was reduced to 1-3 hours (batch RT=4days) the removal efficiencies were significantly reduced almost to zero. Mayes et al. (2009) used high surface area hydrous ferric oxide (HFO) while removing Zn from 1.5-2.2 ppm to 0.9-1.5 ppm and found that the presence of alkalinity and dissolved Fe also helps in removing Zn by precipitation or sorption. Warrender et al. (2010) investigated the use of a range of materials in the circum-neutral removal of Zn at 23.5ppm, RT=15mins, flow rate=1 L/min in beds containing 1.5-12 kg of material. The presence of Fe in the wastewater formed Fe-oxy-hydroxide precipitates adversely affecting flow rates.

A significant advantage of the treatment system trialled is the openness of the IE mesh, which, together with its high surface area combined with agitation from the rotating discs, allows excellent flows whilst providing a variety of charged sites for IE / precipitation / sorption of metals.

Applicability of the technology

The results presented in this paper show the tremendous potential of this technology for the treatment of mine waters. This technology would be suitable for most metalliferous mine waters. However, if the pH of the mine water is highly acidic (pH<2) and alkalinity is low, then pre-treatment for pH and alkalinity is needed. Younger et al. 2002 used Oxic Limestone Drains (OLDs) to increase pH and alkalinity in RT=2-3 hrs.

For mine waters with very high SS, pre-treatment involving settlement might be advisable. If the mine water contains low concentration of metal ions then it may be necessary to increase the RT; longer RTs improve IE and precipitation processes by enhancing contact between metal ions and the active sites on the IE mesh. If the mine water contains an excessively high concentration of Fe then pre-treatment might be necessary to prevent clogging of mesh with ochre. Pre-treatment may avoid competition of Fe with the uptake of the desired metal ions. However, as discussed above the presence of Fe is likely to enhance the precipitation / sorption of the Zn. If the mine water contains low concentrations of Fe then this will be removed together with other metal ions by an IE process and will eventually assist in the co-precipitation / sorption of the other metal ions onto the IE mesh.

Conclusion

The IE mesh developed at DMU and incorporated in the innovative rotating contactor has been successfully applied in the removal of metal ions from mine water heavily contaminated with Zn, Cd and Pb. The order of removal efficiencies was Pb (75.04%) > Zn (64.18%) > Cd (22.37%). Accordingly, 4.15 kg of Zn, 5.55 g of Cd and 5.22 g of Pb were removed from 131.46 m^3 of mine water in 170 days. Amongst the other metals / metalloids removed by the system include Fe, Al, Mn, Cu, Ba, As, Ni, B, Cr and small amounts of Na, K and Sr. Amongst non-metallic water quality parameters include acidity, SS, alkalinity and small amounts of NO_3-N and total anions. Conductivity was also reduced by the system. However, the system generated small amounts of NH_3-N, SO_4-S and hardness. An average rise of pH by ~0.5unit in treated water was also observed.

Performance of the treatment system was not significantly affected by the regeneration of mesh and RS of the discs. The treatment system was successfully regenerated in-situ, indicating minimal downtimes for full scale units. The treatment process was not affected by temperature variations within the range of 0.7°C to 20°C. This suggests that the treatment system can be used for the continuous flow treatment of mine water under high temperature fluctuation throughout the year. The maximized removals of metals were observed when RT $\geq$1.33 hrs. However, this will vary for full-scale treatment schemes depending on the liquor to mesh ratio and water quality.

The system removed the metals mainly by IE and co-precipitation / sorption on the surface of the mesh. The openness of the mesh means that when Zn is co-precipitated / sorbed onto the mesh, this does not result in blocking of the sites and there is no reduction in flow rates unlike particulate systems. This treatment system has been proved to be suitable for mine waters with high alkalinity and circum-neutral pH and would be suitable for the most metalliferous mine waters. However, pretreatment may be required for mine waters of low pH, alkalinity and very high suspended solids. Performance will not be hindered by the presence of Fe, rather it is likely to be enhanced.

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Extreme Recovery Membrane Process and Zero Liquid Discharge Low Temperature Crystallization for Treating Scaling Mine Waters

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Abstract

The paper describes a step change mine water treatment process that increases water recovery from 40-70% to over 95% without the use of chemical softening in a low cost membrane system. The cost of mine water treatment is decreased by eliminating chemicals and the hassles of chemical and sludge handling and reducing the highly expensive downstream evaporative brine management stage. The membrane process beneficially removes all contaminants of concern, unlike biological treatment where only specific ions are removed. Moreover, the membrane process can start instantaneously, is not temperature dependent, and can operate with fluctuating feed water chemistry. Full analytical results, performance and economics will be presented for an innovative Salt Splitter Reverse Osmosis process treatment of scaling mine waters. Results for a low temperature crystallizer and an advanced targeted removal process for nitrates are also presented.

Key words: Mine water, run-off, tailings, brackish, hardness, water treatment, electrodialysis, reverse osmosis, evaporator, crystallizer, calcium, sulfate, nitrates, selenium, cadmium, zinc

Introduction

The Salt Splitter Reverse Osmosis system offers mine operators an economical alternative to biological treatment systems. It provides reliable treatment of mine waters without intolerance of fluctuating temperature or feed chemistry of biological plants. It also beneficially removes all contaminants of concern rather than a select ion that is specific to that biological culture. As will be shown in this paper, the Salt Splitter Reverse Osmosis process demonstrated extreme high recovery of 96% operating on a highly calcium sulfate scaling mine runoff water. This reduces the brine discharge volumes by 90% compared to lime softening followed by reverse osmosis. It also eliminates large tanks, chemical material handling equipment, and sludge disposal associated with lime softening. The SS-RO reduces overall projects costs by reducing the cost of the more expensive brine management systems.

Mine operators seek economical, reliable treatment of tailings and run-off waters for contaminants of concern, such as selenium and other heavy metals, spanning the entire mine lifecycle. Biological treatment methods are appealing due to lack of brine discharge. However, recent results from full-scale treatment plants have shown inconsistent and unreliable performance, largely due to challenges in fluctuating feed water chemistry and low temperature.

Reverse osmosis (RO) is typically the lowest cost treatment method. However, due to the high scaling potential of many mining and hard brackish groundwater and industrial wastewaters, the performance and recovery of RO systems is often limited. Scale precipitates on the surface of the membrane, resulting in plugging of element feed passages and potential membrane damage. Frequent, costly, and time consuming cleanings are required to operate on these scaling waters.

The scaling potential of these waters is due to presence of sparingly soluble multivalent salts. Scaling occurs when a multivalent anion (SO_4^{2-} or CO_3^{2-}) pairs with a multivalent cation (Ca^{2+}, Mg^{2+}, Ba^{2+}, or Sr^{2+}) forming low solubility compounds such as $CaSO_4$, $CaCO_3$, and $BaSO_4$. The multivalent cations contribute to water hardness.

Conventional lime and ion exchange softening are often used for hardness removal. Lime softening has costs associated with chemical procurement, handling, and added safety risk as well as a sludge by-product. Ion exchange softening has high costs associated with regeneration due to chemicals and disposal of spent regeneration fluid.

Salt Splitter Reverse Osmosis (SS-RO) enables extreme recoveries on highly scaling waters, such as mine discharge and hard brackish water and wastewaters. An ion exchange membrane separation process produces two non-scaling streams from a single stream with high scaling potential. This separation process is followed by reverse osmosis. This lowers total project costs by eliminating chemical softening and reducing expensive downstream brine management requirements: smaller ponds, less deep wells, and lower capacity evaporative and crystallizer systems.

The Salt Splitter leverages electrodialysis, an industrial technology, for scale through addition of membrane packaged stacks (Figure 1). Electrodialysis operates by using a direct potential to flux dissolved salts through ion exchange membranes with water flowing parallel to the membranes. It operates at 100 kPa without pressure differences across the ion exchange membranes. This, along with water not being fluxed through the membranes, makes electrodialysis tolerant to inorganic scaling and organic fouling.

The main difference between electrodialysis and Salt Splitter is the SS uses specialized mono-selective ion exchange membranes for splitting the scaling salts and a proprietary process and control. These specialized ion exchange membranes have monovalent ion selectivity of up to 98% to facilitate the salt splitting process.

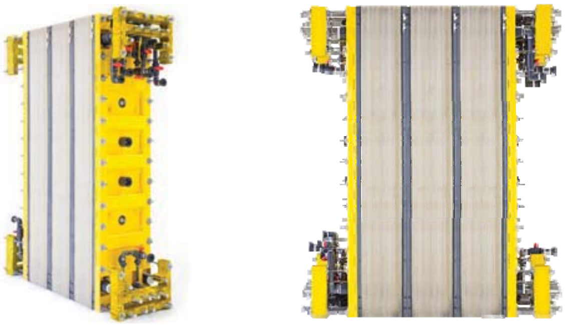

Figure 1: *Electrodialysis Membrane Packaged Stack*

The SS-RO eliminates the scaling potential of hard water. It works by separating multivalent cations from multivalent anions (Figure 2). Ions are transported from the process stream to form two separate highly concentrated brines. Partially electrochemical pre-treated water is fed to an RO unit, with the RO brine re-circulated to the Salt Splitter feed. A small portion of the RO brine is bled to prevent accumulation of organics.

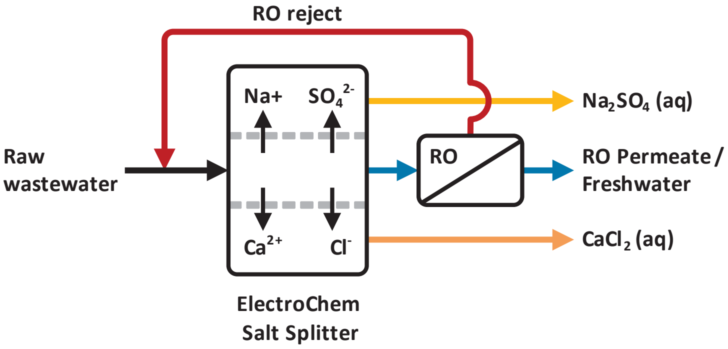

Figure 2: *Salt Splitter Reverse Osmosis Simplified Process Flow Diagram*

A feed water containing calcium sulfate and sodium chloride can be split into two non-scaling streams: one containing sodium sulfate (Na_2SO_4) and one containing calcium chloride ($CaCl_2$). Both of these streams have a solubility limit nearly 10 times that of calcium sulfate, 195,000 mg/L at 20°C compared to calcium sulfate at 2,550 mg/L at 20°C (Figure 3). This represents a potential brine concentration that is 75 times higher and results in a system that can recover over 96% of the feed water without scaling.

The SS-RO process softens water which allows reverse osmosis to operate at much higher reliability. The RO is fed with Salt Splitter product that has most of the scaling salts removed. The RO further desalinates the product water and produces a high quality RO permeate. The RO brine is sent back to the Salt Splitter for further concentration. Two highly concentrated low volume brines, with the scaling ions largely separated, are produced by the electrochemical Salt Splitter unit.

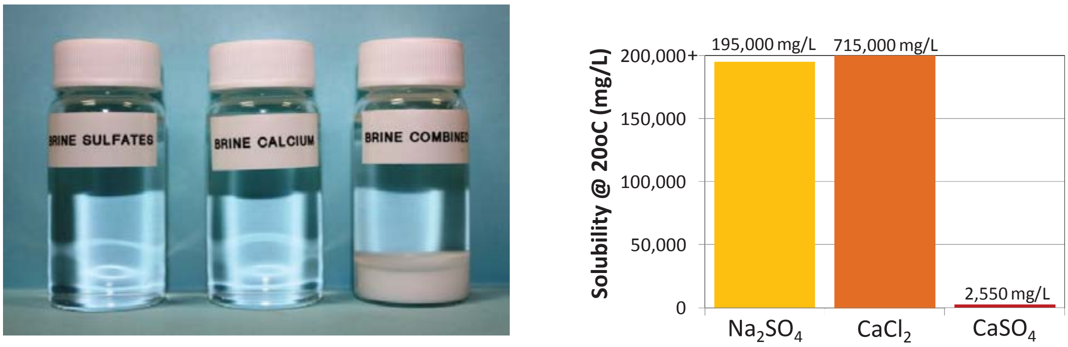

Figure 3: *Solubility Limits of $CaCl_2$ and Na_2SO_4 Solutions*

SS-RO brine can be treated with a low temperature crystallizer for true zero liquid discharge (ZLD). True ZLD is defined as producing only freshwater and solids from the process water. ZLD is practiced when projects have no access to ponds or deep wells and trucking great distances for disposal is too expensive.

The low temperature crystallizer uses a four effect humidification-dehumidification (HDH) cycle to concentrate wastewater or brine to greater than 30% solids by mass and produce freshwater (Figure 4). It is designed to operate on scaling and challenging fluids. Moderate grade heat (i.e. 90°C) generated from waste heat or natural gas, is used to evaporate and condense the wastewater in successive "effects". Latent heat of condensation is recycled as it is downgraded four times. This produces distilled water and requires only one quarter the heat required by conventional, open to atmosphere evaporators. It produces a highly concentrated brine or solids for true zero liquid discharge.

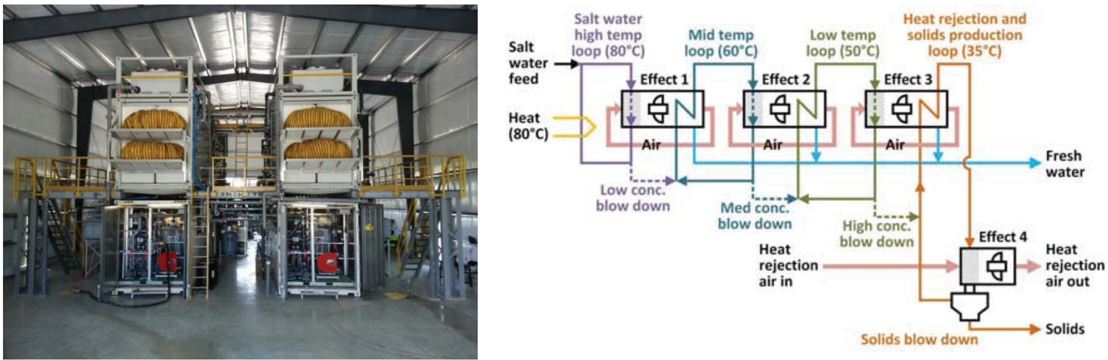

Figure 4: *100 m^3/day Low Temperature Crystallizer (left) and Simplified PFD (right)*

Project Overview

A small Salt Splitter Reverse Osmosis pilot project (~80 L/day) was completed for a Canadian miner. Runoff from the mine required treatment for contaminants of concern, such as sulfate, selenium, and other heavy metals. The runoff was predominantly gypsum salts near saturation. Calcium and sulfate comprised 71% of the runoff's's total dissolved solids (Table 1). The mine runoff contained relatively few monovalent ions. The Salt Splitter process requires sufficient monovalent ions to split scaling $CaSO_4$ into non-scaling $CaCl_2$ and Na_2SO_4. Sodium chloride was used to supply the required monovalent ions to complete the salt splitting process. Sodium chloride represents approximately 10% of the total cost of treatment.

***Table 1:** Mine Run Off Water Chemistry*

Parameter (mg/L)	RAW Mine Runoff Water
pH	7.60
Total Dissolved Solids	4048
Total Hardness (as CaCO3)	3082
Alkalinity (as CaCO3)	593
Calcium	507
Chloride	23.2
Magnesium	442
Sodium	18.5
Sulfate	2369

The miner previously pilot tested conventional membrane based systems to treat the runoff. This included the following:

- Lime Softening followed by RO achieving 65% recovery. This process required the use and handling of chemicals and management of sludge waste.
- Electrodialysis Reversal softening followed by RO (EDR-RO Hybrid) achieving 80% recovery. This process did not require chemical addition or produce sludge. EDR is not a pressurized filtration process. Thus water is not being fluxed through the membrane, and it is more tolerant of inorganic scaling and organic fouling than reverse osmosis. However, the recovery of the EDR-RO hybrid plant is still limited by the concentration of $CaSO_4$ in the brine stream. Even using antiscalants and advanced EDR cleaning systems, the brine concentration is limited to four times the solubility limit of $CaSO_4$.

Previous piloting results showed that the maximum recovery for the EDR-RO hybrid process for this application is 80%. A 20,000 m^3/day plant would produce 4,000 m^3/day of brine to be managed. Managing this volume of brine increases the overall project costs. Therefore, a low cost process to reduce brine discharge volumes would significantly reduce total project costs.

Project Objectives

The objective of the pilot project was to demonstrate that the SS-RO process can reduce brine volume and operate reliably on a high scaling mine water. Specific objectives were as follows:

- Determine the size of the full sized plant by determining the brine concentration limits
- Produce high quality RO permeate that meets regulatory discharge requirements.
- Demonstrate pilot plant reliability by operating continuously.

Pilot Plant Description

The SS-RO project was completed on Saltworks' small pilot plant. Capacity ranges based on stack size and test water availability. This projects capacity was set to produce roughly 80 L/day. The plant is an integrated Salt Splitter Reverse Osmosis system with full automation and data acquisition (Figure 5).

The plant has internet login capabilities for remote monitoring and operation of the system. The runoff was pretreated with 50 µm and automatically acidifed to remove particles and reduce carbonate scaling risk.

Figure 5: *Salt Splitter Stack (left), Salt Splitter Reverse Osmosis Hybrid Pilot (middle and right)*

Project Results

The SS-RO pilot achieved 96% recovery, met regulatory discharge requirements, and operated continuously for more than 1,500 hours (60 days). The SS-RO treated 5,300 L of water producing 5,100 L of permeate. Approximately 100 L of Na_2SO_4 brine, and 100 L of $CaCl_2$ brine, both with TDS > 120,000 mg/L, were produced.

Extreme Recovery

Brine concentrations of greater than 120,000 mg/L TDS were produced from mine runoff water near calcium sulfate saturation. The two brine streams steadily increased in concentration and then plateaued at a conductivity limit of ~130 mS/cm (Figure 6).

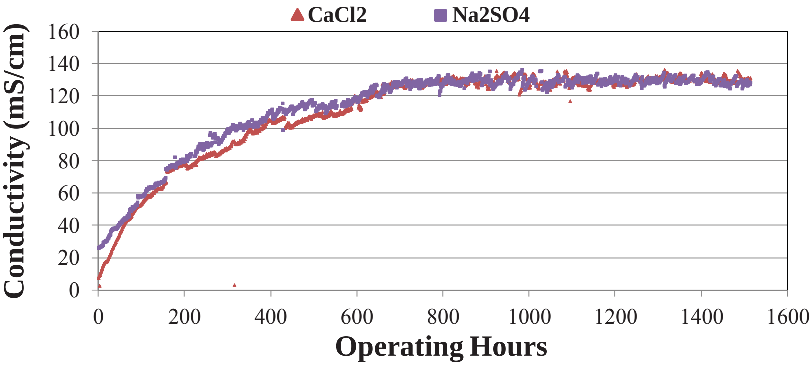

Figure 6: *Achieving High $CaCl_2$ and Na_2SO_4 Brine Concentrations*

Samples of the two brines at steady state were collected and submitted to an independent laboratory for analysis. The laboratory results for the two streams are summarized in Table 2. Results show the following:

- The TDS of both brines are >120,000 mg/L.
- The Salt Splitter successfully separated the $CaSO_4$ solution into two non-scaling brines
  - The $CaCl_2$ brine has sulfate concentrations <300 mg/L
  - The Na_2SO_4 brine has hardness <200 mg/L as $CaCO_3$
- The pH of both brines were <5, due to acid dosing to mitigate carbonate scaling risk. Minimal NaOH or lime would be required to neutralize the pH of these brines.

***Table 2:** Salt Splitter Brine Chemistry for $CaCl_2$ and Na_2SO_4*

Parameter (mg/L)	RAW Mine Runoff Water	Salt Splitter $CaCl_2$ Brine	Salt Splitter Na_2SO_4 Brine
pH	7.60	3.88	4.89
Total Dissolved Solids	4048	125000	157000
Total Hardness (as CaCO3)	3082	65700	176
Alkalinity (as CaCO3)	593	<1	1
Calcium	507	10200	39
Chloride	23.2	67400	37600
Magnesium	442	9770	19
Sodium	18.5	13800	59200
Sulfate	2369	297	64100

Meeting Discharge Limits

The RO produced 5,100L of permeate from 5,300L of mine runoff water. A sample of the RO permeate was submitted to an independent laboratory for analysis. The results are summarized in Figure 7 and are compared to regulatory discharge limits. Key results are as follows:

- High quality RO permeate was produced with a TDS of 18 mg/L
- All regulated parameters met discharge requirements

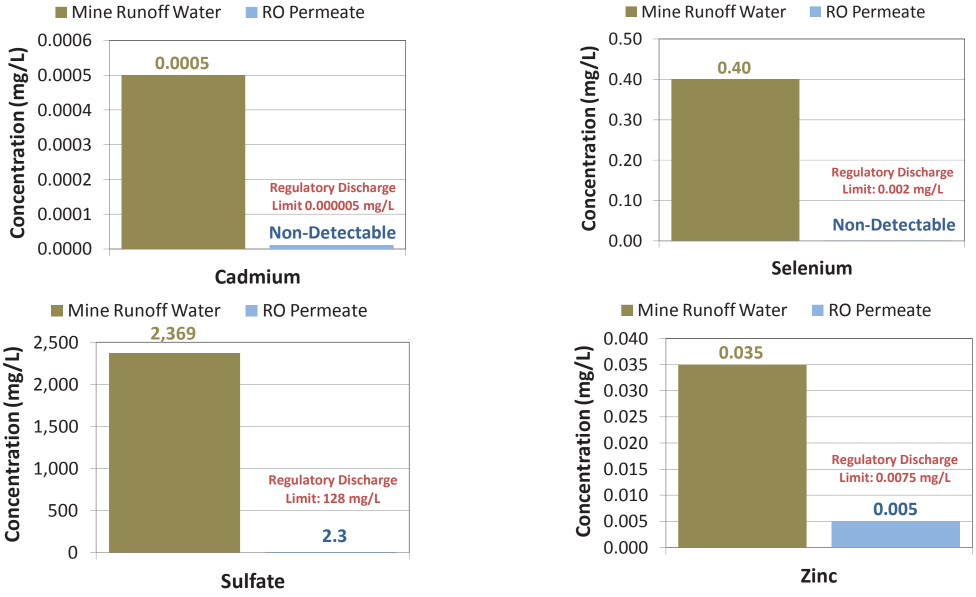

***Figure 7:** RO Permeate Water Chemistry Compared to Regulatory Discharge Limits*

Reliable Operation

The SS-RO pilot went through a series of trials to find brine concentration limits and refine process controls specific to this mine water. In the final test run, the plant was operated continuously for over 1,500 hrs (60 days) and continues to operate at the time of writing.

Low Temperature Crystallizer

The high solubility, low volume SS-RO brines were to be treated with a low temperature crystallizer for additional freshwater and solids production. However, since the SS-RO operated at 96% recovery, there was not enough brine produced to pilot the crystallizer at the time of writing. Table 3 and Figure

8 show typical freshwater data and ZLD solids pictures for the low temperature crystallizer from projects completed on shale gas produced water, landfill leachate, and oil sands produced water evaporator blowdown.

***Table 3:** Exemplary SaltMaker Feed Water and Freshwater Quality*

	Oil Sands Evaporator Blowdown		Shale Gas Produced Water		Landfill Leachate	
Parameter (mg/L)	Raw	Freshwater	Raw	Freshwater	Raw	Freshwater
Total Dissolved Solids	66,300 to 147,000	103	54,600 to 230,000	95	12,000 to 90,500	135
Total Hardness (as CaCO3)	229 to 725	<2	725 to 41,200	5	500 to 14,000	5

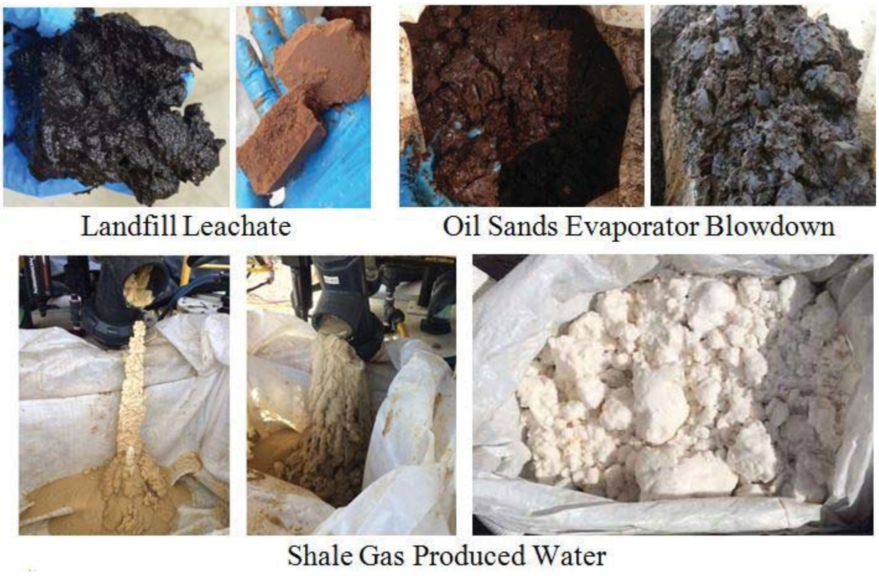

***Figure 8:** Low Temperature Crystallizer True ZLD Solids*

Nitrate Removal

The project also demonstrated selective nitrate removal with 97% recovery. The miner operates a biological system to remove selenium from their run off. Nitrate concentration spikes in the feed water reduce treatment efficiency. Nitrates, due to explosives residuals, in the mine runoff were treated by adapting the advanced electrodialysis system for selective nitrate removal (EDR-N). The EDR-N system uses the same equipment with a different configuration of membranes. The test results show that it reduces nitrate concentrations from 131 mg/L as N down to 5.3 mg/L as N (Table 4). 97% recovery was achieved by concentrating the nitrate in the brine to over 4800 mg/L as N. EDR-N selectively removes nitrates (96% removal) with ion specific ion exchange membranes (Figure 9).

Parameter (mg/L)	**Raw Mine Runoff Water**	**EDR-N Product Water**	**EDR-N Brine**
pH	7.60	8.22	7.70
Total Dissolved Solids	4048	2780	47800
Hardness (as CaCO3)	3082	1860	32100
Calcium	507	300	5980
Magnesium	442	270	4160
Nitrate (as N)	131	5.29	4830
Sulfate	2370	2350	3570

***Table 4:** EDR-N Water Chemstry Demonstrating Selective Nitrate Removal*

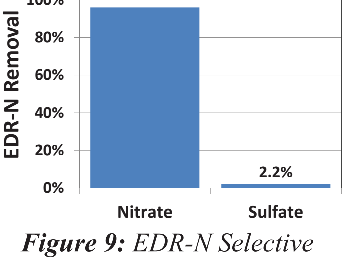

***Figure 9:** EDR-N Selective Nitrate Removal*

The brine from the EDR-N system can also be treated by a low temperature crystallizer for true ZLD. The brine is a predominantly nitrate/calcium/magnesium solution. Results show that the brine can be solidified and encapsulated to pass the necessary leaching tests to meet non-hazardous landfill acceptance criteria for final disposal.

Economics

The total cost of ownership for the SS-RO-Low Temperature Crystallizer treatment process is estimated at \$3 USD/m^3 plant inlet, assuming efficient construction, 8% interest rate, and 10 year project life. Lifecycle costs are based on the small pilot test results and for a full-scale plant capacity of 20,000 m^3/day. The lifecycle costs are summarized in Table 5.

***Table 5:** Economics for a 20,000 m^3/day Salt Splitter Reverse Osmosis Crystallizer Plant*

SS-RO	Capex (includes site construction)	\$0.99/m^3 plant inlet
	Opex (labor, maintenance, and consumables)	\$0.41/m^3 plant inlet
	Opex (NaCl)	\$0.20/m^3 plant inlet
	Opex (Energy)	\$0.26/m^3 plant inlet
Low Temperature Crystallizer	Capex	\$0.80/m^3 plant inlet
	Opex (Non-Energy)	\$0.14/m^3 plant inlet
	Opex (Energy)	\$0.17/m^3 plant inlet
Total Cost of Ownership (SS-RO-Low Temperature Crystallizer)		**\$2.97/m^3 plant inlet**

Conclusions

The Salt Splitter Reverse Osmosis system offers mine operators an economical alternative to biological treatment systems. It provides reliable treatment of mine waters without intolerance of fluctuating temperature or feed chemistry of biological plants. The Salt Splitter Reverse Osmosis process demonstrated extreme high recovery of 96% operating on a highly scaling mine runoff water. This reduces the brine discharge volumes by 90% compared to lime softening followed by reverse osmosis. It also eliminates large tanks, chemical material handling equipment, and sludge disposal associated with lime softening. High quality RO permeate was produced that met regulatory discharge limits. The SS-RO reduces overall projects costs by reducing the cost of the more expensive brine management systems. The non-scaling brines can be treated by a low temperature crystallizer for true zero liquid discharge and a complete cradle to grave solution. Total cost of ownership for a Salt Splitter Reverse Osmosis and Low Temperature Crystallizer treatment process is USD \$3/m^3 plant inlet.

The advanced electrodialysis system can also be adapted to remove nitrate spikes from the feed of existing biological systems. EDR-N selectively removes nitrates from 130 mg/L as N to 5 mg/L as N to improve existing biological plants' performance and reliability. High recovery of 97% reduces brine volume and minimizes the costs of a downstream low temperature crystallizer for true ZLD.

The complicated role of CO_2 in mine water treatment

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Abstract

Elevated concentrations of CO_2 are common in discharges from abandoned coal mines. The CO_2 is a problem in lime treatment systems because of its tendency to react with lime and prepiciate as calcite. In passive systems elevated CO_2 can maintains pH values between 5.5 and 6.5, which is low enough to substantially slow Fe and Mn oxidation reations. The typcial solution for elevated CO_2 is degassing through aeration which lessens the formaton of calcite in lime systems and raises pH is passive systems. However, CO_2 can also provide benefits in treatment systems. Most passive treatment systems generate alkalinity through limetone dissolution. CO_2 enhances the dissolution and results in higher concentrations of alkalinity. This study evaluated the effect of CO_2 on limestone dissolution by measuring alkalinity generation of limestone that recived fresh mine water with high CO_2 and stale mine water with low CO_2. Fresh mine water which retained elevated CO_2 generated twice the alkalinity as stale mine water. The results demonstrate that effect of CO_2 on a treatment system's performance varies with the technology being utilized.

Key words: mine water treatment, limestone, carbon dioxide

Introduction

Metal and sulfate contaminated mine waters discharging from coal mines or spoil piles commonly contain elevated concentrations of CO_2 (Hedin et al. 1994a; Jarvis 2006). As the mine water flows through a treatment stream the CO_2 can degas to the atmosphere, precipitate into a solid, or discharge in the liquid effluent as carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-) or carbonate ion (CO_3^{2-}). In lime treatment systems where the dissolution of CaO or $Ca(OH)_2$ creates high concentration of Ca^{2+} and high pH, the formation and precipitation of calcite, $CaCO_3$, is favored.

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$
$$H_2CO_3 + CaO \rightarrow CaCO_3 + H_2O \qquad (2)$$
$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \qquad (3)$$

The formation of $CaCO_3$ results in treatment inefficiencies because neutralization is transferred to the solid sludge, not to the mine water. In the coal fields of northern Appalachia, many lime treatment plants operate inefficiently due to the formation of $CaCO_3$. Means et al (2016) analyzed the treatment efficiency of four systems that treated high-CO_2 Fe-contaminated mine water with lime. Calcite formation consumed 29-58% of the alkaline addition in the systems. A recent study of the chemical composition of solids produced by mine water treatment plants in Pennsylvania found that eight lime sludges averaged 54% $CaCO_3$ (TU 2016).

CO_2 is an important factor in passive treatment systems. Alkaline mine waters with high CO_2 have high concentrations of carbonic acid (reaction 1) which generally buffers between 5.5 and 6.5. This pH range is low enough to slow oxidation rates for Fe^{2+} and Mn^{2+} to impractical levels. The degassing of CO_2 though passive means or mechanical aeration increases pH (reaction 5) which can significantly increase rates of Fe and Mn removal (Hedin et al. 1994b)

$H_2CO_3 \rightarrow H^+ + HCO_3^{--}$ (4)
$HCO3^- \rightarrow CO_2$ (degas) + OH^- (5)

These examples of the benefits provided by decreasing CO_2 suggest that degassing should be a primary interest in systems dealing with high CO_2. However, there are circumstances where CO_2 is advantageous to treatment. The dissolution of limestone, the most commonly used alkaline reagent in passive systems, is enhanced by CO_2.

$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$ (6)

The significance of reaction 6 in passive systems has not been quantified so it is difficult to estimate the impact of CO_2 degassing on the treatment performance of a passive system.

In this paper the effect of CO_2 management in limestone-based treatment systems is measured through limestone incubation experiments. In the two mine waters tested, the degassing of CO_2 from mine water prior to contact with limestone is found to decrease the alkalinity-generating capacity by 40-50%. The results illustrate the complexity of CO_2 management between types of treatment systems and even between treatment units within the same system.

Methods

Alkalinity generation potential was measured with a device referred to as an *Alkast* (alkalinity forecaster). The device consists of a 140 ml plastic syringe, a mesh bag of sieved, washed, and weighed material that fits inside the syringe, and an airtight cap (Figure 1). The mesh bag fills approximately ½ of the syringe volume. This allows the plunger to be moved so that water can be drawn into and dispelled from the device. Once the device is filled with water, the plunger is pushed so that it is flush with the syringe contents, and the syringe tip is capped. The device is then incubated for a set period of time. The incubation ends when the water contents are flushed out using the plunger. After its use the *Alkast* device is rinsed with tap water and is ready to be used in another test.

In these experiments, the *Alkasts* were filled with 120 grams of sieved (2-4 mm) washed calcitic (90% $CaCO_3$) limestone. The water samples produced were filtered (0.22 µm) and measurements were made of pH, temperature, and conductivity with a calibrated Hanna HI 991300 meter. Alkalinity was measured by titration with 1.6 N H_2SO_4 to pH 4.5. Alkalinity and acidity are expressed as mg/L $CaCO_3$.

Two treatments of mine water were considered in the experiments. Fresh mine water was collected from is source with minimal exposure to the atmosphere. When testing fresh mine water *Alkast* devices were filled with water withdrawn from the discharge zone or water collected from the discharge zone and maintained in a closed container until use in experiments. Stale mine water was collected at a point downstream of the discharge after it had been aerated or was generated by allowing fresh mine water to equilibrate with the atmosphere over at minimum 2-day period.

Samples of the influent and effluent of limestone treatment systems were collected and analyzed in the field for pH, temperature, alkalinity, and conductivity and by a laboratory for acidity, Fe, Mn, Al, and sulfate using standard analytical procedures.

Figure 1 *The standard composition of an Alkast is a 140 mL syringe, a mesh bag with material, and an airtight cap.*

Study Sites

The Woodlands passive treatment system is located at the Pittsburgh Botanic Garden, Pennsylvania, USA, and has been operating since April 2013. The system includes a 409 mton open limestone bed followed by a polishing pond and flush pond. The system treats acid water containing Al (Table 1). This project focused on the influent and effluent of the limestone bed. The influent to the bed is a buried pipe that connects to an underground coalmine. Water flows directly from the mine into the bed without aeration and is considered fresh mine water. The limestone bed was installed open to the atmosphere, however the Botanic Garden has since constructed a walking trail on top of it by covering it with geotextile and fine aggregate and the bed operates as a closed system.

The Fall Brook South and North passive treatment systems are located near Blossburg, Pennsylvania, USA and have both been operating since November 2015. The South system contains 9,091 mton of calcitic limestone in three parallel limestone beds followed by two ponds. The North system contains 1,680 mtons of calcitic limestone in a single limestone bed followed by one pond. The limestone beds receive acid water from a common abandoned underground coal mine, but the chemistry varies somewhat (Table 1). The Mine Water (MW) at the North system is collected underground and transferred to the system with minimal aeration. Water samples were collected for *Alkast* testing at the system influent. Because of landowner issues, the MW at the South system could not be collected at its source. Instead it flows approximately 50 m down a steep rocky channel before it is collected into a pipe that delivers the water to the limestone beds. Water samples were collected for Alkast testing at the discharge point (fresh) and at the collection pipe influent after aeration (stale).

Table 1 *Influent characteristics of Woodlands, Fall Brook South, and Fall Brook North treatment system*

	flow	pH	Alk	Acid	Fe	Al	Mn	SO4
	L/min		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Woodlands	30	3.2	0	143	0.6	16.3	0.8	474
Fall Brook South	3,125	3.5	0	89	0.6	10.6	13.2	360
Fall Brook North	512	3.5	0	67	2.7	11.5	9.4	213

Results

Figure 1 shows *Alkast* alkalinity concentrations for the Woodlands influent at varying incubation periods. Over short incubation periods of 1-2 hours the *Alkast* results were variable. Beyond ten hours the alkalinity concentrations stabilized at similar values and averaged 221 mg/L. The DLB during this period had a theoretical retention time of approximately 40 hours and discharged water with 197 mg/L alkalinity.

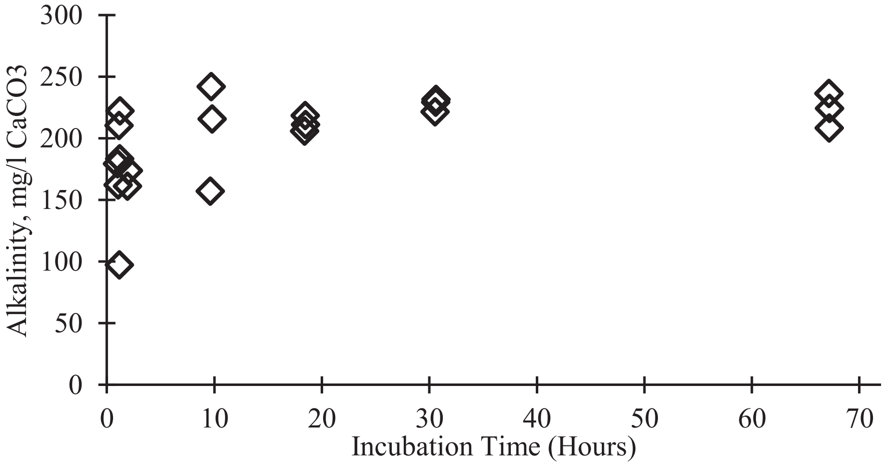

Figure 2 *Alkalinity concentrations for Alkasts containing fresh Woodlands MW at different incubations periods. The limestone at this time discharged 197 mg/L alkalinity*

Table 2 shows alkalinity measurements for the treatment system effluents and the *Alkast* testing on a variety of mine waters collected at the sites. The Fall Brook South system was sampled under average and high flow conditions (15 and 5 hour retention times, respectively). Variation in alkalinity generated by *Alkast* incubation of the system effluent was similar to variation in the alkalinity generated by the limestone beds (compare "System effluent" and "*Alkast*, system effluent"). The *Alkast* method overestimated alkalinity generation by the limestone beds by 12% at the Woodlands site and 25% at the Fall Brook sites. The cause of the overestimation is suspected to be related to limestone particle size (much smaller in the *ALkasts*) and the loss of CO_2 in the mine water between its sampling point and its entry into the limestone beds.

The Woodlands and Fall Brook North system receive a fresh influent while the Fall Brook South system receives an aerated stale influent. When the Woodlands mine water was allowed to equilibrate with the atmosphere, the *Alkast* alkalinity for the stale water was 40% lower than the fresh water. When the Fall Brook South MW was collected at its source, the *Alkast* alkalinity for this fresh water was 80-110% higher than was obtained for the stale system effluent.

Table 2 *Concentrations of alkalinity for samples collected at the Woodlands (Wood), Fall Brook South (FBS), and Fall Brook North (FBN) passive limestone treatment systems.*

System influent	Type	Wood Fresh	FBS Stale	FBS Stale	FBN Fresh
System theoretical retention	hr	36	15	5	14
System effluent	Alk	197	78	61	125
Alkast, system influent	Alk	221	97	76	158
Alkast, system effluent	Alk	na	97	89	147
Alkast, fresh influent	Alk	---	206	162	---
Alkast, stale influent	Alk	128	---	---	na

When pH is measured on *Alkast* effluents, the CO_2 partial pressure can be calculated from the pH, alkalinity, and carbonate equilibria constants. The Woodlands fresh and stale waters had CO_2 partial pressure of $10^{-1.70}$ and $10^{-2.32}$, respectively. For context, water in equilibria with the atmosphere has a CO_2 partial pressure of $10^{-3.5}$.

Discussion

Calcite formation is a costly side reaction in lime treatment that can avoided in chemical treatment systems by switching to a non-Ca reagent or by removing CO_2. Means et al (2016), working only with net alkaline discharges, found that switching to hydrogen peroxide eliminated calcite formation and decreased treatment costs substantially. For acid waters that require the addition of alkaline reagent, the removal of CO_2 via aeration prior to lime addition is a recommended practice. The recently constructed Hollywood treatment system in Elk County Pennsylvania treats a low-pH acidic mine water with lime. The mine water is vigorously aerated prior to lime addition and the sludge produced is only 10% $CaCO_3$. Two nearby lime plants that treat similar water but without aeration generate sludge that is 40-70% $CaCO_3$. Calcite formation in lime plants without CO_2 management decreases useful alkalinity generation by 50-100% with major cost impacts.

In passive systems, the impact of the CO_2 on alkalinity generation is opposite what is observed in lime systems. Where limestone is utilized as the alkaline reagent, CO_2 enhances dissolution of the limestone and increases the generation of useful alkalinity. In the limestone incubation tests fresh mine water with elevated CO_2 produced water with 93-109 mg/L higher alkalinity than tests conducted with stale water with decreased CO_2. Many passive systems that treat acid mine water discharge to streams degraded by untreated mine water from abandoned mines. In these cases, treatment systems should generate as much alkalinity as possible. The simplest method for ensuring the maximum amount of alkalinity is to prevent any degassing of CO_2 prior to treatment with limestone.

In some cases, maximum alkalinity generation is not a priority and the generation of excessive alkalinity may be viewed as wasteful. In these cases, the current solution is to decrease the quantity of limestone and thus lessen contact time. This approach is problematic when flows increase or when the limestone dissolves, both of which could decrease the retention time below a critical minimum. The results here suggest an alternative method where alkalinity generation is controlled through CO_2 management.

CO_2 management strategies can vary within a treatment system. As noted earlier, CO_2 can buffer pH less than 6.5 which impacts Fe and Mn removal. Degassing increases pH. A common situation in Pennsylvania coal fields is acid water with Fe concentrations greater than 100 mg/L where passive treatment consists of limestone pretreatment followed by oxidation and settling ponds. In this case, CO_2 should be maintained as high as possible in the limestone treatment units and decreased as low as possible in the oxidation ponds.

Conclusions

Mine waters commonly contain elevated concentrations of CO_2. The handling of CO_2 should differ depending on the treatment technology. In lime treatment systems, where CO_2 promotes treatment inefficiency due to calcite formation, CO_2 should be removed. In limestone treatment systems, where CO_2 promotes alkalinity generation, CO_2 should be conserved.

The *Alkast* methodology presented here provides a simple procedure for experimentally measuring the effect of mine water handling on limestone dissolution. In experiments on mine water from two sites, the *Alkast* testing indicated that CO_2 degassing decreased the alkalinity generation capacity of limestone treatment by 80-100 mg/L.

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Performance of synthesized hybrid hydrogel nanocomposite applied for the removal of metal ions from aqueous solutions

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Abstract

The removal of metal ions from mine effluents by a copolymerized gelatine (GL-cl-PAAm) and the hybrid hydrogel nanocomposite was investigated in the present study. Both adsorbents were characterized using fourier transformed infra-red spectrometer (FTIR) and their adsorption behaviour was studied through the determination of the effects of adsorbent dosage and temperature on the adsorption capacity. The thermodynamic study at 20, 30 and 40°C showed that the adsorption process using GL-cl-PAAm and the hybrid hydrogel nanocomposite were both exothermic ($\Delta H = 351$ KJ/mol > 0 and ($\Delta H = 17.71$ KJ/mol > 0, respectively) while the values of the Gibbs free energy ($\Delta G < 0$) for both adsorbents was negative indicating that for the initial concentrations of Cd considered, the adsorption process was of a spontaneous nature. The adsorbents were found to effectively remove uranium (U), nickel (Ni) and lead (Pb) from mine effluents achieving a maximum removal of 100%.
The developed adsorbents have shown the potential to remove metals in synthetic and complex solutions.

Key words: Clinoptilolite, hybrid hydrogel nanocomposite, adsorption, mine effluent, thermodynamic

Introduction

Hydrogels also referred to as hydrophilic gels are network of polymer chains with the ability to adsorb water arising from hydrophilic functional groups attached to the polymeric backbone. They have a wide range of applications in food industry, bioengineering, biomedicine and water treatment processes. Hydrogels made from biopolymers are renewable, safe and can be afforded at relatively low cost; they can be easily modified through biochemical and chemical mechanisms, making them suitable for the synthesis of composites. During synthesis of hydrogels important consideration must be taken to ensure that the polymer does dissolve, this is done by systematic introduction of cross-links, several methods have therefore been developed for preparation of suitable hydrogels (Park et al. 1993). Akhtar et al. (2015) have identified the physical cross-linked gels and the chemical cross-linked gels as the major methods for synthesis of hydrogels. The physical cross-linked gels can be achieved by hydrogen bonds, amphiphilic graft and block polymers, crystallization, ionic interaction and protein interaction (Yokoyama et al. 1986; Gacesa 1988; Mathur et al. 1998; Forster and Antonietti 1998; Miyata et al. 1999); the chemical cross-linked gels is done by complementary groups chemical reaction, high energy radiation, free radical polymerization and by the use of enzymes (Sperinde and Griffith 1997; Martin et al. 1998; Coviello et al. 1999; Ray et al. 2010; Amin et al. 2012; Zu et al. 2012; Fosso-Kankeu et al. 2015). Hydrogels have been filled with other adsorbents to add new properties to the natural polymers such as to improve its adsorption capacity. According to Jing et al. (2013) hybrid hydrogels have three major advantages over their components, these include: biological materials introduced into the hybrid hydrogels can lower the cost of the resulting composite; the composite being made of different materials results into hydrogels with various active groups and remediation potentials, therefore capable to remove more than one contaminants from polluted water (Im et al. 2010; Yun et al. 2010; Tang et al. 2010; Rao et al. 2011); finally hybrid hydrogels have good mechanical properties and tolerance to vigorous stirring (Pan et al. 2008; Chatterjee et al. 2010). Hydrogels have been effectively used for the removal of pollutants from water; Mandal et al. (2012) preparaed a semi-IPN (interpenetrating polymer network) and IPN based on poly(vinyl alcohol) and poly(AA-co-2-hydroxylethyl methacrylate) with various compositions that they used for removal of rhodamine B and methyl violet from solution; they observed that the sorption capacity of both dyes increased with the increase of the copolymer content in the gel. In a separate study, semi-IPN composite hydrogels prepared by the incorporation of cellulose derivatives in a matrix of poly(methacrylamide) was used by Chauhan and Mahajan (2002) for the removal of Fe^{2+}, Cu^{2+} and Cr^{6+} from solution and they found that the functional groups on the gels have a considerable impact on their adsorption capacity and mechanism.

Metals found in surface water have an influence on the aquatic life as well as human; when these contaminated sources are used for irrigation or domestic purposes the metal pollutants can negatively affect the health of people consuming the water and the crops. It is therefore important to use a sustainable method such as adsorption to effectively remediate water pollution (Fosso-Kankeu et al. 2011; Mittal et al. 2013; Fosso-Kankeu et al. 2016a, b).

This study investigates the characteristics of a zeolite-hydrogel composite and its potential as adsorbent for the treatment of acid mine water.

Methods

Water samples

Water samples from the mine effluent were collected from mine dams in the Mpumalanga and the North-West provinces of South Africa. A polypropylene plastic bottle of a capacity of 500 mL was used to collect the water at the subsurface of the dams; the physicochemical parameters of the water samples such as pH, electrical conductivity, oxido-redox potential and temperature were determined in situ using a portable Lovibond SensoDirect 150 multi-parameter water quality pH meter. The samples were then stored in cooler box containing ice packs and transported in the laboratory for further analyses.

Synthesis of adsorbents

GL, acrylamide (AAm), N,N-methylene-bis-acrylamide (MBA), potassium persulfate (KPS) were purchased from Sigma-Aldrich, South Africa. Clinoptilolite was obtained from a local company in South Africa.

GL-cl-PAAm and hybrid hydrogel composite were synthesized using the free radical graft co-polymerization technique. For the synthesis of GL-cl-PAAm hydrogel, initially GL (1 g) was dispersed in 20 mL deionized water and stirred vigorously followed by the addition of KPS (20 mg) and MBA (30 mg). 1 g AAm was added in the reaction vessel and stirred again. Finally, the reaction temperature was maintained at 60 °C and the reaction was allowed to proceed for 2 h without any further disturbance. After, the completion of reaction, the reaction vessel was allowed to cool down at room temperature. The homopolymer, unreacted monomers and the crosslinkers were separated by repeated washings with hot water followed by acetone. Finally, the synthesized hybrid hydrogel composite was dried in hot air oven for 24 h and powered using the ball mill.

For the synthesis of hybrid hydrogel composite, initially, 20 mg clinoptilolite was dispersed in 20 ml deionized water by sonicating the solution for 2 h using the ultrasonicator, thereafter, the same procedure used to synthesize the GL-cl-PAAm hydrogel was followed.

Characterization

The graft co-polymerization of the PAAm onto GL and the effect of the incorporation of Clinoptilolite within the hydrogel polymer matrix on its physico-chemical properties were studied using FTIR. The FTIR of samples were recorded on the Perkin-Elmer Spectrum 100 spectrometer (USA) using the KBr pellet method in the spectral range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

Adsorption experiments

The adsorption behavior of the GL-cl-PAAm and the hybrid hydrogel composite for the adsorption of metal ions was studied in batch mode. Initially, the varied mass of the adsorbents were added in the metal ion solutions taken in plastic bottles. The bottles were agitated on a thermostatic water bath shaker (Labcon, South Africa) for 1 h. After the completion of the adsorption experiment, the bottles were removed from the water bath shaker. The solutions were filtered using syringe filters and the concentration of remaining metal ions in the solution were measured using an inductively coupled plasma optical emission spectrometer (ICP Expert II, Agilent Technologies 720 ICP-OES). The percentage adsorption was calculated using Eq. (1) (Mittal et al. 2015; Mahdavinia et al. 2013).

$$\% \, Adsorption = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (1)$$

Where, C_o and C_e are the initial and equilibrium concentrations (mg/L) of the metal ion, respectively. The investigation of the effect of temperature on the adsorption potential of adsorbents was done by varying the temperature between 20, 30 and 40°C while keeping the other parameters constants.

Results and discussion

Characterization of the clinoptilolite and the hybrid hydrogel composite

The FTIR spectra of the clinoptilolite and hybrid hydrogel composite are shown in Figure 1. The FTIR of clinoptilolite has shown the characteristic peaks of the hydrated water at 3610 and 1641 cm^{-1}, these bands were due to the water molecules associated with Na and Ca in the channels and cages of clinoptilolite structure. Some other peaks were observed at 1178 cm^{-1}, due to the asymmetric stretching vibration modes of internal T-O bonds in TO_4 tetrahedra (T=Si and Al), 786 and 694 cm^{-1}, due to the stretching vibration modes of O-T-O groups and the bending vibration modes of T-O bonds, respectively(Vasylechko et al. 2003; Korkuna et al. 2006). On the FTIR spectrum of the hybrid hydrogel composite, the characteristic peaks of clinoptilolite at 1601, 786 and 615 cm^{-1} were observed along with the peaks at 3455 cm^{-1}, due to the –OH stretching vibrations, 2929 cm^{-1}, due to the aliphatic –CH_2 stretching vibrations, 1713 cm^{-1}, due to the C=O stretching in AAm, 1449 cm^{-1}, due to the amide –NH in-plane bending and 1173 cm^{-1}, due to the amide –CN stretching vibration. The presence of the characteristic peaks of the clinoptilolite as well as the characteristics peaks of the AAm in the FTIR of the hybrid hydrogel composite confirm the successful grafting of AAm onto the GL as well as the incorporation of clinoptilolite within the hydrogel polymer matrix.

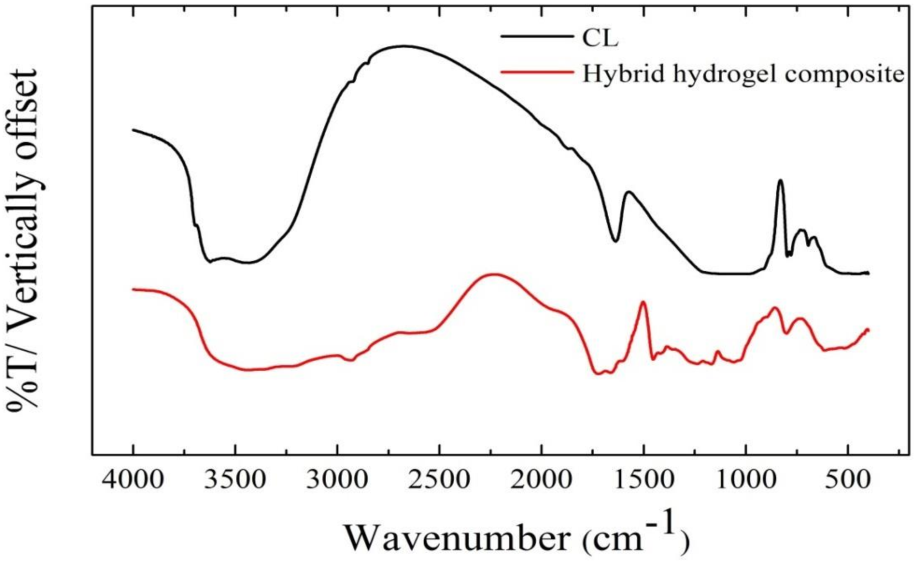

***Figure 1** FTIR spectra of clinoptilolite and the hybrid hydrogel composite*

Effect of the adsorbent dosage

The effect of the adsorbent dose on the adsorption efficiency of the GL-cl-PAAm and the hybrid hydrogel composite was investigated with varied mass of the adsorbents (25-150 mg) and the results are depicted in Figure 2. It was observed that for both the adsorbents the adsorption efficiency increased with increasing polymer dose and attained the optimum value beyond which no noticeable increase in the adsorption efficiency was observed with further increase in the dosage of adsorbents. The adsorption efficiency increased initially due to the availability of more adsorption sites with increased mass of the adsorbent. The saturation in the adsorption efficiency at much higher mass of the adsorbents was due of the fact that, with higher amounts of the adsorbents, the total available surface area decreased through the aggregation of adsorption sites and the increased diffusion path (Mittal et al. 2015; Mittal et al. 2016).

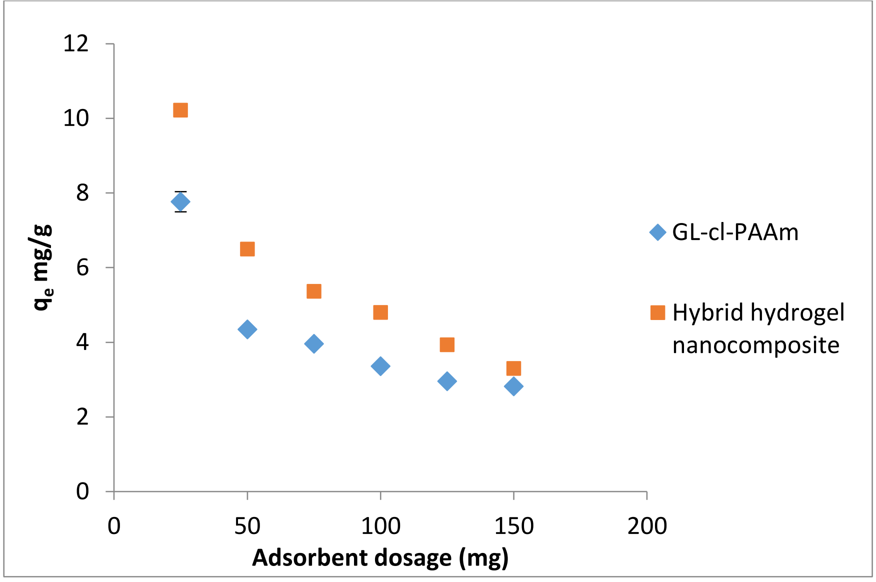

***Figure 2** Adsorption of cadmium at various dosages of GL-cl-PAAm and hybrid hydrogel composite*

Thermodynamic study

To determine the temperature dependency of cadmium removal from solution, adsorption experiments were carried out at three different temperatures (20, 30 and 40°C). An increase of adsorption was observed from 20°C to 30°C, follow by a sudden decrease at 40°C. Metal ions removal is strongly dependent on solution temperature, similar trend was observed by several researchers (Kula et al. 2008; Karami 2013; Abdelwahab et al. 2015) who explained this phenomenon as a result of the exothermic nature of the adsorption; furthermore, adsorption mainly occurs through electrostatic interaction which is usually associated with low adsorption heat (Karaca et al. 2006). The thermodynamic behaviour of the adsorption of cadmium onto GL-cl-PAAm and the hybrid hydrogel nanocomposite was investigated through the determination of parameters such as the standard free energy change known as Gibbs free energy (ΔG°, KJ mol-1), entropy change (ΔS°, J mol-1 K-1) and enthalpy change (ΔH°, KJ mol-1) (Table 1). The Gibbs free energy (ΔG°) for the adsorption of cadmium onto GL-cl-PAAm and the hybrid hydrogel nanocomposite was calculated using the van't Hoff equation below:

$$lnK_a = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{2}$$

Where Ka (q_e/C_e) is the equilibrium constant or the linear adsorption distribution coefficient, T is the solution temperature (K), and R is the gas constant (8.314 x 10-3 KJ mol-1 K-1).

The values of ΔS° and ΔH° were obtained from the intercept and slope of the plot lnKa vs 1/T, these values are shown in Table 1. The negative value of ΔG° indicates the spontaneous nature of the adsorption of cadmium onto GL-cl-PAAm and the hybrid hydrogel nanocomposite; while the values of ΔS° and ΔH° were both positive. The positive value of ΔS° suggests increased randomness at the solid/liquid interface with some structural changes obtained in the adsorbate and adsorbent system (Onal et al. 2006; Hiwarkar et al. 2015). The positive value of ΔH° confirms the endothermic nature of the process.

Table 1 *Thermodynamic parameters for the removal of cadmium from solution*

Adsorbent	Kc	Temp	ΔG (KJ/mol)	ΔS (J/mol/K)	ΔH (KJ/mol)
GL-cl-PAAm	1.620974	293.15	-1177.25814	2914.72	43.36
	1.630947	303.15	-1232.87589		
	1.635984	313.15	-1281.57248		
Hybrid hydrogel nanocomposite	5.85189	293.15	-4306.0458	148.06	0.34
	5.314635	303.15	-4210.22016		
	5.033183	313.15	-4207.43968		

Removal of metal pollutants from mine effluents

Surface waters were collected around mines in Orkney (mine effluent A) and Clewer (mine effluent B) located in the North West Province and the Mpumalanga Province of South Africa. Analysis of the water quality (Table 2) showed that the mine effluent A was less polluted; with pH close to neutral and conductivity within the guideline value; however metal ions such as U^{+6}, Fe^{+2}, Ni^{+2} and Pb^{+2} occurred in relatively high concentrations exceeding the recommended values in the guideline (SABS, 2005). The mine effluent B on the other side was highly polluted, a typical acid mine drainage (AMD), characterized by acidic pH (~2.5), abnormal conductivity and very high concentrations of metals (Table 2) such as U^{+6}, Cd^{+2}, Co^{+2}, Fe^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2} which exceeded the recommended values in the guideline (SABS, 2005).

Table 2 *Physicochemical characteristics of mine effluents*

Parameters	**Unit**	**Recommended value SABS (2005)**	**Samples**	
			Mine effluent A	**Mine effluent B**
pH		5 – 9.5	7.74	2.55
Eh	mV	NA	-42	216
EC	mS/cm	< 150	3.36	6.55
Sulphate	mg/L	< 400	1360	7035
Chloride	mg/L	< 200	180	400
Nitrate	mg/L	< 10	8.5	123.2
Cyanide	mg/L	< 0.050	65	242
Cd	mg/L	< 0.005	nd	0.45
Co	mg/L	< 0.5	nd	12.18
Fe	mg/L	< 0.2	0.24	2516.72
Mn	mg/L	< 0.1	4.92	104.86
Ni	mg/L	< 0.15	nd	13.06
Pb	mg/L	< 0.02	1.26	43.57
U	mg/L	NA	0.41	2.378
Zn	mg/L	< 5	nd	8.82

The synthesized adsorbents were used to remove metal ions from mine effluents A and B. The results in Table 3 show that the adsorbents performed relatively well for the removal of metals in mine effluent A, achieving a total removal of U^{+6}, Fe^{+2}, Ni^{+2} and Pb^{+2}. On the other hand only Co^{+2}, Ni^{+2} and Pb^{+2} were removed above 80% in mine effluent B. There was no major difference observed when the solution temperature was varied from 25°C to 45°C; the adsorption performance in this case varied with the metal ions as some metal ions were easily removed at high temperature while the others were poorly removed at such temperature.

Table 3 *The concentrations of different metal ions in the mine effluents before and after adsorption*

Metal in solution	**Concentration mg/L**							
	Mine effluent A				**Mine effluent B**			
	Before adsorption	**Fitness**	**After adsorption**	**Fitness**	**Before adsorption**	**Fitness**	**After adsorption**	**Fitness**
U^{+6}	0.41	No	0	Yes	2.38	No	0.83	No
Cd^{+2}	0	Yes	0	Yes	0.45	No	0.18	No
Co^{+2}	0	Yes	0	Yes	12.18	No	1.44	No
Fe^{+2}	0.24	No	0.14	Yes	2516.72	No	2260	No
Ni^{+2}	1.52	No	0	Yes	13.06	No	1.10	No
Pb^{+2}	1.26	No	0	Yes	43.57	No	2.58	No
Zn^{+2}	0	Yes	0	Yes	8.82	No	7.59	No

Overall the hybrid hydrogel composite performed better than the GL-cl-PAAm and the performance of the former was considered to evaluate the suitability of the treated water. After treatment it was found that metal ions such U^{+6}, Fe^{+2}, Ni^{+2} and Pb^{+2} initially present at unacceptable concentrations in mine effluent A were reduced to acceptable values based on the SABS guideline (2005); while the concentrations of all the metal ions in mine effluent B remained unacceptable after treatment; such solution requires a pretreatment process prior to the application of our adsorbents.

Conclusions

The hybrid hydrogel nanocomposite was successfully synthesized in this study as demonstrated by the FTIR results; the developed adsorbent was found to perform better than its components at relatively high temperature. The adsorption process occurred through an endothermic and spontaneous reaction. The application of the newly developed adsorbent for the treatment of mine effluent resulted into the total removal of trace metals from solution while the major metals were not totally removed. The developed adsorbent can therefore play a role of polishing to complement a treatment method applied upstream.

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Feasibility study on seepage water treatment at a uranium TMF site by ion exchange and ferric hydroxide adsorption

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Extended Abstract

Uranium and arsenic retention by ion exchange and ferric hydroxide adsorption, respectively, was investigated as seepage water treatment option for the WISMUT TMF - site Helmsdorf. The conducted feasibility study involved geochemical modeling, laboratory tests and pilot scale field tests.

Helmsdorf TMF seepage water is alkaline (pH ~ 9) and contains up to 10 mg / l uranium, ~ 1 mg / l arsenic and 1 - 2 g / l hydrogen carbonate, sulfate and sodium, respectively. Seepage water pollutant speciation was calculated by PhreeqC using an extended Wateq4f database. Calcium uranyl carbonate and hydrogen arsenate species dominate dissolved uranium and arsenic, respectively. While hydrogen arsenate adsorbs to ferric hydroxide preferentially, alkaline earth carbonate complexation is known to hinder uranyl sorption [1]. Prior to laboratory tests, optimal geochemical conditions for uranium and arsenic retention by ion exchange and ferric hydroxides were modeled. Both pollutant speciation and surface properties of ferric hydroxide adsorbent depend on pH. A drop in treatment pH from pH ~ 9 to pH $\leq$ 6 facilitates uranium and arsenic retention by suppression of alkaline earth uranyl carbonates complex formation and increase in the number of positively charged ferric hydroxide surface sites, respectively.

Laboratory experiments were conducted to test uranium and arsenic retention from original seepage water at different ion exchange resins and ferric hydroxide adsorption materials. Different pH values were adjusted using hydrochloric acid. Uranium retention of all tested ion exchange resins improved from insignificant at original seepage water pH to technically feasible levels at adjusted seepage water pH of pH = 5.5 - 6. Arsenic retention was tested with GEH, FerroSorp and Bayoxide as adsorbent. Despite differences in pzc and total loading capacities, the different ferric hydroxides showed comparable arsenic sorption at pH = 6 - 6.5. Next to pH, contact time was found to be of capital importance for ferric hydroxide adsorption.

Pilot testing was performed using a multi-stage ion exchange and a single-stage ferric hydroxide adsorption unit subsequent to pH controlled hydrochloric acid dosage and sand filtration. The treatment tests were performed on-site at seepage water pH adjusted to pH = 5.5, pH = 6 and pH = 6.5. For prevention of CO_2 degassing, the pilot installation was operated at a pressure of 3 bar. At a flux of 500 l / h, seepage water treatment was demonstrated successfully over a period of one year. Uranium and arsenic effluent concentrations were reduced to < 0.2 mg / l. The identified operational parameters met or even slightly exceeded the range of typical ion exchange and ferric hydroxide adsorption applications in water treatment.

Key words: Uranium mining, seepage water treatment, geochemical modeling, ion exchange, ferric hydroxide adsorption, laboratory test, pilot plant test

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Research and development of waste waters vibroacoustic purification methods for mining enterprises

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Abstract

Purpose. Intensification of effluents treatment process and increase in the quality thereof due to use of vibroacoustic oscillations. Development of the technique and technology of vibroacoustic filtration.

Methods. We studied a physical mechanism of filtration process during application of elastic oscillations on the basis of research of hydrodynamic situation during filtration and behavior of suspended particles. Effectiveness and fineness of filtration were examined for various filter materials depending on the mode of oscillations.

Results. Parameters of waste waters filtration were found to improve under the effect of vibroacoustic oscillations. The performance and effectiveness of filtration do depend on characteristics of filtering material, the amplitude of oscillating velocity and frequency of oscillation. Methods of calculation of the optimal mode to conduct vibroacoustic filtration have been developed.

Scientific novelty. Under the effect of oscillations, hydrodynamic conditions of the filtration process change. There emerge counter-current and tangential fluid flows due to which regeneration of filter elements takes place. Conditions for appearance of such flows have been determined.

Practical utility. We have designed and developed a pilot of a vibroacoustic filter which has already passed verification in industrial conditions. Results of these tests have shown application perspectiveness of this method in water-sludge systems of mining enterprises.

Key words: purification, waste waters, vibroacoustic filter, counter-current flows, filter regeneration.

Task setting.

The issue of effluents purification from highly dispersed mechanical admixtures is rather critical for most of mine enterprises. Certainly one can treat waste waters to bring them to standard norms using filter materials. Nevertheless, these have one essential drawback: filter pores become clogged very quickly and the process performance sharply drops down.

We propose a cardinal solution to this problem with the help of vibroacoustic oscillations method. The innovative element of the proposal is purification of waste waters on filtering materials with simultaneous impact of vibroacoustic oscillations on the suspension. The gist of our proposal is to change the modes of suspension passing through a filter element due to the pulse-wave effect. As a result, continuous filter regeneration takes place and conditions of particles extraction from the suspension are improved. So, we can solve the critical task of waste waters purification from highly dispersed suspended solids.

Basics of the principle.

The intensifying effect of vibroacoustic oscillations on separation of multiple-phase suspensions is based on physical effects such as counter-current regeneration (restoration) of filter elements due to varying pressures and liquid flows, as well as to change in the velocity of suspended particles movement [1, 2]. The point is that at a certain moment the pressure behind the filter partition exceeds the pressure in front of the partition, leading to a «reverse» pressure difference [3, 4]. Under this effect, counter-current flows appear in the fluid the direction of which is counter to the main flow, the so called «counter-current» flows. Due to these flows, filter pores are cleaned and suspended particles on its surface are destroyed [5, 6]. After this, hydrodynamic characteristics of the grid partition are restored (the hydrodynamic resistance is reduced). The filter regeneration takes place with a frequency equal to oscillations frequency.

We studied conditions for emergence of such counter-current flows and dependences of performance and effectiveness of filtration on the dynamic and frequency range of vibroacoustic oscillations on the laboratory unit (Fig. 1).

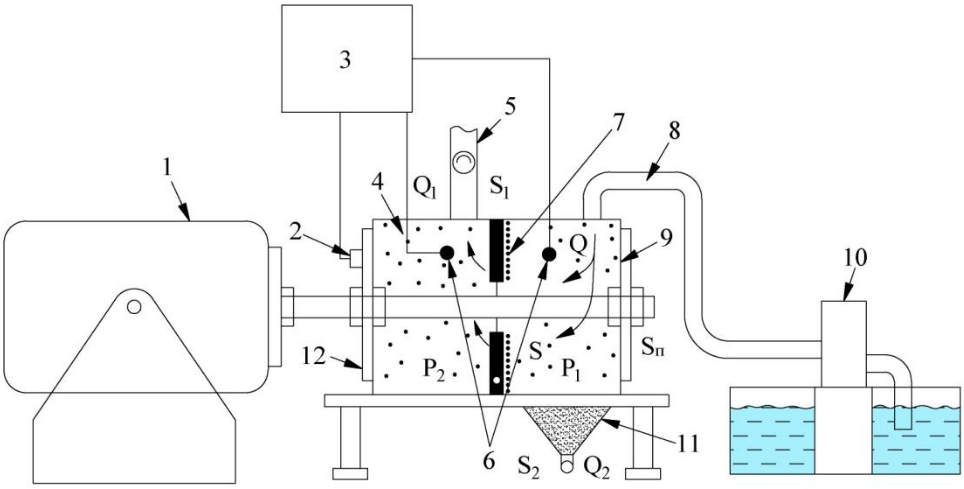

Figure 1 *Schematic diagram of a vibroacoustic filter*

1 – vibration exciter; 2 – acceleration meter; *3* – measurement unit; *4* – filtration chamber; *5* – outlet connection with pressure gauge; *6* – pressure sensor (strain gage transducer); *7* – filtering partition; *8* – inlet connection; *9,12* – pistons; *10* – pump; *11* – discharging gear.

The vibroacoustic filter is a chamber *4* separated with filtration partition *7* into two sections - initial suspension section and purified fluid section. Each section has pistons. Pistons *9* and *12* are driven with a vibration exciter *1* and make in-phase vibrations thanks to rigid connection between themselves through a metal rod. The suspension is fed to the filtering unit with a pump *10*. Pressure and performance in the initial suspension section are adjusted with the help of a valve installed in the input connection *8*. The pressure drop in the filter and the pressure in the sections are monitored with membrane strain gage transducers *6*, while the vibration parameters of the pistons are measured by acceleration strain gage transducer *2*. Signals from the transducers are furnished to measurement unit *3*. In the lower initial suspension section there is a conical discharging gear *11* for condensed product. The flow meter in the outlet connection *5* determines the filter performance.

During the study, we used various filter materials differing in method of their manufacture and structure: double twill-woven metal gauze, bronze and nickel metal-ceramic filters, filtering belting, and nitron. The filter element is designed in a «sandwich» from consisting of two perforated plates with filtering material located between them. As perforated plates, slotted screen (*Humboldt*) was used with the mesh size of 50÷70 µm. Fig. 2 shows hydraulic characteristics of these filters.

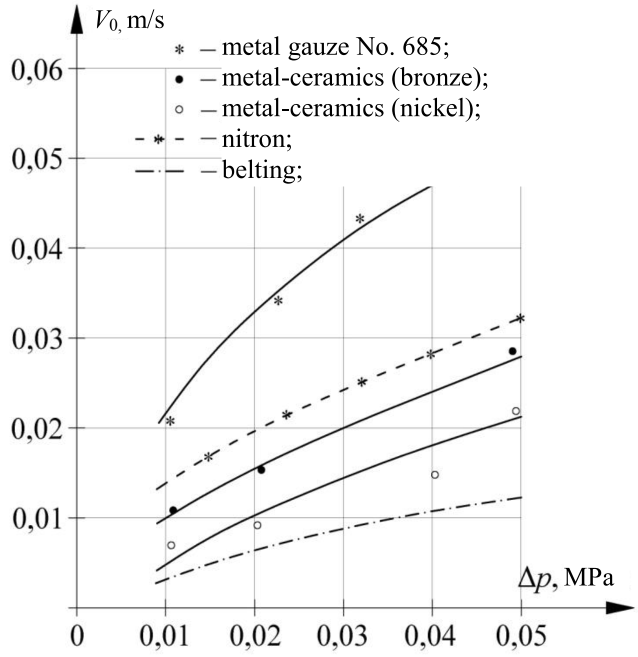

***Figure 2**. Hydraulic characteristics of filter materials*

During the experiment, suspension with its particles concentration from 100 to 2000 mg/l of a specified granulometric composition, typical for well waters, was fed to the filter element with simultaneous application of vibroacoustic oscillations of 5 to 120 Hz and oscillation velocity amplitude of 0.01 to 0.1 m/s. The pressure drop on the filters changed from 0.02 to 0.05 MPa. Different filter materials were used. The obtained results are presented in Figure 3. The diagrams show that regeneration of any filtering materials happens with certain vibration velocity amplitudes subject to conditions for counter-current flows occurrence.

It should be noted that there are three modes of impact of vibroacoustic oscillations. In the first mode, there are no counter-current flows ($V_m<V_0$) and there is no regeneration of the filter. In the second mode (transition zone), the amplitude of the oscillating velocity increases to cause sharp increase of filtration productivity ($V_m \approx V_0$). For the third mode, the filtration capacity ($V_m>V_0$) is maximum and continuous. Subsequently, the performance does not depend on the dynamics of impact and is practically equal to the productivity of purified water.

The transient mode is determined by the following [7]. For this range of dynamic impact, a gradual increase in the counter-current flow velocities is characteristic. Turbulent flows of fluid appear along the filtering material surface. All that contributes to more efficient filter regeneration. At a certain amplitude of oscillation velocity, a full restoration of the filtering material takes place, and further increase of oscillation velocity does not bring any increase in productivity. A dynamic mode of full regeneration of the filter depends on the type of filtering material used. Also, a mode of stable regeneration begins for dense filters with greater intensity of oscillations. Fig. 4 presented a graph of dependence of the required oscillating velocity amplitude on the filtering material and filtration process conditions (pressure difference).

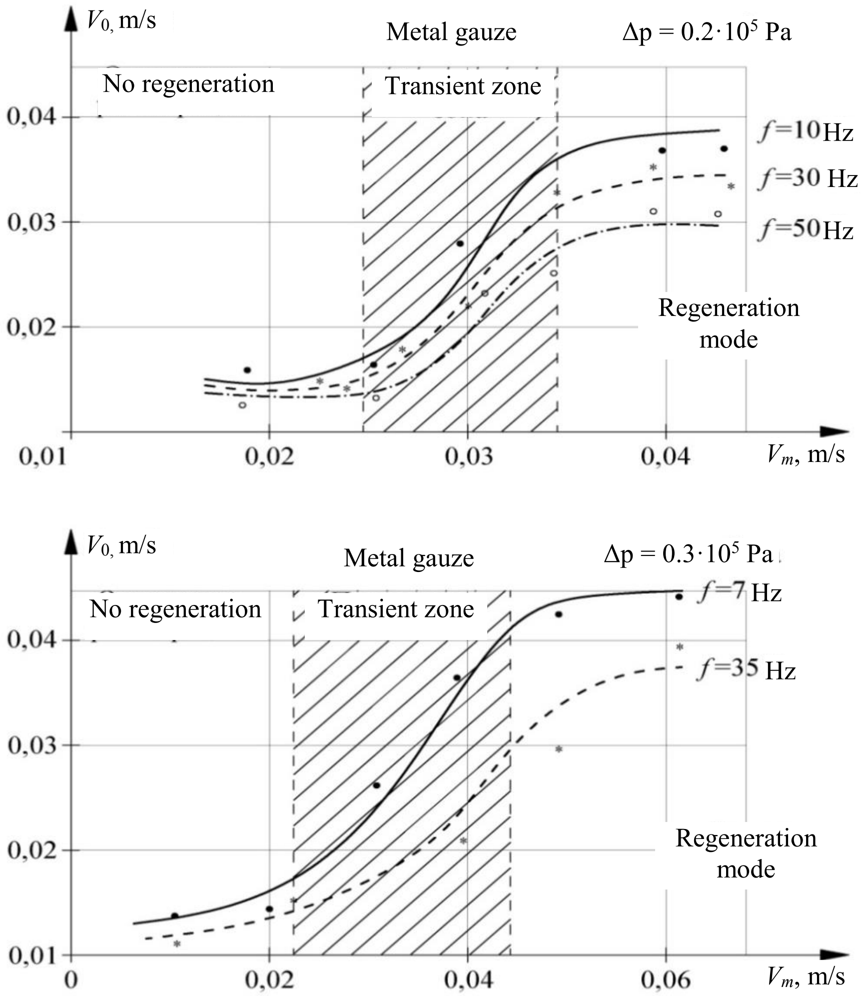

Figure 3. *Dependence of the filter specific productivity on the oscillating velocity V_m amplitude for metal ceramics (bronze) and metal gauze.*

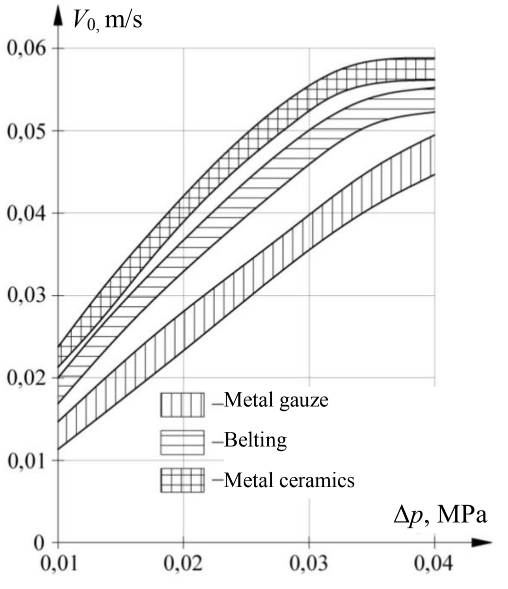

Figure 4. *Graph of dependence of the required oscillating velocity amplitude on the type of filtering material and conditions of filtration process (ΔP).*

The efficiency of waste water purification during the vibroacoustic filtering process was determined by the suspensions weight distribution depending on their granulation sizes. The following algorithm was employed to establish the filtration fineness. First, the dispersion composition of the initial suspension was determined, then the one of the treated suspension. The particle sorting coefficient for each interval was determined which value indicated the degree of filtration fineness of the filter under test.

The degree of filtration was established by the difference in the weight content of impurities in the initial fluid and in filtrate. Measuring of the weight content of suspended particles in the fluid was conducted either by filtration of 0.5 liter of fluid through a biological membrane filter or by using nephelometer LMF-69. The obtained results are presented in Fig. 5 and in Table 1.

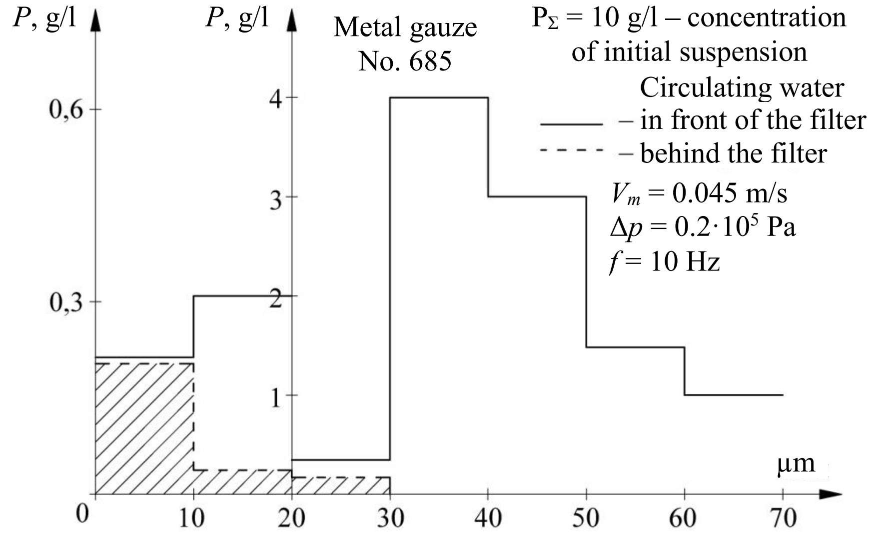

Figure 5. *Efficiency of vibroacoustic waste water purification with a metal filter*

The analysis of the obtained results makes it possible to conclude that filter materials with applied vibroacoustic oscillations can treat effluents to the required condition. In the purified water the suspensions concentration is always less than 150÷200 mg/l.

Table 1 *Dependence of the efficiency of purification on the type of the filtering material*

Type of filter material	Amplitude of oscillatory velocity, m/s	Suspensions weight distribution in filtrate as per grain size, g/l		
		0-10 μm	10-20 μm	20-30 μm
Metal gauze	0.045	0.14	0.09	0.07
	0.06	0.1	0.07	0.05
Belting	0.05	0.08	0.06	0
Metal ceramics (bronze)	0.05	0.07	0.03	0

When using metal gauze, the minimum size of captured particles is 25÷30 μm, and with metal ceramics filter (bronze) and belting – 20÷25 μm. Notably, metal ceramics and belting can treat water to a concentration of 100÷150 mg/l. Higher oscillating velocity amplitude results in higher purification effect. Clearly, it is associated with the fact that with great dynamic loads the number of particles accumulated in the area near the gauze increases.

Theoretical and experimental studies conducted have allowed developing and creating of a test prototype of a vibroacoustic filter for waste waters purification (Fig. 6).

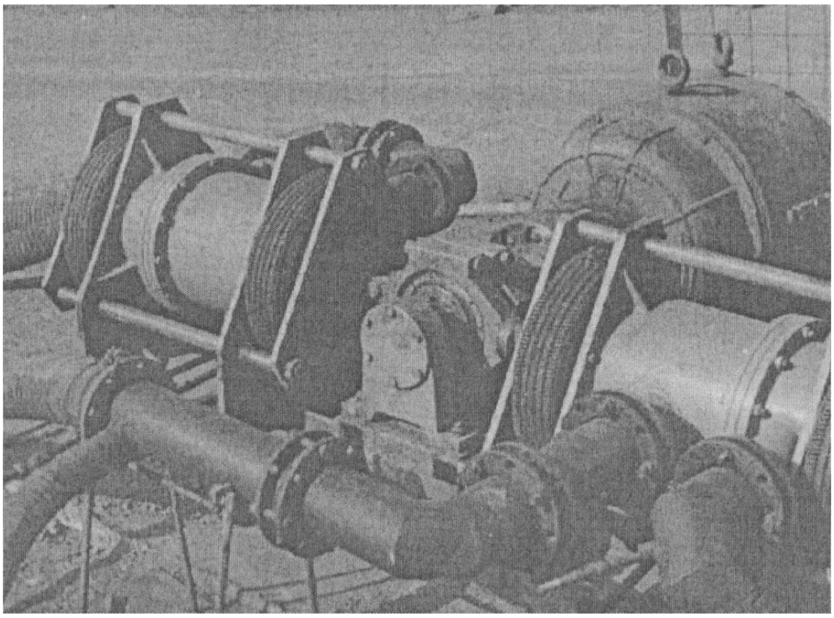

***Figure 6**. External appearance of the vibroacoustic filter (a pilot prototype)*

The filter contains two bodies arranged symmetrically relatively to the source of oscillations. A mechanical vibration drive is employed. Each body is divided with filtering partition into two sections. Pistons are installed into the end walls of the bodies using flexible elements with rigid interconnection. All four pistons are driven to oscillate from one vibration drive.

The task of the test research was to (i) determine the performance of the developed construction in the conditions close to production site and (ii) mastering the technology of effluents purification with our vibroacoustic apparatus in various stages of complex treatment schemes. Parameters of vibroacoustic filtration were studied relative to their granulometric composition, concentration of suspensions and physical and mechanical properties as well as modes of elastic oscillations.

During the experiment, we registered the flow rate of well waters under treatment; measured concentrations of suspended particles in initial well waters, in filtrate and in condensed product. The dispersion analyses of well waters and obtained product were conducted. Operation values of the vibroacoustic apparatus and current treatment facilities were also compared. Slime water was periodically taken from a conical sludge container. While conducting the tests, the vibroacoustic filter was built into a traditional circuit of purification. Experimental amplitude of the pistons oscillation velocity was changed (oscillation frequency from 5 Hz to 50 Hz) and the pressure drop on the filter element was varied in the range from 0.01 MPa to 0.1 MPa. Flat filter elements and cylindrical filter elements (cartridge-type) were employed. The pilot prototype was tested in wells of different regions of the Russian Federation. Qualitative and quantitative indicators of treated well waters are given in Table 2.

Table 2 *Results of industrial tests of the vibroacoustic filter.*

Type of filtering material	Parameters of vibroacoustic filtration process					Concentration of suspended matter in sludge container filtrate, mg/l
	Filter specific productivity m/hour	Concentration of suspended matter, mg/l in			Coefficient of filtration completeness, %	
		Initial suspension	Filtrate	Sludge		
Metal gauze	70	35	11	5000	69	20
Belting	25	35	5	4500	85,7	20
Metal gauze	70	100.8	33,6	23500	67	51
Metal ceramics (nickel)	32	100.8	28,4	19900	72	51
Metal ceramics (bronze)	38	100.8	30.4	24700	70	51
Metal gauze	70	200	100	400	50	170
Lavsan	70	202	79	8500	60.5	170

Results of industrial studies show potential perspectives of using vibroacoustical filters in water-sludge systems of mining enterprises.

The filter high specific productivity (up to 70 m/hour) ensures a high level of purification (70÷80% clarification). The developed construction shows its high performance and reliability; it does not require expensive servicing. Technological possibilities of vibroacoustic filters are practically unlimited and seem to have no analogs in the world.

Conclusions

Our investigations demonstrate that vibroacoustic filtration makes it possible to drastically increase the speed of waste waters purification of highly dispersed admixtures and increase the process efficiency. Introduction of the process will eventually reduce capital and operational expenses.

The developed vibroacoustic module is simple in manufacture, reliable in operation, is small-size and mobile.

The innovative element of this development is a possibility to use ultrathin cell filter elements manufactured with the use of nanotechnologies. This will help to essentially increase the quality of treated effluents and successfully solve environmental issues.

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Sorption of arsenate on ettringite formed in sulphate removal from mine drainage water

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Abstract

There is a current need for effective treatment methods for water pollutants such as sulphate and arsenic. Circular economy thinking is also increasing. Ideally, waste from one stream could be valuable in another. The aim of this research was to investigate arsenate sorption on ettringite formed in sulphate removal from underground gold mine drainage water. Batch sorption experiments were conducted at room temperature using a synthetic solution with an initial As(V) concentration of 1.7 ± 0.1 mg/L, which was chosen to model typical arsenate containing mine water. The effect of ettringite dosage was studied, and Langmuir and Freundlich sorption isotherms were fitted to the results. The maximum sorption capacity (1.8 mg/g) of the ettringite was determined from the Langmuir isotherm, which corresponded well with the maximum experimental sorption capacity. Furthermore, the effect of contact time was studied, and pseudo-first order and pseudo-second order kinetic models were fitted to the experimental data. The kinetics of the arsenate sorption on ettringite were best described by the pseudo-second order model. This paper offers one possible method of extracting value from mine water, as its results indicate that the precipitate produced during sulphate removal from mine water by precipitation as ettringite could be further used as a sorbent for arsenate removal from aqueous solutions.

Key words: Mine water, sulphate removal, ettringite, sorption, arsenic removal

Introduction

Sulphate emissions cause environmental problems. Mine water can contain up to tens of thousands of milligrams of sulphate per litre, and must be treated before discharge from a mine site. Precipitation as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) is an efficient method of sulphate removal from mine water. In this method, the pH of mine water is raised to approximately 12 using lime, and conventional aluminium chemical is added in order to precipitate sulphate as ettringite. For example, quicklime or hydrated lime and sodium aluminate or aluminum hydroxide can be used. The purified water can be treated with carbon dioxide (CO_2) precipitating calcite ($CaCO_3$) to lower the pH so as to be in accordance with mine discharge limits. With precipitation as ettringite, mine water sulphate concentration can be reduced to less than 200 mg/L (i.e., less than the drinking water guideline in Finland). In comparison, the conventionally used lime treatment (Tolonen et al. 2014, Tolonen et al. 2015) can reach sulphate levels of only 1500—2000 mg/L. When ettringite precipitation is used for waters with high sulphate concentration (>3000 mg/L), it may be economical to use traditional lime precipitation as a pre-treatment to remove some of the sulphate. After partial sulphate removal, a smaller dosage of the more expensive aluminium chemical is required for the ettringite precipitation step. Sulphate removal from mine water with precipitation as ettringite offers a means of reducing environmental pollution and simultaneously recovering a useful mineral that could be used, for example, as a construction material or as a sorbent in arsenic removal from water.

As arsenic is toxic and carcinogenic, arsenic contamination in natural waters is a significant problem. The World Health Organisation (WHO) has set a 0.01 mg/L guideline for arsenic in drinking water, which is the same value set as the permissible limit for drinking water in Finland. Arsenic occurs in the aqueous environment mainly at two oxidation states: arsenite As(III) and arsenate As(V). As(III) is 10 times more toxic than As(V). Eh and pH conditions control arsenic speciation. As(III) is dominant at intermediate to low redox potentials, whereas As(V) is dominant at high redox potentials. Arsenic is a significant mine water contaminant that mainly occurs as As(V) in acid mine drainages (AMD) (Williams 2001, Bednar et al. 2004, Paikaray 2015). While the sorption of arsenate on ettringite has been studied by Myneni et al. (1997), to our knowledge, there are no studies of isotherm and kinetic models fit to data obtained from arsenate sorption experiments on ettringite.

In this research, arsenate sorption on ettringite that formed during sulphate removal from underground gold mine drainage water by adding hydrated lime and sodium aluminate was investigated. The sorption experiments were conducted using synthetic solution with 1.7 ± 0.1 mg/L As(V), which was chosen to model arsenic containing mine water. The effect of sorbent dosage was studied, and Langmuir and Freundlich isotherm models were fitted to the experimental data using OriginPro software. Futhermore, the effect of contact time was studied, and pseudo-first order and pseudo-second order kinetic models were fitted to the data from the experiments using OriginPro software.

Materials and methods

Ettringite

The sorbent (referred to as ettringite) that was used in the sorption experiments contained approximately 90 % ettringite and 10 % calcite, which was determined via quantitative X-ray diffraction data Rietveld analysis. The ettringite formed during sulphate removal from ferric sulphate treated mine drainage water from an underground gold mine (sampled after settling pond). The initial sulphate concentration of the mine drainage water was 1400 mg/L. The sulphate precipitation was done in batch-mode using programmable paddle stirrer equipment at room temperature (20 ± 2 °C). The sample volume was 800 mL for each 1 L glass beaker, with 1.5 g/L of hydrated lime (JT Baker 93+ %) and 0.5 g/L of sodium aluminate (Eka WT A 83, 40—50 % $NaAlO_2$) used as reagents. Each batch was mixed at 50 rpm for 5 hours and then left to settle overnight. The precipitates were filtered with Schleicher & Schuell 589 blue ribbon quantitative low ash filter paper by vacuum filtration. They were then air-dried, weighed, crushed, sieved to a 63—125 µm particle size fraction, and stored in a desiccator prior to the sorption experiments.

The sorption of arsenate on ettringite

The effect of the sorbent dosage on arsenate removal from synthetic solution was studied via 24 h batch sorption tests using a reciprocal shaker at room temperature (20 ± 2 °C). An arsenate model solution was prepared by dissolving arsenic (V)oxide (Acros Organics 99.9+ %) into ultrapure water. Then, 0, 0.2, 0.5, 1, 2, 3, 4, 5, 7 or 10 g/L of the synthesized ettringite was dosed to 0.025 L of 1.7 mg/L arsenate model solution and agitated at 250 rpm for 24 h in a reciprocal shaker (POL-EKO LS 700). After shaking, the samples were centrifuged at 4000 rpm for 5 min with Thermo Scientific SL 8 Centrifuge, after which the supernatant pH was measured. The supernatant was saved for arsenic analysis. The arsenic concentration was analysed using inductively coupled plasma optical emission spectrometry ICP-OES according to the standard SFS-EN ISO 11885 in an accredited laboratory (Ahma Ympäristö, Finland). Furthermore, the effect of contact time was also studied. One litre of the 1.8 mg/L arsenate model solution was stirred at 250 rpm in a 2 L glass beaker with a magnetic stirrer, and 1 g/L of ettringite was dosed into the solution. Samples were taken at 0, 1, 3, 5, 7, 10, 30 minutes, as well as 1, 2, and 5 hours after ettringite addition. The samples were centrifuged for 1 min at 4000 rpm, and the supernatant was saved for arsenic analysis.

Results and discussion

The effect of ettringite dosage

Figure 1 shows the As(V) removal percentages as a function of ettringite dosage. The As(V)removal percentage increases as the ettringite dosage increases from 0 to 4 g/L and then stabilizes thereafter. With a 4 g/L ettringite dosage, an arsenic concentration below the drinking water limit was obtained. However, the increase of sorption efficiency after 1 g/L dosage was quite moderate. The best arsenate removal from the techno-economical point of view (90 %) was obtained with a 1 g/L ettringite dosage.

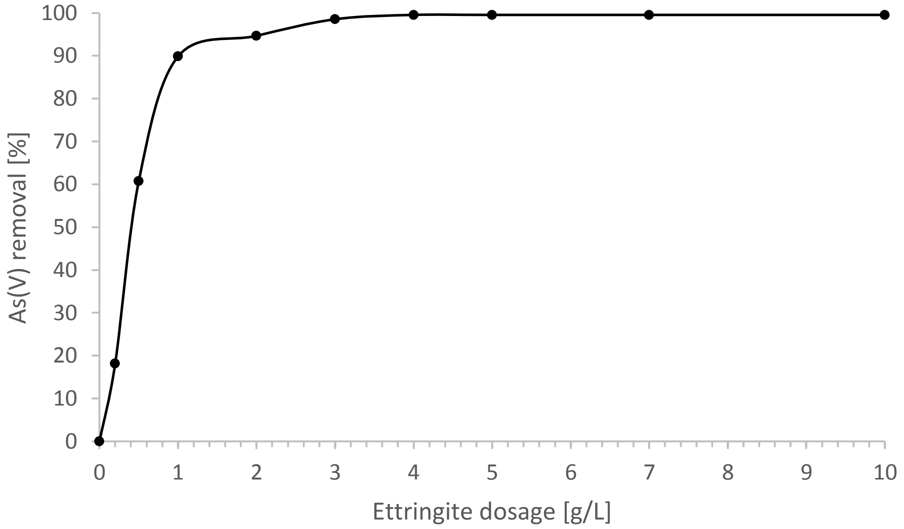

Figure 1 *The effect of sorbent dosage on the sorption of arsenate on ettringite. Initial As(V) concentration = 1.7 mg/L, ettringite dosage = 0—10 g/L, temperature = 20 ± 2 ◦C, agitation = 250 rpm, contact time = 24h, and solution volume = 25 mL. Values are presented as the average of duplicate experiments.*

Isotherms

Figure 2 shows Langmuir and Freundlich isotherm models fitted to the data gained from the experiments concerning the effect of ettringite dosage on arsenate removal. The Langmuir (1918) and Freundlich (1906) isotherms, which are the most commonly used isotherm models, are represented by the following equations 1 and 2, respectively. The Langmuir isotherm model assumes monolayer sorption that occurs on a homogenous surface with no interactions between sorbates. The Freundlich isotherm model is empirical and assumes that sorption occurs on a heterogenous surface.

$$q_e = \frac{Q_{\max} b c_e}{1 + b c_e} \tag{1}$$

$$q_e = K c_e^{\frac{1}{n}} \tag{2}$$

where q_e (mg/g) is the amount of arsenate sorbed on ettringite at equilibrium, Q_{max} (mg/g) Langmuir isotherm constant relating to maximum sorption capacity, b (L/mg) Langmuir isotherm constant relating to the energy of sorption, c_e (mg/L) the equilibrium solution concentration, K (L/g) Freundlich isotherm constant related to sorption capacity, and 1/n Freundlich isotherm constant relating to intensity of sorption.

The fit of each isotherm model was compared according to the adjusted correlation coefficient R^2_{adj} values. The Langmuir and Freundlich isotherms fitted equally well to the experimental data. The isotherm parameters are presented in Table 1. The Freundlich parameter 1/n was < 1, indicating favourable sorption. The maximum sorption capacity obtained from the Langmuir isotherm was 1.8 mg/g, which was in the same range as the maximum experimental adsorption capacity. The low initial arsenate concentration used in the experiments could be the cause of the relatively low sorption capacity. A similar observation was made by Luukkonen et al. (2016) for the sorption of arsenite on geopolymers. The experimental equilibrium sorption capacity was calculated according to equation 3 as follows:

$$q_e = \frac{(c_0 - c_e) \cdot V}{m_{ads}} \qquad (3)$$

where c_0 (mg/L) is the initial solution concentration, c_e (mg/L) the equilibrium solution concentration, V (L) the volume of the solution, and m_{ads} (g) the amount of the sorbent.

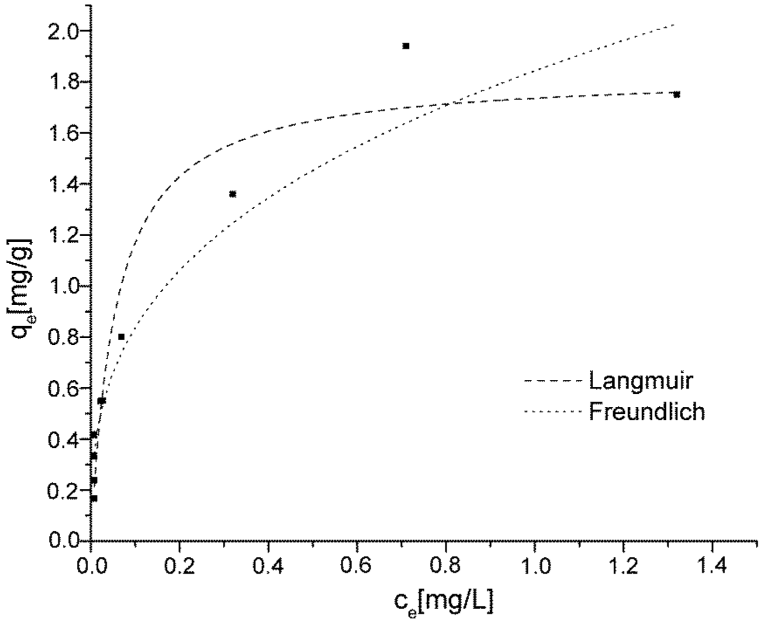

Figure 2 *Isotherm for the sorption of arsenate on ettringite, and the fit of the Langmuir and Freundlich models. Initial As(V) concentration = 1.7 mg/L, ettringite dosage = 0—10 g/L, and temperature = 20 ± 2 °C.*

Table 1 *Isotherm parameters.*

Parameter	Langmuir	Parameter	Freundlich
Q_{max}	1.835	K	1.844
Standard error of Q_{max}	0.109	Standard error of K	0.101
b	17.616	n	2.914
Standard error of b	3.619	Standard error of n	0.249
R^2	0.943	R^2	0.937
R^2_{adj}	0.938	R^2_{adj}	0.932
reduced chi-square, X^2_{red}	0.022	reduced chi-square, X^2_{red}	0.024
residual sum of squares, RSS	0.259	residual sum of squares, RSS	0.284
root mean square error, RMSE	0.147	root mean square error, RMSE	0.154

The effect of contact time and kinetic modelling

Figure 3 shows arsenate removal as a function of time. In the beginning of this process, the uptake of arsenate on ettringite was rapid, which was due to many available sorption sites on the surface of the ettringite for arsenate sorption. However, the sorption later proceeded at slower rate and reached equilibrium within 10 minutes contact time. Thus, the saturation of the sorption sites on the surface of ettringite led to the slower rate of arsenate sorption as time passed.

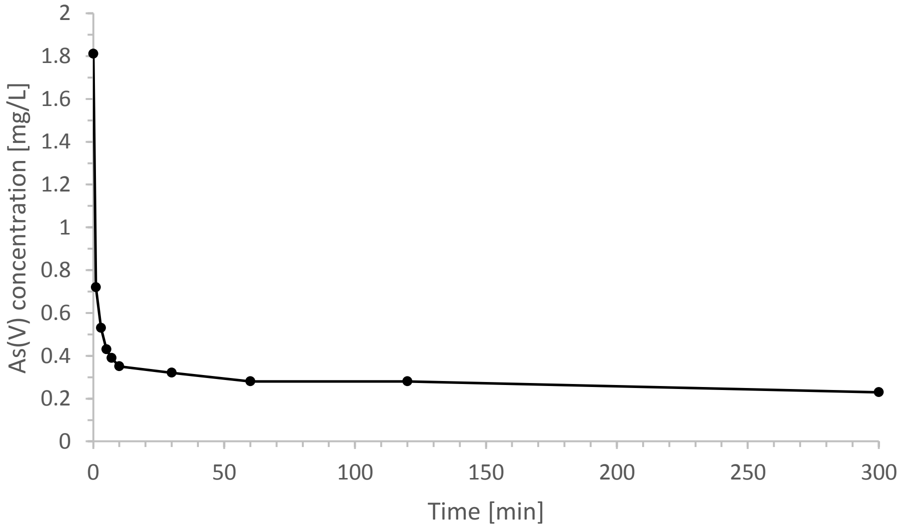

Figure 3 *The effect of contact time on the sorption of arsenate from a model solution on ettringite. Initial arsenate concentration = 1.8 mg/L, ettringite dosage = 1 g/L, temperature = 20 ± 2 ◦C, initial solution volume = 1 L, stirring 250 rpm, and samples taken between 0-5 h.*

Figure 4 shows the pseudo-first order and pseudo-second order kinetic models that were fitted to the experimental data. The Lagergren pseudo-first order model (1898) and the pseudo-second order model (Ho and McKay 1999) are represented by equations 4 and 5, respectively.

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{4}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{5}$$

where k_1 (1/min) is the pseudo-first order rate constant, k_2 ((g/(mg*min)) the pseudo-second order rate constant, q_e (mg/g) the amount of arsenate sorbed on ettringite at equilibrium and q_t (mg/g) the amount of arsenate sorbed on ettringite at time t (min).

The parameters of the kinetic models are presented in Table 2. The fit of the models was evaluated by comparing the adjusted correlation coefficient R^2_{adj} values. Following this, the pseudo-second order model was found to best fit the experimental data. The adsorption capacity obtained from the pseudo-second order model was 1.5 mg/g, which was in agreement with the experimental equilibrium adsorption capacity value.

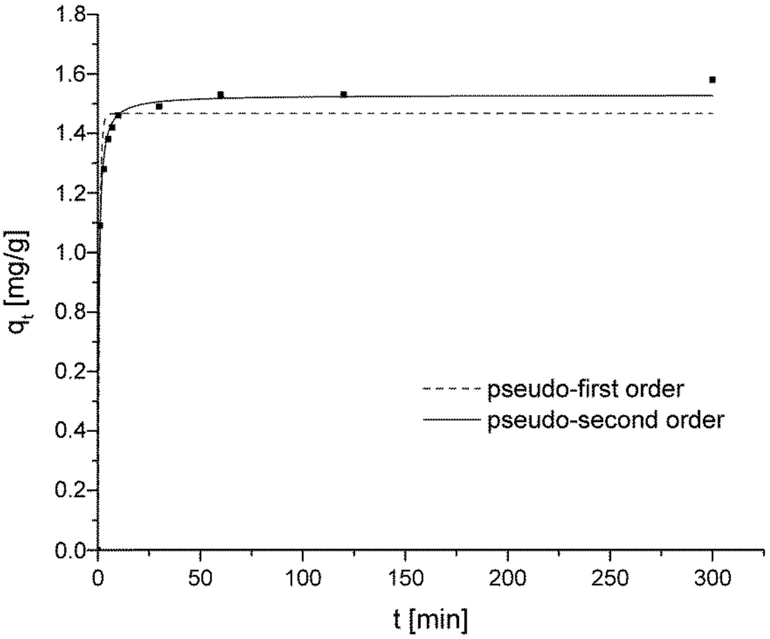

Figure 4 *Pseudo-first order and pseudo-second order kinetic models fitting for the sorption of arsenate on ettringite. Initial As(V) concentration 1.8 mg/L and ettringite dosage 1 g/L.*

Table 2 *Parameters from the kinetic models.*

Parameter	Pseudo-first order	Parameter	Pseudo-second order
q_e	1.467	q_e	1.530
Standard error of q_e	0.030	Standard error of q_e	0.014
k_1	1.257	k_2	1.437
Standard error of k_1	0.206	Standard error of k_2	0.146
R^2	0.972	R^2	0.996
R^2_{adj}	0.969	R^2_{adj}	0.996
reduced chi-square, X^2_{red}	0.007	reduced chi-square, X^2_{red}	0.001
residual sum of squares, RSS	0.056	residual sum of squares, RSS	0.008
root mean square error, RMSE	0.083	root mean square error, RMSE	0.031

Conclusions

The results of this study indicate that ettringite formed during sulphate removal from mine water could be utilized as an arsenate sorbent. A ninety percent arsenate reduction from the initial 1.7 mg/L arsenate concentration was obtained with a 1 g/L ettringite dosage. The maximum sorption capacity of ettringite for As(V) obtained from the Langmuir isotherm was 1.8 mg/g. This relatively low sorption capacity could be due to a low initial arsenate concentration, which was chosen to model the arsenic-containing mine waters. The adsorption capacity of ettringite could possibly be increased with heat treatment, but this would also increase the cost of the treatment. The sorption of arsenate on ettringite was fast, reaching equilibrium within 10 minutes. The Langmuir and Freundlich isotherm models fitted the sorption data equally well with an R^2_{adj} value of 0.94. The pseudo-second order model (R^2_{adj} > 0.99) best fitted the kinetic data of the arsenate sorption on ettringite.

Acknowledgements

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Iron and arsenic removal rates in a continuous flow reactor treating As-rich acid mine drainage (AMD)

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Abstract

Arsenic is one of the most hazardous elements associated to acid mine drainage with concentrations ranging from ≤ 1 µg L^{-1} to hundreds of mg L^{-1} in these leachates. To date, there is no affordable method to efficiently treat As-rich AMD over the long term. Natural attenuation processes based on oxidation of iron and arsenic by autochthonous bacteria present in AMD promote precipitation of these elements. The exploitation of these processes offer a promising method for the treatment of As-rich acid mine drainage (AMD).

In the present study, the Fe(II) oxidation rates and Fe and As removal rates have been investigated in a laboratory pilot-scale system with a continuous circulation of AMD water under controlled conditions (temperature, light, water-height and residence time). The system was fed with AMD from the Carnoulès mine with a permanent acid character (pH 2-4), an average iron concentration of 0.5 g L^{-1} in the reduced form (Fe(II)) and an average arsenic concentration of 40 mg L^{-1} predominantly under As(III) oxidation state.

The efficiency and rates of Fe(II) oxidation and of Fe and As removal were determined in the pilot as a function of experiment duration and for a range of residence times, in presence or absence of a floating film that develops naturally at the surface of the water. The Fe- and As-rich biofilms formed in the pilot were characterized for their mineralogy, redox As speciation, and bacterial quantification.

During the early stage of experiment, results evidenced that the gradual coverage of the pilot channel bottom with an Fe-As precipitate, that contained $6 \pm 3 \times 10^6$ bacterial cell/g (dry wt.), increased the Fe(II) oxidation efficiency and the Fe and As removal by two orders of magnitude. At the steady state, ~ 90 % Fe(II) was oxidized and ~ 30 % Fe and ~ 80 % As were precipitated within a residence time of 200 min. Rate values were slightly lower than those measured in the field in the natural AMD stream at Carnoulès. The development of a thin floating film at the surface of water in the pilot channel affected oxygen diffusion and retarded these rates. All these results improve our understanding of natural processes responsible for arsenic attenuation in AMD, and give some indications that might be considered when designing an Fe and As removal passive treatment in AMDs.

Key words: Acid mine drainage, arsenic removal, bioremediation, laboratory pilot

Introduction

Arsenic is an ubiquitous and toxic element associated to acid mine drainage (AMD) (Paikaray 2015; Williams 2001). Nowadays there is no treatment able to remove As efficiently over the long term without the need for expensive reactants and filter materials. In this context, bacterial oxidation of iron followed by the precipitation of Fe-As minerals provide an opportunity to conceive a bioremediation system to effectively treat As-rich AMD. This natural attenuation process has been described in many mining sites around the world: France (Casiot et al. 2003; Egal et al. 2010), Spain (Asta et al. 2010), Japan (Fukushi et al. 2003), Australia (Gault et al. 2005), Cuba (Romero et al. 2010) or Taiwan (Chen and Jiang 2012). It could be exploited for the treatment of AMD waters containing arsenic. However, the factors controlling this natural process and the subsequent variations of As removal efficiency are still poorly understood. Therefore, it is essential to identify key parameters controlling the rates of Fe oxidation and As removal. For this purpose, experiments were conducted in a continuous flow reactor where natural attenuation of Fe and As takes place under controlled conditions of temperature, light, flow rate and water height. The effect of the gradual coverage of the bottom of the channel by a biofilm and the effect of residence time on Fe(II) oxidation and Fe- and As- removal efficiency was investigated in presence or absence of a thin film floating that formed at the water surface in low flow conditions in the pilot channel.

Materials and methods

The experiments were conducted in a laboratory continuous-flow reactor made of four channels of 1 m length and 6 cm large (Fig.1). Water is circulating through these channels by pumping through a 3.17 mm i.d. tygon tubing at the inlet and at the outlet in order to maintain a stable water height of 4 mm during the experiment. Accurate flow rate is obtained with peristaltic pumps (Gilson, Minipuls 3). Channels are illuminated (T5 Superplant 216W CROISSANCE 6500 K) in the 400-500 nm spectra with a day/night cycle of 12 h and thermo-regulated at 20 ± 0.5 ºC using a refrigerated-heating circulator (Julabo F34-EH) and circulation of thermostatic fluid in a double-envelope underneath the channels. The bottom of the channels is covered with a biodegradable canvas facilitating the natural attachment of the Fe- and As-rich deposit that forms during the experiments.

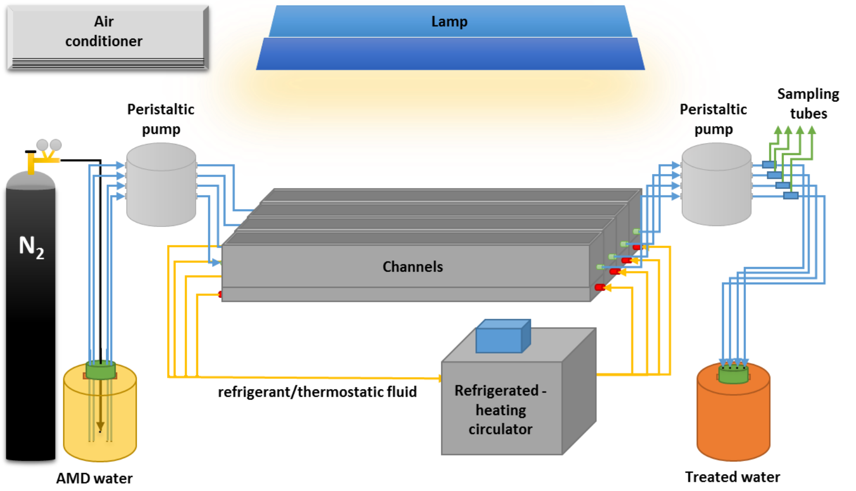

***Fig.1**. Laboratory continuous flow reactor treating As-rich AMD*

The feeding water used in all experiments is AMD water from the Reigous creek (Carnoulès mine, France). On average, this water had a pH ~ 3, an Fe concentration of 0.5 g L^{-1} in the reduced form (Fe(II)) and an As concentration of 40 mg L^{-1}, predominantly under As(III) oxidation state. Natural attenuation processes leading to the partial removal of arsenic have been evidenced in Reigous Creek (Egal et al. 2010) and Fe- and As-oxidizing bacteria were identified (Bruneel et al. 2011). Once collected, the water was purged with N_2 and preserved under N_2 atmosphere in the laboratory until use. Nitrogen bubbling in the feeding AMD water was carried out during the whole experiment duration to limit Fe oxidation prior to channel inlet.

During the experiments, the main physicochemical parameters of the water (pH, Electrical Conductivity (EC) and Redox Potential (Eh)) were monitored at regular time intervals at the inlet and at the outlet of the channels. Dissolved Oxygen (DO) profiles in the water column were performed with an oxygen microoptode (50 µm tip diameter, Unisense), coupled to a microoptode-meter and fixed in a micromanipulator. Water samples were taken at the inlet and outlet for analyses of Fe(II), total Fe (Fe(T)), As(III), As(V) and total As (As(T)). They were preserved using routine procedures as described elsewhere (Egal et al. 2010). Fe(II) and Fe(T) were analyzed by molecular absorption spectrophotometry at 510 nm wavelength, and As(III), As(V) and As(T) were analyzed by High Performance Liquid Chromatography ICP-MS (Héry et al. 2014).

In Exp 1a, the four channels were fed continuously during 13 days with a fixed water flow of 0.5 mL min^{-1} which set the residence time to 324 ± 30 min. During this experiment, the bottom of the channels gradually covered with an orange deposit while an iridescent floating film progressively formed at the surface of the water. Inlet and outlet water chemistry were monitored until reaching a steady state for Fe(II) oxidation in the channels. Then, a kinetic experiment was conducted; a range of residence times (from 24 to 366 min) were applied successively by regulating the flow rate. For each residence time, after a stabilization period corresponding to at least three times the residence time duration, inlet and outlet water chemistry were determined, allowing to calculate the proportion of Fe(II) oxidized and As removed for each residence time. After this kinetic experiment, the floating film was removed and the Fe-As deposits at the bottom of two of the four channels (which had an age of 17 days) were collected to analyze the mineralogy by X-Ray Diffraction (XRD), As speciation by X-ray Absorption Near Edge Structure (XANES) spectroscopy (Maillot et al. 2013), and bacteria cells counting by Gallios™ flow cytometer (Lunau et al. 2005). Then, a new kinetic experiment (Exp 1b) was conducted with the two remaining channels. The range of residence times applied to the channels was 30 - 252 min. At the end of Exp1b, 34 days after the start, the Fe-As deposits were collected and analyzed as in Exp 1a.

In each experiment, rates of Fe(II) oxidation, Fe and As removal were calculated with Eq. 1,

$$Rate\ (mol\ L^{-1}\ s^{-1}) = \frac{[X]inlet - [X]outlet}{\Delta t} \qquad (1)$$

where [X] is the dissolved concentration of Fe(II), Fe(Total) or As(Total) in mol L^{-1}, and Δt is the residence time in seconds.

Results

Variation of iron oxidation and iron and arsenic removal as a function of experiment duration

At early stage of Exp 1a, during the first two days, the proportion of Fe(II) oxidized during the course of the water from the inlet to the outlet of the channel was lower than 1 %, corresponding to Fe(II) oxidation rate of 3 ± 2 x 10^{-9} mol L^{-1} s^{-1}. The proportion of Fe removed from the dissolved phase was also lower than 1 %. After this "lag time", the proportion of Fe(II) oxidized increased up to ~ 90 % within the first ~ 9 days, then stabilised (steady state) during the next 4 days. The proportion of Fe removed from the dissolved phase increased simultaneously up to 28 % (Fig. 2) and the accumulated amount of Fe precipitated inside the channel reached 0.9 mg cm^{-2}, corresponding to the gradual coverage of the bottom of the channel with an orange precipitate that looked like natural Fe-rich deposit in AMD streams. Once the steady state was reached, Fe oxidation rate averaged 3.3 ± 0.4 x 10^{-7} mol L^{-1} s^{-1},

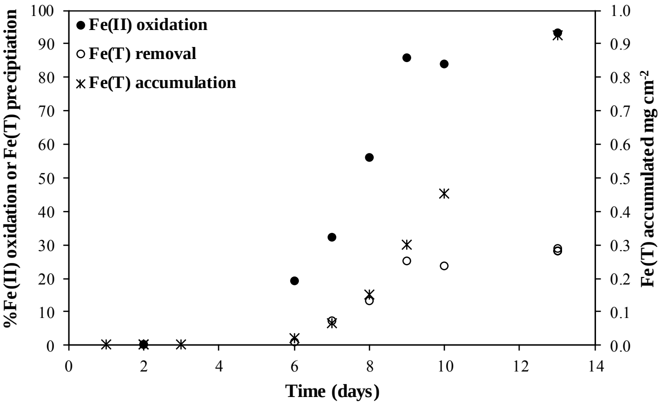

Fig. 2. Variation of the proportion of Fe(II) oxidized, the proportion of Fe(T) precipitated between inlet and outlet of the channels as a function of experiment duration and the Fe(T) accumulated inside the channel per unit of area in Exp 1a and Exp 1b. Residence time was fixed at 324 ± 30 min. Physico-chemistry of the AMD water: pH = 3.01 ± 0.07; Fe(II) = 433 ± 28 mg L^{-1}; Fe(T) = 449 ± 13 mg L^{-1}; As(III) = 16 ± 14 mg L^{-1}; As(V) = 8 ± 2 mg L^{-1}; As(T) = 24 ±17 mg L^{-1}.

corresponding to a rate increase of approximately two orders of magnitude with respect to the rate value at the early stage of experiment, while Fe removal rate reached 1.1 ± 0.1 x 10^{-7} mol L^{-1} s^{-1} and As removal reached 65 %, corresponding to an As removal rate of 3.5 ± 0.1 x 10^{-9} mol L^{-1} s^{-1}.

Variation of iron oxidation and iron and arsenic removal as a function of residence time

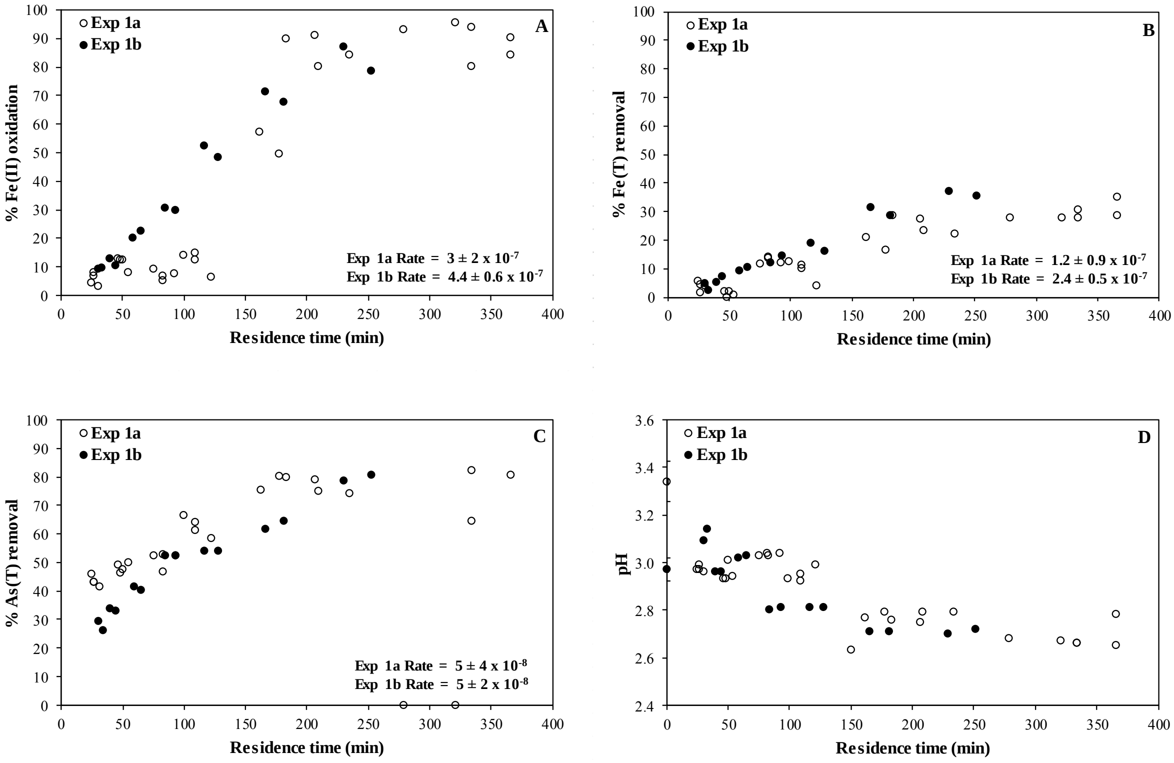

Fig. 3. *% Fe(II) oxidation (A), % Fe removal (B), % As removal (C), pH (D) as a function residence time in Exp 1a (with floating film) and Exp 1b (without floating film), and associated rates in mol L^{-1} s^{-1}. Physico-chemistry of the AMD water from Exp 1a: pH = 2.97 ± 0.05; Fe(II) = 447 ± 31 mg L^{-1}; Fe(T) = 460 ± 24 mg L^{-1} ; As(III) = 13 ± 4 mg L^{-1}; As(V) = 17 ± 6 mg L^{-1}; As(T) = 30 ± 9 mg L^{-1}. Physico-chemistry of the AMD water from Exp 1b: pH = 3.34 ± 0.08; Fe(II) = 414 ± 11 mg L^{-1}; Fe(T) = 419 ± 13 mg L^{-1} ; As(III) = 26 ± 3 mg L^{-1}; As(V) = 7 ± 2 mg L^{-1}; As(T) = 34 ± 2 mg L^{-1}.*

Kinetic experiments Exp 1a and Exp 1b showed an increase of Fe(II) oxidized by increasing the residence times from ~ 25 to 200 min, then, a plateau was reached with ~ 90 % of Fe(II) oxidized (Fig. 3A). The shape of the curve differed from Exp 1a to 1b; Fe(II) oxidation was delayed for residence times lower than ~ 120 min in Exp 1a compared with Exp 1b (Fig. 3A). Measurement of dissolved oxygen concentration along the water column showed a drastic decrease of this parameter until anoxic condition at 1 mm depth below the floating film that developed in Exp 1a (Fig. 4, Exp 1a). Such a drastic oxygen depletion was not observed in the absence of floating film in Exp 1b (Fig. 4, Exp 1b). Fe removal (Fig. 3B) was also delayed in Exp 1a for residence times lower than 120 min, as a consequence of retarded Fe(II) oxidation, but As removal did not seem to be affected (Fig. 3C). pH decreased up to ~ 0.5 units for residence times higher than ~ 200 min (Fig. 3D).

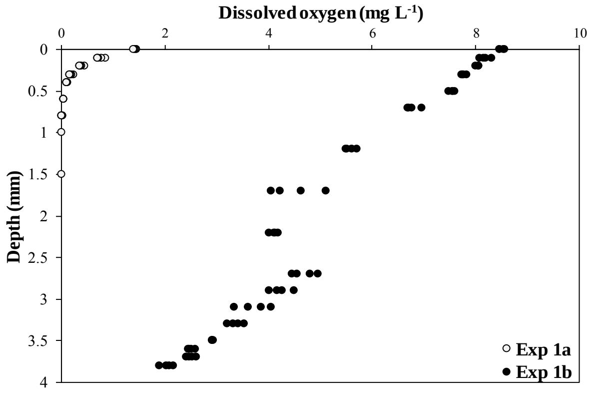

Fig. 4. *Dissolved oxygen profile along the water column (0 mm depth = water surface) in the channel. Profile Exp 1a corresponds to middle channel position under the floating film, experiment time = 21 days, residence time = 300 min. Profile Exp 1b corresponds to outlet channel position, experiment time*

Characterisation of the Fe-As rich deposit precipitated in the channels

The deposit that covered the channel bottom contained 348 mg Fe g^{-1} (dry wt.) and 67 mg As g^{-1} (dry wt.) in Exp 1a, and 334 mg Fe g^{-1} (dry wt.) and 70 mg As g^{-1} (dry wt.) in Exp 1b, with a corresponding As/Fe molar ratio of 0.14 and 0.16, respectively. XRD analyses showed that the dominant crystalline phase that precipitated in the channels was schwertmannite. XANES analyses indicated that the deposits contained both As(III) and As(V) species, with 16 ± 2 % As(III) and 85 ± 2 % As(V) in Exp 1a, and 24 ± 2 % As(III) and 78 ± 2 % As(V) in Exp 1b. Bacterial cell counting indicated 8.4×10^6 bacterial cell g^{-1} (dry wt.) in Exp 1a, and 4.5×10^6 bacterial cell g^{-1} (dry wt.) in Exp 1b.

Discussion

Increased efficiency of Fe(II) oxidation and Fe precipitation with time (Exp 1a) was associated to the gradual coverage of the bottom of the channel with an orange deposit made of iron and arsenic that also contained bacterial cells. Such deposits that naturally form in AMD streambeds were shown to contain Fe-oxidizing bacteria (Leblanc et al. 1996; Druschel et al. 2004). The formation of these bacterial rich deposits has been shown to increase the rate of Fe(II) oxidation in batch experiments with the AMD from Carnoulès mine (Casiot et al. 2003). It is well known that Fe(II) oxidation is mediated by bacterial catalysis at acid pH (Kirby and Kostak Jr 2002; Kirby et al. 1999). Results from this research show that this activity also takes place in our laboratory continuous flow channel reactor, where the presence of this bacterial rich deposit attached to the channel bottom increases Fe(II) oxidation rate by two orders of magnitude compared to the rate obtained with only free bacterial cells in the water. After ~ 9 days, a steady state was reached for Fe(II) oxidation, which seems to coincide with the complete coverage of the channel bottom with the bacteria rich deposit. DeSa et al. (2010) also observed improved Fe(II) oxidation in gutter reactors that contained iron mound sediment compared to the ones without any sediment as well as an improved Fe(II) oxidation over time as sediment aged. Fe(II) oxidation rates (~ 4×10^{-7} mol L^{-1} s^{-1}, Fig. 3A) obtained in the present study were close to those measured in the field in AMD from the Iberian Pyrite Belt (3.4 to 4.3×10^{-7} mol L^{-1} s^{-1}, in Asta et al. (2010) and 8×10^{-7} mol L^{-1} s^{-1} in Sánchez-España et al. (2007)) but were lower than those measured *in-situ* in the Reigous creek at the Carnoulès mine (3.8×10^{-6} mol L^{-1} s^{-1} in Egal et al. 2010). Lower rates were also observed in laboratory compared to the field by Sánchez-España et al. (2007). Differences in the amount of Fe(II) oxidizing bacteria and community distribution between laboratory reactors and field streams might explain such differences and will require further research.

As removal rate obtained in the present study (~ 5×10^{-8} mol L^{-1} s^{-1}) was ten-fold lower than in the field (3.58×10^{-7} mol L^{-1} s^{-1} in Egal et al., 2010), in accordance with lower Fe(II) oxidation rate in laboratory experiments. The Fe-As solids in the channel bottom resembled to those found in Carnoulès streambeds (Maillot et al., 2013), with the predominance of schwertmannite and the coexistence of both As(III) and As(V) species. Thus, the As removal in the pilot(~ 80 % within 200 min of residence time) is attributed to the natural attenuation of both As(III) and As(V) species, as a result of biological Fe(II) oxidation.

Comparison of kinetic experiments 1a and 1b showed the influence of the floating film, that develops naturally at the surface of low flow AMD water, on Fe(II) oxidation rates. Fe(II) oxidation was delayed for shorter residence times (<120 min) in presence of this floating film and this was ascribed to dissolved oxygen depletion along the water column. Elbaz-Poulichet et al. (2006) had previously observed a detrimental effect of the floating film on Fe and As removal in experimental pool at the Carnoulès mining site and suggested an oxygen diffusion inhibition.

The importance of water oxygenation for Fe(II) oxidation rate has been evidenced in many laboratory and field studies. Chen and Jiang (2012), in a field study at Chinkuashih mining area in Taiwan observed that AMD creek sections exhibited Fe(II) oxidation rates that were 1 to 2 orders of magnitude lower than in waterfall sections, where it reached 6.1 to 6.7×10^{-6} mol L^{-1} s^{-1}; and suggested that waterfall aeration was the main factor driving Fe(II) oxidation rate. Similarly, Sánchez-España et al. (2007) studied the Fe(II) oxidation rates in batch reactors with oxygenated/suboxic AMD, and showed that high DO concentration increased Fe(II) oxidation rates. These results suggest that oxygenation conditions may strongly affect Fe(II) oxidation rates in laboratory and field conditions. However, the presence of the floating film did not appear to affect As removal efficiency, even at short residence times. A possible explanation is that As can be removed efficiently at low As/Fe molar ratios in the aqueous phase (< 0.1) (Maillot et al. 2013), and thus, only small amount of particulate Fe may be sufficient for As precipitation, since As(V) is effectively retained onto Fe solids at acid pH (Cheng et al. 2009). Additionally, it was found that arsenite can coprecipitate with amorphous phases, with schwertmannite, and/or be incorporated in tooeleite ($Fe_6(AsO_3)_4SO_4(OH)\cdot 4H_2O$) in AMD. This last was observed in batch experiments carried out with strains of *A. ferrooxidans* in Carnoulès mine water (Egal et al. 2009).

Field and laboratory results agree with the predominant role of the Fe-bacterial-rich precipitates in the so called "natural attenuation" processes. Any human or natural activity (like heavy rains) that could remove these ochreous precipitates from AMD streambeds, would considerably affect the natural As removal efficiency. This is important to consider because the full recovering of this attenuation would probably need some time to be achieved, in accordance with the coverage of the whole riverbed with the bacterial-rich precipitates. Furthermore, the efficiency of the natural attenuation process can also be diminished at low stream flow rates, like in summer season, by standing waters that can limit oxygen diffusion along the water column. Therefore, the oxygenation has to be improved, by, for example, promoting the formation of cascades.

Conclusion

First experiments from this pilot showed the importance of some key factors affecting Fe and As removal that have to be considered in the conception of field bioremediation systems that aim to treat As-rich AMD. The deposits covering the channels bottom were found to improve Fe and As removal, due to the biotic Fe(II) oxidation. Water oxygenation was a key factor controlling the Fe(II) oxidation rate, which is the basis of natural attenuation process. This means that, for an efficient bioremediation system, the oxygenation of water has to be maximized and standing water should be avoided.

Acknowledgements

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Passive Treatment of Radioactive Mine Water in Urgeiriça Uranium Mine, Portugal

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Abstract

Environmental remediation of old uranium mine sites in Portugal in particular the importance of finding alternatives in water treatment processes has led to the research of passive treatment techniques in order to establish and improve long term sustainability. As so, this kind of innovative technology gathering in the same site chemical, physical, phyto and bioremediation has become a pilot ground or study area in Portugal.

The paper is focused in the main features of the applied techniques and their use on specific infrastructures to control uranium and radium contaminated effluents and seepage control. The aim of this paper is to, based upon three years of water samples analytical data, to better understand the behavior and efficiency of Mine Water Passive Treatment (MWPT) Systems alternatively to Active Treatment Systems (ATS) as well as to develop and systematize MWPT systems. Regardless the variation in the beginning of the MWPT's parameters concentrations, the results show that this kind of treatment on mine water or seepage, throughout the system stabilization in less than 2 years, highly reduces concentrations of radioactive elements mainly Uranium (total) from 487µg/l to nearly 11µg/l, with a 98% efficiency, and Ra_{226} with 99% efficiency, varying 1Bq/L to <DL, 0,01Bq/l. Metals Fe-oxides and Mn are also reduced from ~6mg/l in the first passive treatment pond to values below detection limits in the final pond (<1mg/L). Metalloids mainly Mg^{2+} and K^{+} show stable concentrations with values up to 15mg/l and 10mg/l, respectively, along passive treatment. Ca^{2+} and Na^{+} show also stable values up to 100mg/l and 40mg/l, respectively.

Keywords: Remediation, Uranium, Mine water passive treatment, seepage control.

Introduction

Portugal has an important legacy of degraded former mining sites with clear environmental and public health impacts and safety problems. Since 2001 they are being subjected to environmental rehabilitation operations by EDM- *Empresa de Desenvolvimento Mineiro, S.A.* under a legal regime of concession assigned by the Portuguese State and approved by the Decree-Law Nº 198-A/2001. EDM is covering the environmental rehabilitation of 175 abandoned mining areas, 61 of which in radioactive minerals and 114 in the Polymetallic mines set. In the radioactive ore mines the most relevant are Urgeiriça, Quinta do Bispo, Cunha Baixa and Bica mines, all located in the Beiras Granitic Region. By the year of 2015, 95 out of 175 mine sites have been intervened. Actually main strategic areas of EDM were to develop the remediation works of the remaining mining sites, the development of safety actions and medium and long term monitoring/maintenance operations in air, water, soils, sediments.

EDM started the Urgeiriça Environmental Remediation works in 2001 and started with the underground mine flooding at controlling at the same time in the surroundings 252 monitoring points (wells, piezometers, sediments, soil and streams) measuring in situ parameters (pH, electrical conductivity, EC, redox potential, Eh and temperature, t) and laboratory analysis of chemical and radiological parameters such as total uranium, Ra_{226}, sulphates, chlorides, manganese, calcium and sodium as hydrochemical contamination indicators.

In the meantime EDM started in this site some experiments with small pilot scale projects of passive treatments using some natural neutralizing and fixing agents such as barite, limestone, expanded clay and proportional flows with the purpose of scale up for large scale projects. Additionally the projects were upgraded with species of bioaccumulation heavy metals macrophytes (phytoremediation) taking in consideration the work of Favas et al (2013), and with the natural creation of adapted aquatic ecosystems for uranium and other metals reduction bacteria.

The results of final heavy metals concentrations were promising and led to final passive treatment projects, where the hydraulic retention times were optimized regarding the higher winter flows and lower temperatures. Therefore EDM implemented in 2012 the first MWPT with several decantation stages settling remediation efficiency supported by a tight chemical analysis and monitoring program, first on a weekly basis and then monthly till now.

The results associated with groundwater natural attenuation processes and hot-spot contamination containment led to the generalization of passive treatment projects in other old uranium mining areas. Afterwards, and after the stabilization of the groundwater, the need of low flow seepage water control arose letting to the use of some other tests supported by independent structures in the passive treatment filled with activated carbon and also with some physical specific plastic frames for the growth of uranium bacteria.

In fact the streamlined passive treatments with lower associated operational costs, has led to the decline of chemical active treatments importance in EDM´s context. Optimization of these passive systems can lead to an improvement in terms of associated maintenance costs and rehabilitation projects sustainability.

Study Area

Geographical and Geomorphological setting

The Urgeiriça Uranium mine is located in the parish of Canas de Senhorim, in the SE part of the municipality of Nelas, around 20 km south of Viseu in the center of Portugal, ***Figure 1***. The parish has a population of 3500 and a population density of 136/km^2.

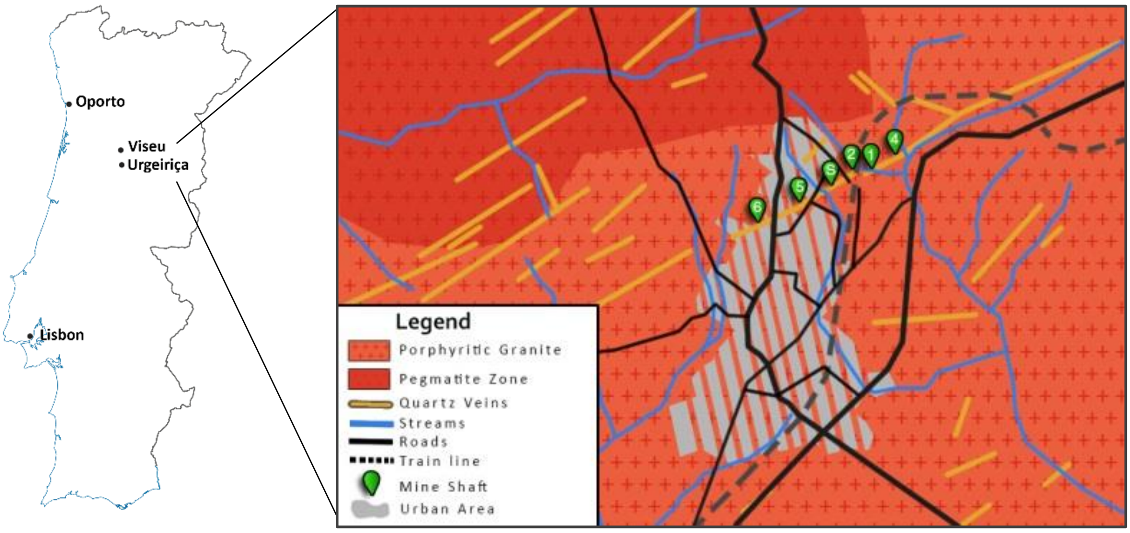

Figure 1 *Localization of the Urgeiriça Mine and simplified geological map of the area*

The geomorphology of the area is characterized by smooth reliefs, the highest point being located at 400 m and the lowest in the stream called "*Ribeira da Patanha*" sitting at 340 m. It belongs to the Iberian Plateau, which is tectonically stable. The study area is bordered by stream which is part of the Mondego watershed. The biggest depressions in the terrain are associated with streams presenting a dendritic pattern. The area is sparsely populated, being a suburban and agricultural area, forested by small bushes, pine trees, olive trees and eucalyptus. The local climate is a moderate Mediterranean climate.

Geology and Mineralizations

Geologically the area belongs to the geotectonic Central Iberian Zone in the Iberian massif. Hercynian Granites are predominant in the region, a porphyritic medium to coarse grained two mica granite, as it can be seen in ***Figure 1***. The granites are considerably altered and the general area is very fractured, having three important faults associated with the mine, a horizontal fault, and two vertical ones, and various smaller ones. Veins are extremely common, with the dominant strike direction of N60ºE.

The exploration was related to the mineralization of one of this vein, trending N60E – 75SE, up to 3 m thick and 7km in length, 2km of it were economically viable. The vein formation is related to the unconformity of *Variscan* granites. The orebody's origin is related to alpine movements that reactivated Hercynian faults and shear zones. According to Rich et al. 1977, volatile rich, high pressure and temperature hydrothermal fluids dissolved country rock, increasing the pH. This factor, combined with lower temperatures which decrease the solubility of UO_2 changed the valence state of Uranium from U^{+6} to U^{+4} which in turn led to the precipitation of Uranium minerals in those shear zones. The most significant mineralizations could be found in the most fractured areas.

The vein main association of minerals is microbotryoidal sooty picheblend and uraninite (UO_2), Pyrite (FeS_2), marcasite (FeS_2) and jasper quartz (SiO_4) as gangue, and sporadically galena (PbS) and chalcopyrite ($CuFeS_2$). The wall rock alteration is frequent, mainly sericitization, cloritization, hematization, jasperization and kaolinisation (Portugal et al. 1971).

Mining activity

The mine began its exploration of Radium Salts in the year 1913. Later during WWII the production shifted towards Uranium due to the demand at the time. In 1951, the Chemical Treatment Plant (CTP) was constructed, allowing Urgeiriça to be a hub for the reception and processing of uranium from mine sites of the *Centro* region, which at the time accounted for 61 uranium mining sites, with an output capacity of 125 t/year of U_3O_8.

The exploration methods were adapted throughout time. The site began as an underground mine using the Cut-and-Fill technique, with the empty stope being filled with gangue and low grade ore. In 1967 it reached its peak depth at 19 levels, roughly 500m deep and 1km in length. After it was concluded that the mineralization was depleted, small scale tests to recover residual uranium resources left behind were implemented. These tests consisted in using Sulphuric Acid to mobilize Uranium to an effluent that would be pumped out to the surface, using an ionic exchange system the uranium content could be extracted, a process denominated *in-situ* leaching. In 1969 the first four levels of the mine were destined to try out leaching *in-situ* on a bigger scale, taking advantage of a horizontal fault at that level. In 1971 the classical exploration was over and *in-situ* leaching was generalized to all floors and lasted until the mine was closed in 1991 (J. Cordeiro Santo 1983).

Methods

Procedures

Mine flooding

In 2001 the pumping of contaminated groundwater to the active treatment plant was interrupted in order to flood the mine in a controlled and progressive way as it can be seen in ***Figure 2***. The objective was to understand the behavior of the groundwater related to the diminishing of oxidation/reduction reactions, creating an anaerobic environment restraining metals mobilization. Within two years of systematic water monitoring control, the water level reached its highest level. As so, in 2003 the groundwater level stabilized at the level between -12m and -8m and the natural hydrodynamic equilibrium was reached.

As the groundwater level rose throughout the mine galleries it started to exit only in the old mine shaft nº4 as expected, being collected, characterized and treated in the existent ATS. This spring is the only place were groundwater from the mine galleries outflows. By that time, some experiments were implemented, in the form of a passive treatment pilot plant, to research on the possibility to decontaminate this seepage water with these type of systems. Afterwards, while the main circuit was built, a second seepage water started to exit next to the former one.

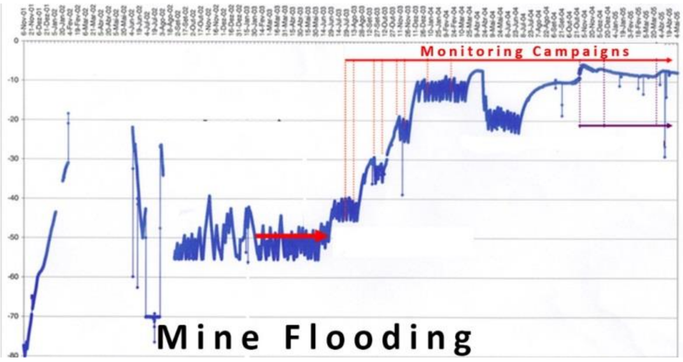

Figure 2 *Mine flooding piezometric evolution*

Structure of the Urgeiriça mine MWPT pilot plant

The MWPT pilot plant (Figure 3) used consisted in a small basin with decantation sectors filled with limestone gravel, expanded clay and barite acting as Permeable reactive Barriers (PRB's) in a total proportional volume related to the hydraulic retention time of existing active treatment basins, around 20 and 40 days, winter and summer, respectively. The final chemical analysis results led to decreasing concentrations of radioactive elements such as U_{total} and Ra^{226}, Fe-oxides and Manganese.

Figure 3 *Mine water passive treatment pilot plant*

Mine water passive treatment project

The main features of the MWPT final project lay down on 6 ponds initially, 3 of concrete with a volume of nearly $V=1000m^3$, and other 3 up to $1700m^3$ as wetlands with macrophytes. Afterward, the system was upgraded to treat the second seepage, with 3 additional concrete ponds of $100m^3$ each, the last of which was divided into 3 as a pilot to test a PRB's with activated carbon filtration. The sampling locations were defined as WAP_i for the first decantation pond, ii for the second, and so on with the last point being WAP_f, the supplementary circuit was named WAP_{bi}, WAP_{bii}, WAP_{Biii1}, WAP_{Biii2}, WAP_{BiiiCA} (Figure 4.1).

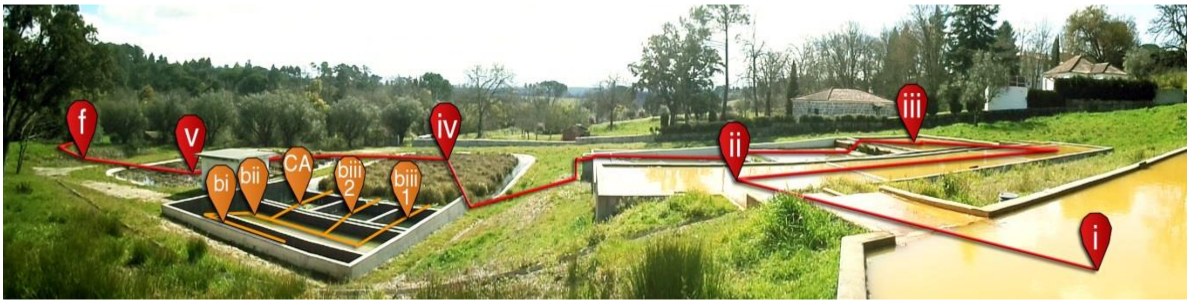

Figure 4 *- MWPT layout*

The existing hydraulic retention time ensure the needed conditions to promote the oxidation and the precipitation of the main contamination elements, allied to the existence of bacteria and macrophytes which improve water quality. The final project was assembled with previously stablished hydraulic and physical data as shown in Figure 5.

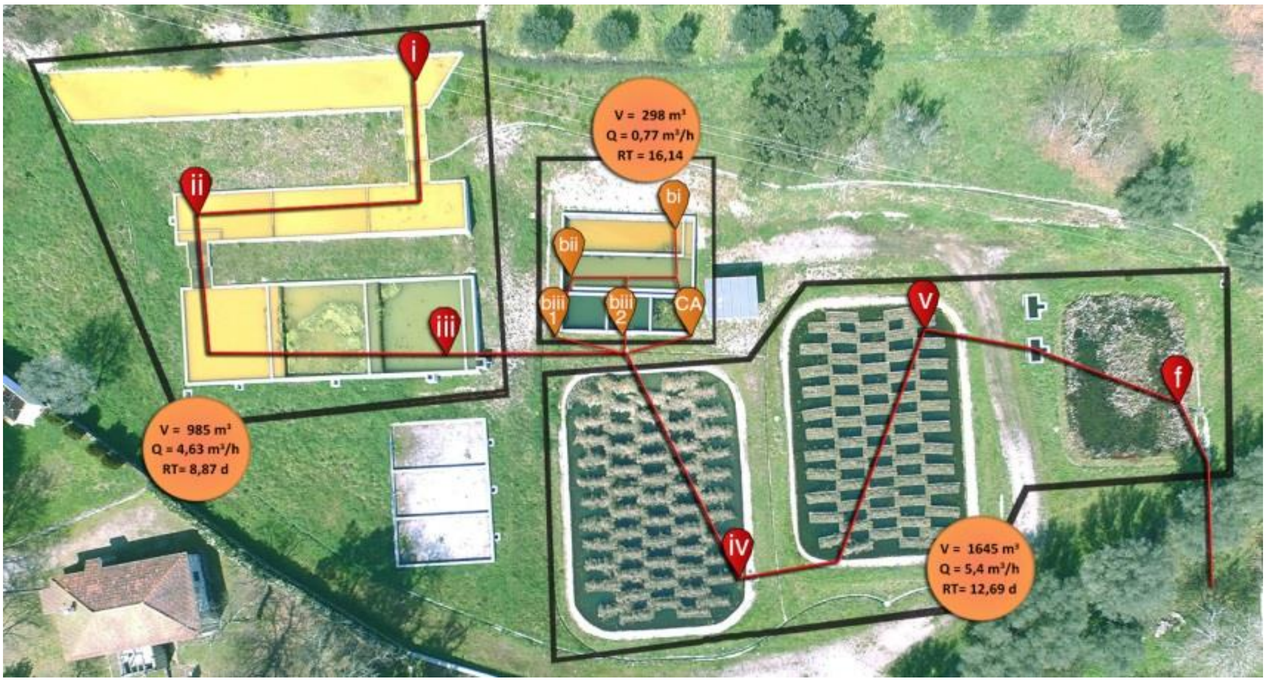

Figure 5 *- MWPT layout and hydraulic data, V=Volume; Q=Flow; RT=Retention Time*

The hydraulic data shows that the flow of the 2nd seepage treatment is six times lesser than the discharge from the main pathway. The historical discharged values are $0.9m^3/h$ (minimum) and $7.2m^3/h$ (maximum) with a mean value of $4.0m^3/h$ for all MWPT. The data used (Figure 5) report to field sampling.

Field sampling and sample treatment

Water samples for chemical analysis were collected in each of the MWPT ponds since September 2012 until present days with a frequency of at least once a month, accounting for 42 series of samples investigated in this study. In the beginning of the monitoring (2012) several chemical and physical parameters were analyzed, however since 2014, most of the trace elements were historically bellow the detection limit, the monitoring was focused in major cations (Ca, K, Na), major anions (HCO_3^-, Cl^-, SO_4^-), radionuclides (U_{total}, Ra_{226}, U_{234}, U_{238}) and trace elements (Fe, Mn).

The water samples were stored and transported in clean and sterile plastic bottles. For the determination of metals the samples were acidified with (65%) HNO_3, being afterwards processed in a certified laboratory. Field parameters (pH, EC, Eh and t) were measured *in situ* at the same time in each sampling site. pH and t were measured using a pH-Electrode Sentix 940 probe from WTW, EC was measured using Tetracon 925 probe from WTW.

Results and discussion

Former studies indicates that bacteria alongside with macrophytes (phytoremediation) upgrade precipitation and coagulation processes being the macrophytes used in this case *Juncus efusus, Iris pseudacorus, Typha latifolia and Carex aquatilis.* The common bacteria present in these kind of contaminated waters tend to use organic matter as electron donors by promoting the removal of uranium from water by reducing U^{6+} to relatively insoluble U^{4+} (Zhang *et al.* 2012), favoring its precipitation. Bacteria studies are still being undertaken in order to maximize their growth.

This MWPT layout favors the oxidation and increase of pH and Eh which in turn increases the mobility of U forms. In general, and in less than two years, the system entered in a chemical balance and reached its equilibrium, as we can see in the charts below.

The standard water quality legislation used for compliance verification was the Portuguese Decree-Law nº 236/98, of 1 of August, Annex XVIII referent to discharge limits of effluents. Concerning radioactive elements we used USEPA 40 CFR *Parts 9, 141, and 142 National Primary Drinking Water Regulations Radionuclides;* USEPA CFR440.32 "*Effluent limitations for mine drainage from open pit and underground uranium mines*". The used references, mainly drinking water regulations for Uranium and Radium, point out the observance of water limit for discharge at values of 30 µg/l and 0,185 Bq/l, respectively. The waters in the MWPT can be classified as calcium bicarbonate according to the Piper diagram.

After the statistical analysis of the data the evolution of concentrations of each parameter were analyzed not only on a temporal evolution basis but also throughout the spatial sequence inside the MWPT.

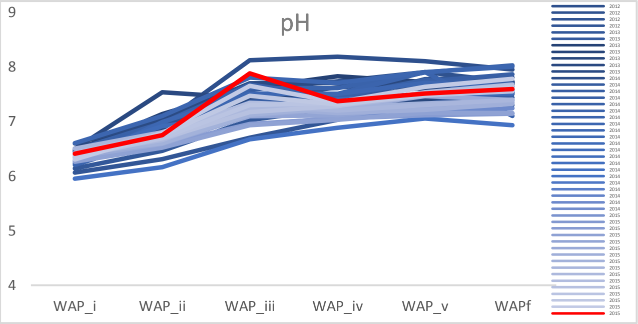

Figure 6 *Spatial evolution of pH*

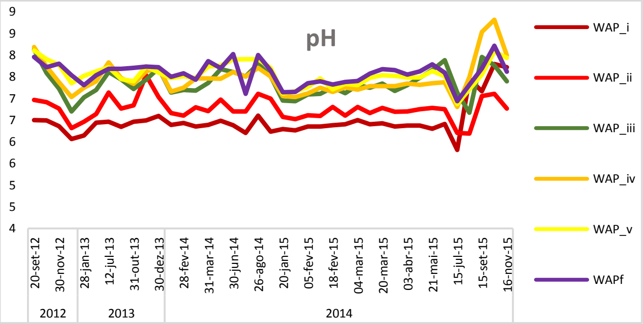

Figure 7 *Temporal variation of pH*

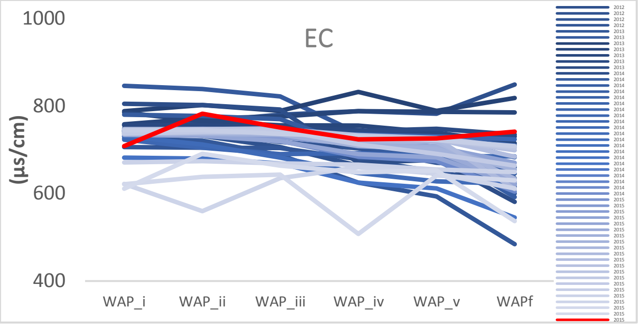

Figure 8 *Spatial evolution of EC*

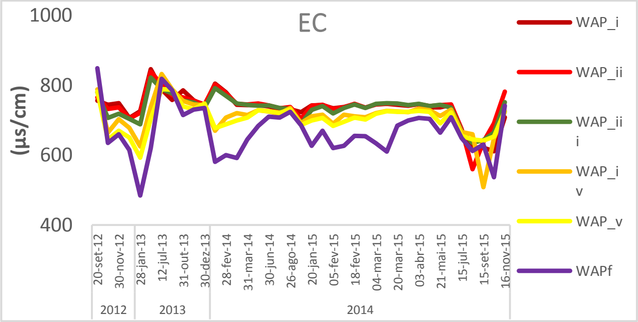

Figure 9 *Temporal variation of EC*

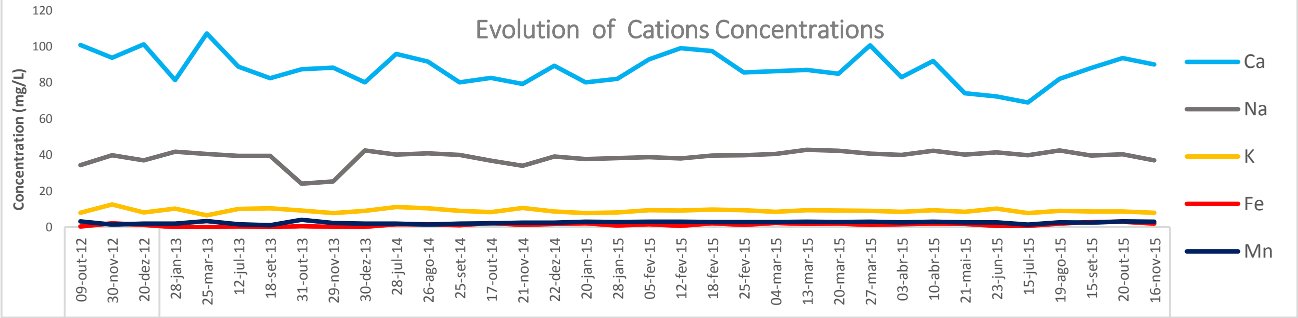

Figure 10 *Temporal variation of average concentrations in MWPT of Ca, Na, K, Fe and Mn in mg.L^{-1}*

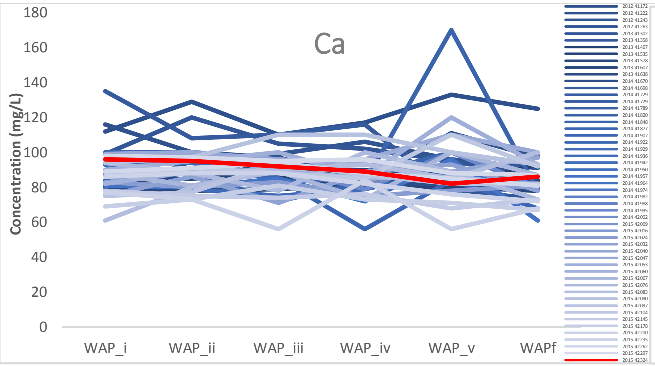

Figure 11 *Spatial evolution of concentrations of Ca in mg.L^{-1}*

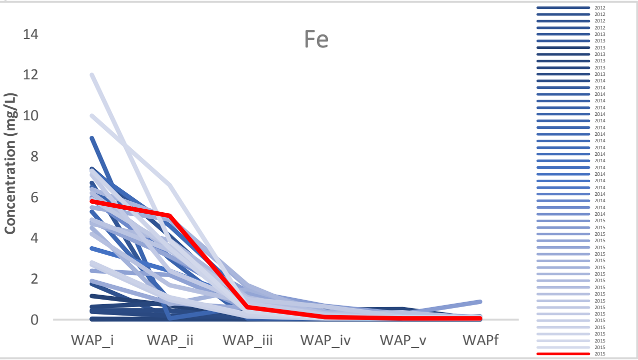

Figure 12 *Spatial evolution of concentrations of Fe in mg.L^{-1}*

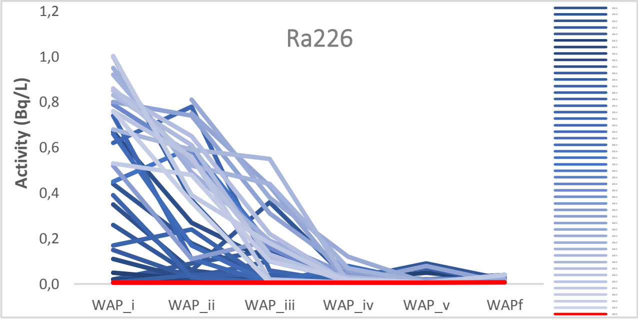

Figure 13 *Spatial evolution of Ra-226 activity in Bq.L^{-1}*

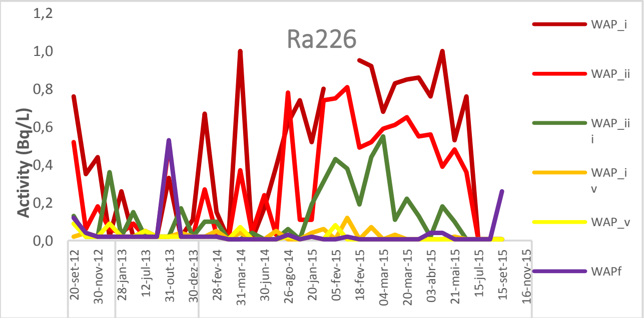

Figure 14 *Temporal variation of Ra226 activity in Bq.L^{-1}*

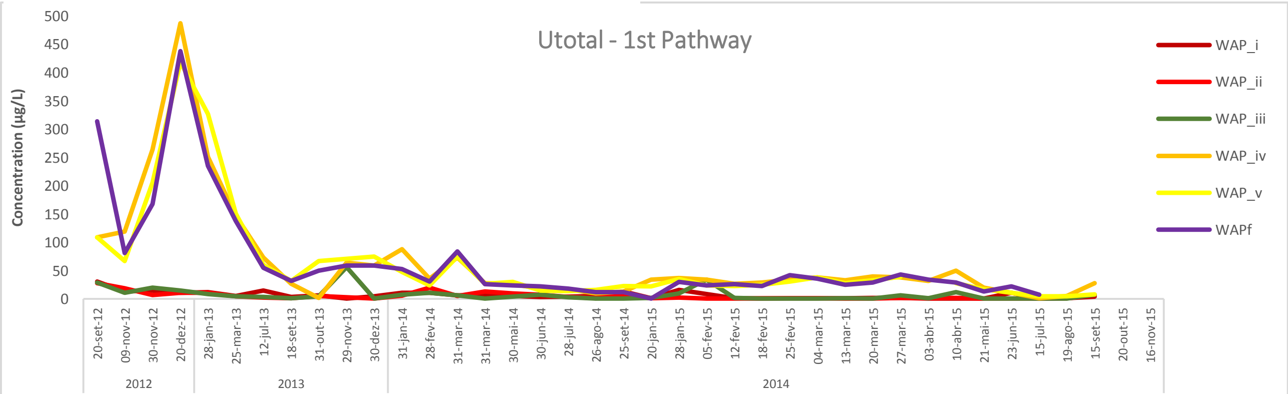

Figure 15 *Temporal variation of U_{total} concentrations in µg/L, in the 1st pathway (2012-2015)*

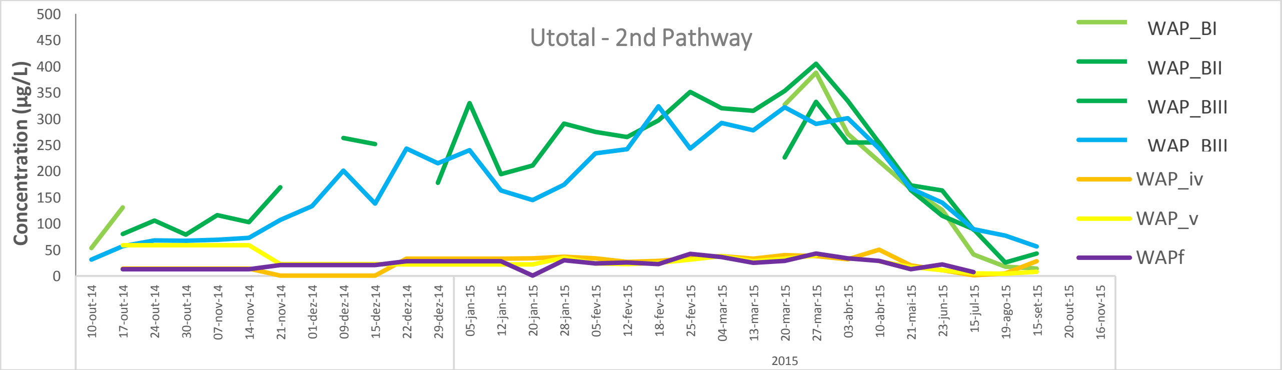

Figure 16 *Temporal variation of U_{total} concentrations in µg/L, in the 2nd pathway (2014-2015)*

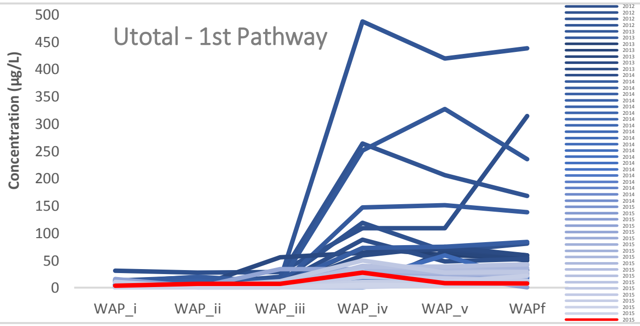

***Figure 17** Spatial evolution of Utotal*

concentrations in µg/L, 1st pathway

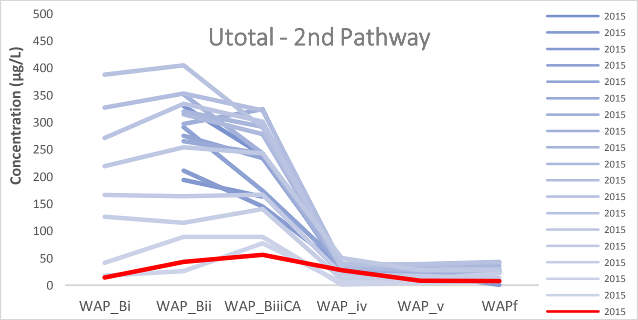

***Figure 18** Spatial evolution of U_{total}*

concentrations µg/L, 2nd pathway

The graphs with spatial evolution are organized according to color series, being the darker colors the oldest series and the most recent samples the lightest. The last series of collected samples taken are marked in red.

The following conclusions were taken from the water quality monitoring results:

Physical Parameters - pH values are within 5.9 – 7,7 ranging from slightly acidic to alkaline (***Figure 6)***. Both, Eh and pH values, increase spatially throughout the system, while EC decreases (***Figure 8***). Temporal variations can be observed in EC ***(Figure 9***), while pH presents a more or less stable behavior (***Figure* 7)**.

Cations (Ca, Na, K, Fe, Mn) **-** In general, these elements have been stable during the monitoring period, as presented by ***Figure 10*** with the average concentrations of these elements along all the sampling points. However, spatial distribution during that same period present two different behaviors: Ca, Na and K maintain stable values during the whole system, being in ***Figure 11*** presented the evolution of concentrations of Ca. Whereas Fe-oxides (***Figure 12)*** and Mn, present a diminishing behavior until WAPiii (third stage) of the system, varying from ~8 mg/L to under detection limits.

Anions (HCO_3^-, Cl^-, SO_4^-) – Regarding temporal evolution of the concentrations of the sampling points: Bicarbonates present a slightly increase over time (300mg/L), sulfates fluctuate from 200-100 mg/L while chlorides tend to stabilize ~50 Mg/L. Spatially, both chlorides and sulfates tend to stabilize throughout the MWPT, bicarbonates on the other hand present a similar behavior to Fe and Mn showing lower concentrations in the late stages of the system.

Radionuclides (Ra^{226}, U_{total}, U^{234}, U^{238}) – Spatially, Radium has been behaving in comparable way as bicarbonates, Fe and Mn do, with progressively lower activities as the MWPT progresses (***Figure 13).*** Temporally has a stable behavior during the period with range values of 1 $Bq.L^{-1}$ to <DL (0,01 Bq/L) (***Figure 14)***. Total Uranium and its isotopes are similar in their performance. Temporal variation of the concentration of U_{total} has been decreasing in both pathways, 1st (***Figure 15)*** and 2nd ***(Figure 16)*** which present a decline over time. However, spatially while 2nd pathway presents a diminishing behavior (***Figure 18***), in the 1st pathway an atypical behaviour can be observed with its concentration slightly increasing in the stage nº4, WAP_{IV}, of the MWPT (***Figure 17)***, decreasing afterwards to values below the ones verified in the initial stages. Most definitely this behavior has to do with two different factors, the first being the entrance of low flow seepage water (2nd pathway) with higher U_{total} concentrations than the initial ones of the first pathway (WAP_i to WAP_{iii}), and the second being the contribution of equilibrium between dissolved (U^{+6}) and particulate (U^{+4}) forms of uranium.

Conclusion

The monitoring results of the constructed MWPT in the last three years shows that this system is efficient by promoting the decrease and significant removal of radionuclides and heavy metals concentrations to levels way below regulatory standard limits.
Analyzing the temporal variation of the different patterns we can see that there is a general tendency overall for the diminishing concentrations (U_{total} and EC) over time, and a group of parameters that have been stable during the whole process.
When examining the evolution of the parameters within the MWPT flow path, we can distinguish three groups, based upon their behavior. The first group (EC, Ra^{226} Fe, Mn, Bicarbonates) have a similar behavior, in which their values decrease as the treatment progresses. The second group (Eh, pH) increase their values in the late stages of the MWPT, and in the last group (Ca, K, Na) they remain with stable values through the system.

Our data seems to indicate that:

- The MWPT has been objectively efficient in terms of removing contaminates from the aqueous phase, within the most important parameters, Uranium (total) from 487µg/l to nearly 11µg/l and Radium from 1Bq/L to <0,01Bq/l, with an efficiency of up to 98% and 99%, respectively, in terms of temporal variation. Concerning spatial variation we have, from the latest series, an efficiency of nearly 90%, ranging ~250µg/l to nearly ~27µg/l.
- When compared with the Active treatment plant, at this efficiency rates, while the WMPT requires a higher monitorization time, it represents lower operational and maintenance associated costs, therefore being a clear option to replace the active treatments.
- There was an improvement in all water quality parameters, both temporally and spatially reaching uranium and Ra-226 values below USEPA standards for drinking water of 30 µg/l and 0,01 Bq/L, respectively.
- The system reached its chemical stabilization in a period of less than 2 years.
- The diminishing concentrations of Fe, Mn are mainly due to their precipitation in the first stages.
- The main mechanisms involved in the precipitation and mobilization of Uranium are thought to come from the increase pH/Eh, complexation with bicarbonates, organic matter and sulfates.
- Present data seems to indicate that Eh increase causes mobilization from U^{+4} which is in particulated uranium form into dissolved U^{+6}.
- The 2nd pathway has higher Uranium concentrations and Eh, with a significantly lower flow (6 times smaller), which contributes to the increase of the dissolved uranium in WAP_{IV}.
- While phytoremediation, specifically placed in stages WAP_{IV}, WAP_{V} and WAP_{f}, and bacteria growth also play a role in the system, it has not been assessed so far the bioremediation influence.

More investigation is undergoing to clarify these hypothesis and improve on the efficiency of the system, by analyzing sediments, plants and rocks in the vicinity of the MWPT and to test pilot the increase of Eh in an earlier stage of the MWPT forcing rapid U mobilization and subsequently its earlier precipitation with more hydraulic retention time to lowering the Eh to a more reduced aquatic environment.

Acknowledgements

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Treatment of Seepage Water from a Tailings Pond of Uranium Mining: Column Tests with a Novel Schwertmannite Adsorbent

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Abstract

Based on biotechnologically synthesized schwertmannite (SHM) from iron and sulfate containing lignite mine water, the agglomerated, filter-stable adsorbent 'SHM-sorpP' was developed by com-pacting SHM in a briquette press (Peiffer et al., 2012; Janneck et al., 2014). As investigated by Fukushi et al. (2003), Regenspurg and Peiffer (2005), and Schroth and Parnell (2005), schwertmannite offers excellent adsorption properties towards arsenic.

Building on several laboratory test regarding the suitability of the new adsorbent for the removal of arsenic from water (Peiffer et al. 2012), SHM-sorpP was tested in this study in comparison to the commercially available iron hydroxide adsorbents Ferrosorp®Plus (HeGoBiotec GmbH) and GEH®104 (GEH Wasserchemie & Co KG) with regard to its suitability for the treatment of seepage water from an uranium tailings pond in column tests. The seepage water was characterized by high pH (8.7–8.9) and significant concentrations of arsenate, molybdate, and phosphate. For the tests, a water pretreatment was realized by decreasing its pH to 7 (pH 7 scenario) and pH 5 (pH 5 scenario) with a dosage of hydrochloric acid (33%), respectively.

In the pH 7 scenario (columns with each of the three adsorbents) no molybdate could be adsorbed by Ferrosorp®Plus, GEH®104, and SHM-sorpP. In contrast, all adsorbents were able to immobilize more or less arsenate and phosphate with SHM-sorpP offering the most efficient adsorption. In the pH 5 scenario (columns with SHM-sorpP and Ferrosorp®Plus each), SHM-sorpP again offered the better performance in the tests: in comparison to Ferrosorp®Plus, about 30% more arsenate and phosphate as well as 100% more molybdate could be adsorbed.

Key words: Schwertmannite, Water Treatment, Seepage Water of a Tailings Pond, Uranium Mining

Introduction

A pilot plant for microbiologically mediated ferrous iron oxidation is operated by the Vattenfall Europe Mining AG and G.E.O.S. company in the open pit lignite mine near Nochten (Lusatia, Germany) where schwertmannite (SHM) is synthesized as a byproduct of a worldwide unique water treatment process (Janneck et al., 2010; DE 102 21 756 B4) for the treatment of iron and sulphate rich mine water from the Nochten pit.

In the framework of a research project funded by the German Ministry of Education and Research (Peiffer et.al., 2012), two methods for the production of agglomerated adsorbents based on the 'byproduct' schwertmannite from the Nochten pilot plant were developed for their utilization in passive water treatment systems. The adsorbent 'SHM-sorpP' was obtained by compacting SHM in a briquette press, the adsorbent 'SHM-sorpX' by curing with an organic polymer (Janneck et al., 2014).

As investigated by Fukushi et al. (2003), Regenspurg and Peiffer (2005), and Schroth and Parnell (2005), schwertmannite offers excellent adsorption properties towards arsenic. Based on this knowledge, batch and small scaled column tests regarding the suitability of the new SHM adsorbents for the removal of arsenic from water were successfully performed (Peiffer et al., 2012). In continuation to the laboratory tests and with the kind support of Wismut GmbH (Chemnitz, Germany), columns filled with SHM-sorpP and two commercially available iron hydroxide adsorbents, respectively, were operated in the bypass of a treatment plant for seepage water from an uranium tailings pond. In this pilot test, which was part of the ongoing research project 'SAWA' and funded by the Federal Ministry of Education and Research (FKZ 02WQ1309), the adsorption potentials of the new Schwertmannite adsorbent to arsenate as well as the structurally similar oxoanions molybdate and phosphate were investigated under real conditions. This study presents selected results of the pilot test.

Methods

Our pilot test could be realized on the location of an active water treatment plant of Wismut GmbH (Chemnitz, Germany) which supported the experiments significantly, especially by the ICP-OES analysis of As and Mo concentrations in influent and effluent water samples. In the water treatment plant (WTP), an alkaline **seepage water** (pH 8.7 -8.9, see table 1 for characteristic components) of an uranium tailings pond in Saxony (Germany) is purified. Officially authorized discharge limit values of the WTP are 0.3 mg As/L and 0.5 mg U/L. Phosphate was analyzed in the laboratory of the Institute for groundwater Management by an UV-VIS spectrometer Lambda 10 (Perkin Elmer). The measurement of pH-values was done on-site by a pH meter 323 and pH probe SenTix41 (WTW).

Table 1 *Concentration (C) range of characteristic parameters of the seepage water used as influent water for the pilot test*

parameter	TOC	HCO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Fe^{2+}	As	Mo	PO_4^{3-}	U
C(mg/L)	10-22	≈ 1000	≈ 1900	≈ 30	≈ 50	<0,01	1-1.3	1-1.3	3-5	7-10

By use of a total of ten columns (figure 1, each 3 cm in diameter and 15 cm in length, total column volume V= 106 cm^3), the new **adsorbent SHM-sorpP** was investigated in comparison to the commercially available **iron hydroxide adsorbents Ferrosorp®Plus** (HeGoBiotec GmbH) **and GEH®104** (GEH Wasserchemie & Co KG) with regard to their suitability for the treatment of the seepage water described above. SHM-sorpP was produced by a briquette press. As shown in table 2, the three adsorbents differ considerably in their bulk densities and therewith their filter bed porosities.

Table 2 *Filter bed parameters of adsorbents used in the pilot test (grain size 0.63-2mm)*

adsorbent		SHM-sorpP	GEH®104	Ferrosorp®Plus
bulk density ρ_d	(g/cm^3)	0.78	1.15	0.47
grain density ρ_s	(g/cm^3)	2.81	2.96	3.02
filter bed porosity *n*	(%)	72	61	84
filter bed volume $BV= n\cdot V$	(cm^3)	76	65	89
adsorbent weight/ column *m*	(g)	99	157	59

Figure 1 *Adsorbent SHM-sorpP*

Figure 2 *Columns of the pilot test*

Figure 3 *Pilot test setup: influent 200L-influent barrels, columns, peristaltic pump and effluent canisters*

In two pilot test scenarios, a pretreatment of the seepage water was realized by decreasing its pH by hydrochloric acid (33%) dosage to pH 7 (‘**pH 7 scenario’**, each two columns with SHM-sorpP, Ferrosorp®Plus and GEH®104 in series) and pH 5 (‘**pH 5 scenario’**, each two columns with SHM-sorpP and Ferrosorp®Plus in series). The flow rate *Q* was set to 7.7 to 8.1 l/d, resulting in a filter bed residence time of 16 to 20 min and 93 to 121 replaced bed volumes (RVB) of the filter bed per day.

Results

Figures 4 and 5 show the breakthrough of As and Mo in the column effluents of the pH 5 scenario. SHM-sorpP retained both oxoanions significantly better than Ferrosorp®Plus. The As discharge limit of the WTP (0.3 mg/L) was exceeded after 60 days (about 5000 RVB) and 66 days (about 5500 RBV) for Ferrosorp®Plus and SHM-sorpP, respectively. At the end of the pilot test (after 176 days), about 10% of the influent As concentration could still be immobilized in the column filled with Ferrosorp®Plus, but only 3% of influent Mo. SHM-sorpP still adsorbed about 30 % of the influent As concentration and about 22% of the influent Mo concentration at this time. The breakthrough behaviour of PO_4 (data not shown) was similar to As (about 10% and 28 % of the influent PO_4 were retained in the Ferrosorp®Plus and the SHM-sorpP column at day 176, respectively).

In the pH 7 scenario no molybdate could be adsorbed by Ferrosorp®Plus, GEH®104, and SHM-sorpP (data not shown). In contrast, all products were able to immobilize more or less arsenic (figure 6) and phosphate (data not shown). SHM-sorpP offers again the most efficient adsorption for As and PO_4. The As discharge limit value of the WTP was exceeded after 28 days (about 2800 RBV), 37 days (about 3700 RBV) and 40 days (about 4000 RBV) in the columns with Ferrosorp®Plus, SHM-sorpP, and GEH®104, respectively. At the end of the pH 7 scenario (after 81 days), about 10% of the influent As concentration could still be immobilized in the columns filled with Ferrosorp®Plus and SHM-sorpP. GEH®104 retained still about 22% of influent As. At a first glance, this might be the best As retention ability. However, the significant higher weight of GEH®104 in the column (see table 2) has to be kept in mind.

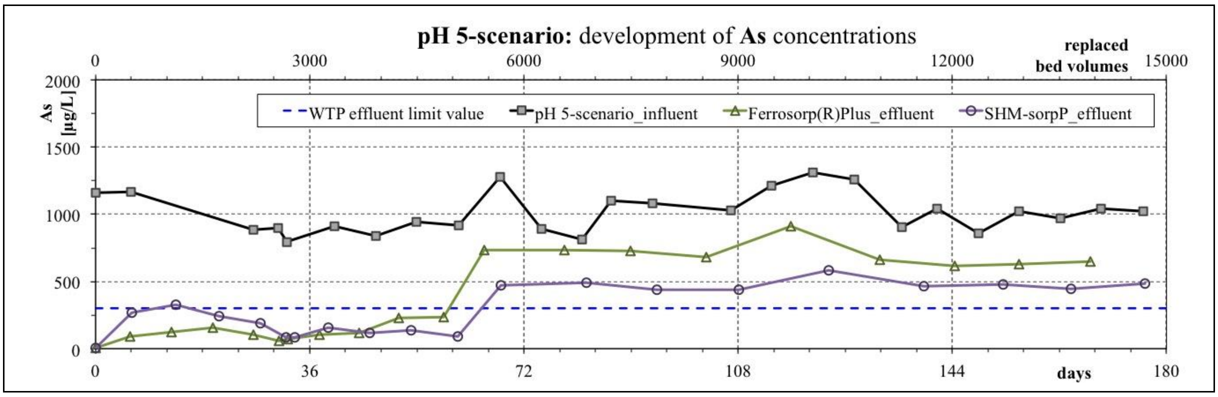

Figure 4 *Development of As concentrations in the first of each two columns filled with SHM-sorpP and Ferrosorp®Plus and seepage water pretreatment by lowering its pH from pH 8.8 to about pH 5 (pH 5 scenario: s)*

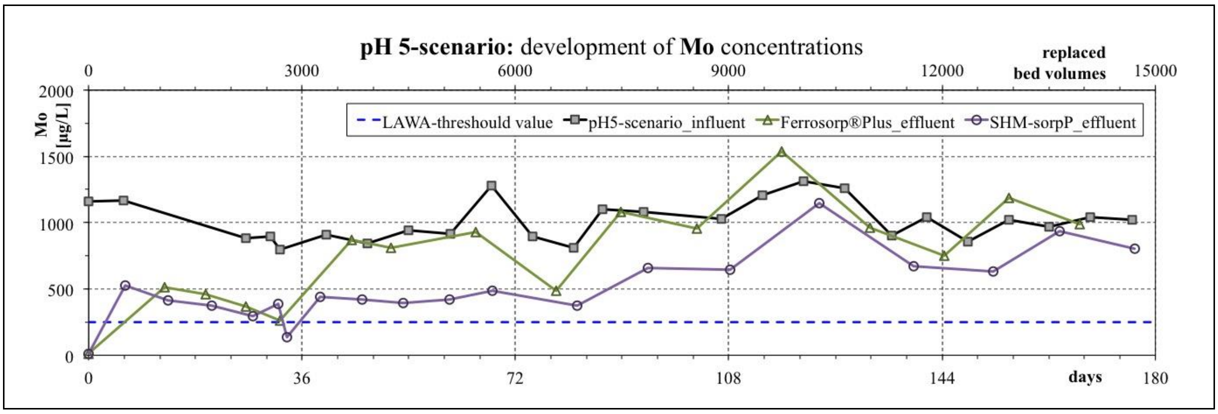

Figure 5 *Development of Mo concentrations in the first of each two columns filled with SHM-sorpP and Ferrosorp®Plus and seepage water pretreatment by lowering its pH from pH 8.8 to about pH 5 (pH 5 scenario)*

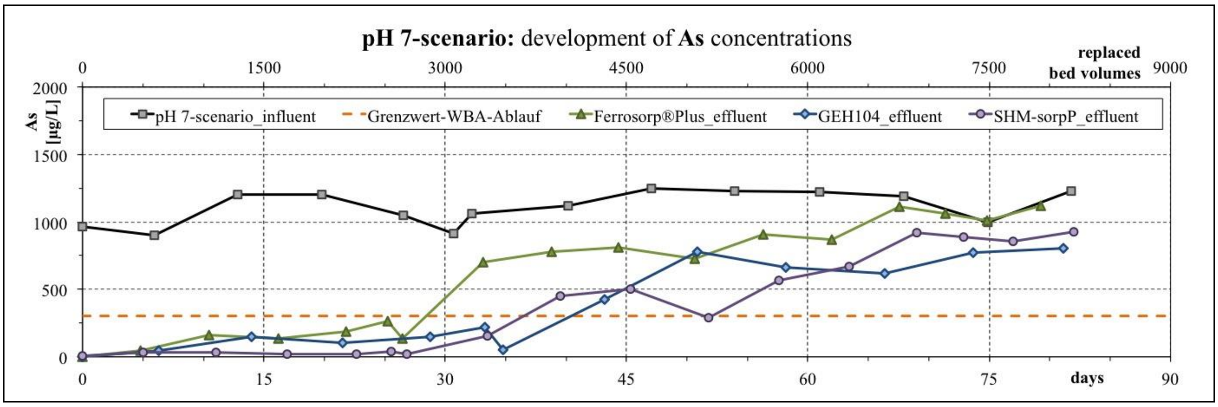

***Figure 6** Development of As concentrations in the first of each two columns filled with SHM-sorpP and Ferrosorp®Plus and seepage water pretreatment by lowering its pH from pH 8.8 to about pH 7 (pH 7 scenario)*

In order to make the oxoanion adsorption behaviour of the three investigated adsorbents comparable, the adsorbent loadings were calculated in mg/cm^3 by use of their bulk densities from table 2. The results are summarized in table 3, proving the excellent suitability of SHM-sorpP for passive filter bed systems in practice. A better adsorbent loading requires less replacements of the filter bed fillings.

***Table 3** Cumulative loading of the investigated adsorbents with arsenate (As), molybdate (Mo) and phosphate (PO_4) after 81 days (pH 7 scenario) and 176 days (pH 5 scenario), where influent concentrations were almost reached in the effluents of the first column of a double series. Adsorbent loadings in mg/cm^3 were calculated by adsorbent bulk densities from table 2.*

scenario	**pH 7:** oxoanion retention (mg/cm^3)			**pH 5:** oxoanion retention (mg/cm^3)		
adsorbent	As	Mo	PO_4	As	Mo	PO_4
Ferrosorp®Plus	3.0	<0.1	7.9	5.1	2.2	11.8
SHM-sorpP	4.9	<0.1	14.3	7.4	5.5	21.1
GEH®104	3.8	0.4	10.6	not investigated		

Conclusions

In order to compare the adsorption ability of the new Schwertmannite-based adsorbent 'SHM-sorpP' and the commercially available iron hydroxide adsorbents Ferrosorp®Plus and GEH®104 with regard to the oxoanions arsenate, molybdate and phosphate under real conditions, a pilot test with two pH scenarios (pH 7 and pH 5) was performed. This the pilot test was friendly supported by Wismut GmbH via providing basic seepage water from a tailings pond of uranium mining (pH 8.7-8.9), the test facility and oxoanion analysis.

In the pH 5 scenario, the retention of the oxoanions As, Mo, and PO_4 was significantly better than in the pH 7 scenario, whereas SHM-sorpP offers the best adsorption ability for all three oxoanions. However, a pretreatment of the seepage water by lowering the pH with hydrochloric acid is a significant cost factor. A cost comparison resulted in a compensation of the additional hydrochloric acid costs (pH 5: 0.20 € versus pH 7: 0.05 € per m^3 seepage water) already by the better retention of arsenate.

For a practical application, clogging of the filter bed systems by secondary precipitates or CO_2 should be prevented by further pretreatment of the seepage water in a column packed with gravel (pH 7 scenario) and by stripping of CO_2 (pH 5 scenario), respectively.

Acknowledgements

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Advanced chemical oxidation for arsenic treatment at a flooded uranium mine with a bio-geochemically reduced mine water pool

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Abstract

Mine water from the flooded WISMUT mine at Pöhla-Tellerhäuser requires long-term treatment regarding arsenic and radium before river discharge. The mine water pool is characterized by geochemically reduced conditions with dissolved methane and hydrogen as well as overall redox potentials of 0 - 100 mV. Sulfate concentrations are < 5 mg/l, and uranium concentrations dropped below the regulatory limit (0.2 mg/l) only five years after flooding was complete. Those conditions, however, induce quasi constant mine water arsenic and radium concentrations of 1.5 - 2 g/l and ~4,000 mBq/l, respectively. Speciation analysis of dissolved arsenic revealed arsenite and arsenate as major species with a dominance of arsenite (>65% of total arsenic), while thioarsenates were detected in traces. Mine water treatment is performed by iron oxide and barium sulfate precipitation, leading to co-precipitation and adsorption of arsenic and radium. Reducing conditions, however, hamper ferric hydroxide formation and thus restrict the treatment performance of the precipitation plant. Generally, mixed ferrous-ferric hydroxides are known to be less effective with respect to pollutant binding and cause problems in sludge treatment. For technology optimization, oxidation of dissolved arsenite, ferrous iron and other reduced mine water solutes was tested using aeration and hydrogen peroxide dosage prior to ferric iron precipitation. Moreover, pH was adjusted to pzc for promotion of ferric iron flocculation and arsenic co-precipitation. Lab and field tests revealed hydrogen peroxide pre-oxidation in combination with pH adjustment to pH ≤ 7 most effective in decreasing dissolved arsenic concentrations. The residual concentrations of dissolved arsenic in the reaction chamber effluent were diminished from 250-400 µg/l to < 50 µg/l by reducing the ferrous fraction of the total iron concentration from ~ 10 % to 1-2 %. Advanced chemical oxidation speeds up colloid coagulation preceding flocculation and results in a stable and substantially complete arsenic removal from reduced mine water.

Key words: Uranium mining, mine water treatment, microbial reduction, arsenic and iron species, ferric hydroxide precipitation, chemical oxidation, laboratory test, field test

Introduction

After East German uranium industry was decommissioned in 1990, an unprecedented close-out and remediation programme was launched immediately thereafter. The programme is run by Wismut GmbH, a governmentally owned remediation enterprise, headquartered in Chemnitz, Saxony. The corporate purpose of Wismut GmbH is to decommission its former uranium mining and milling facilities and to rehabilitate the devastated land for further use.

While the physical clean-up and rehabilitation activities are chiefly completed, active mine water management is still required at all major remediation sites. By 2016 Wismut operates six water treatment plants to clean up effluents from four flooded underground mines and seepage water from several tailings management facilities. A total annual throughput of ~ 20 Mm^3 of water is treated for uranium, arsenic, radium-226 and heavy metal removal, basically by modified lime precipitation. According to current estimates, water treatment is expected to continue beyond 2040. Changes in water composition and the permanent need for cost optimization necessitate adjustments in water treatment methods on a regular basis. The paper illustrates most recent experiences regarding the water treatment approach practiced at the flooded uranium mine at Pöhla-Tellerhäuser, with a particular focus on arsenic removal from bio-geochemically reduced mine waters.

Site history

Between 1967 and 1990, the Pöhla-Tellerhäuser deep mine produced approximately 1,200 t U from polymetallic hydrothermal veins situated in a metamorphic host rock environment. Ore mineralization comprised pitchblende, Co-Ni-arsenides, native arsenic, loellingite, magnetite, pyrite, marcasite, chalcopyrite and native silver; quartz and calcite were the main gangue minerals (Hiller & Schuppan 2012). Mine development comprised a main access tunnel of 8 km total length and two blind shafts reaching a depth of 900 m below ground at the Tellerhäuser mine field.

After decommissioning the mine was flooded between early 1991 and autumn 1995. Floodable mine voids total approximately 1 Mm^3. In 1995, a conventional water treatment plant (WTP) was commissioned for the removal of uranium, manganese, arsenic and radium from the decanting mine waters. Unexpectedly, uranium concentrations declined much faster than modeled for a first flush discharge from a perfectly mixed flow reactor (Paul et al. 2013). Five years after reaching the final post-flooding water level, uranium and manganese concentrations in the mine effluent were even already below regulatory limits (Tab. 1), and treatment for uranium became redundant. Geochemically reduced conditions and the detection of microbial activity in the mine (Gagell 2015) are evidence that microbially induced uranium reduction and precipitation are causing the uranium retention. Unfortunately, those conditions favor at the same time the mobilization of arsenic and radium, which are the major aim of the recent treatment efforts.

The mine water is pH-neutral with low redox potential. In 2015, mean mine water quality has been characterized as follows: pH 7-7.5, Fe 5 mg/l, Mn 0.18 mg/l, As 2 mg/l, U 12 µg/l, ^{226}Ra 4.2 Bq/l, SO_4 < 5 mg/l, TDS 286 mg/l. Both prevention of precipitation reactions and mineral dissolution in the mine induce quasi constant mine water arsenic and radium concentrations which are well above the discharge limits (As 100 µg/l, ^{226}Ra 300 mBq/l). Speciation analysis of dissolved arsenic revealed arsenite and arsenate as major species with a dominance of arsenite (>65% of total arsenic), while thioarsenates were detected in traces. Moreover, dissolved methane and hydrogen as well as overall redox potentials of 0 - 100 mV indicate reduced geochemical conditions in the mine.

***Table 1** Quality evolution of the Pöhla mine effluent after fully-fledged flooding*

Element	Limit value	Mine water quality (mean values)				
		1995	1997	1998	2008	2015
Mn (mg/l)	2.0	3.68	1.60	1.14	0.23	0.18
As (µg/l)	100	487	2,017	2,200	2,091	2,050
U (mg/l)	0.20	1.75	0.20	0.19	0.02	0.012
Ra-226 (mBq/l)	300	1,057	3,910	4,520	4,001	4,210

Today, an annual mine water overflow of ca. 0.13 million m³ from the deeper, flooded part of the mine is collected in the still open drainage adit and led by pipelines to the WTP, while at the same time approximately 0.25 million m³ of penetrating surface water are collected separately along the main access tunnel and drained directly to the natural water system.

Water treatment plant

After having tested the efficiency and robustness of a semi-passive constructed wetland approach over a 10 year period with an unsatisfactory overall outcome, mine water treatment is most recently performed by an iron oxide and barium sulfate precipitation unit, leading to arsenic and radium retention by co-precipitation and adsorption. Fig. 1 depicts a flow chart of the WTP. Briefly, the precipitation plant treatment scheme comprises aeration, addition of chemicals, mixing, coagulation, flocculation, filtration as well as sludge separation and storage. It is important to note that the plant has been designed for a remote-control operation mode without permanent workforce at the site. Low density sludge is collected in a storage tank and discontinuously transported to Wismut's Schlema WTP some 25 km away, where it becomes introduced into the local sludge management procedure of thickening, immobilization and disposal at an in-house disposal area.

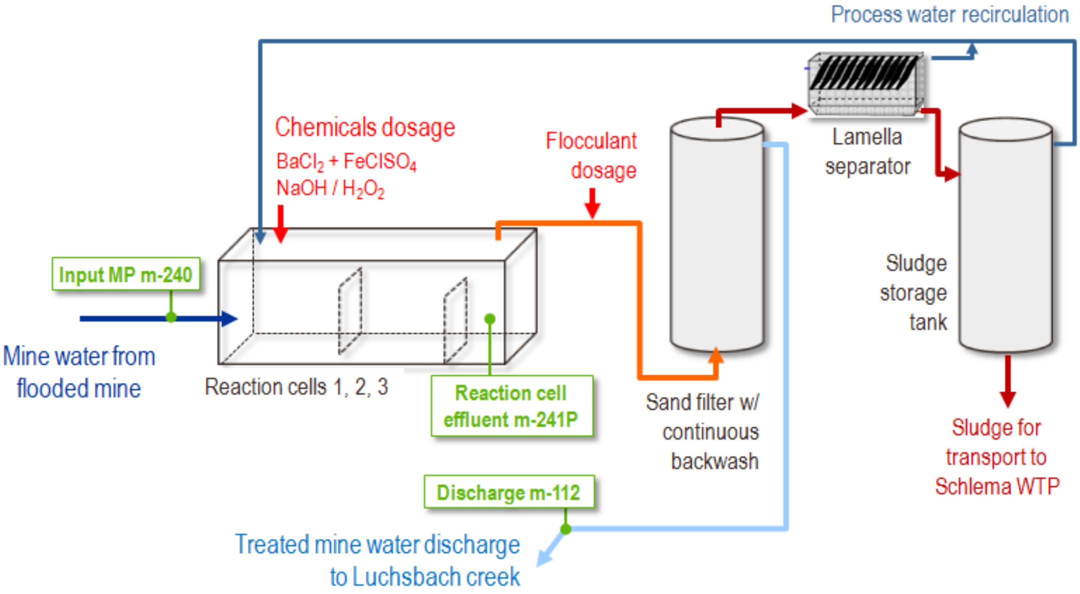

***Figure 1** Principle flow chart of the Pöhla WTP with selected monitoring points*

The Pöhla treatment plant was built in 2013/2014 and has been operated in testing mode since 2014. The treatment capacity of the plant is 10 - 60 m^3/h. At present, the plant is operated at an average flow rate of 12 m^3/h.

The original treatment sequence design comprises

- addition of $FeClSO_4$ (33%) and $BaCl_2$ (24%) with dosage rates of 0.16 - 0.2 l/m^3 and 0.08 l/m^3, respectively (mixing in coagulation basins)
- pH adjustment to pH = 7.5 - 7.7 by addition of 25% NaOH (mixing in coagulation basins)
- flocculant addition (0.05% AP99E (PolyChemie GmbH), 5 l/h) in piping to sand filter
- flocculation and filtration in sand filter with continuous backwash

During the first months of operational testing in 2014, arsenic concentrations in the plant effluent met regulatory limits (100 µg/l) but with values only marginally below it. At the same time, a lag in iron hydroxide flocculation was observed. As illustrated by Fig. 2, flocculation proceeded downstream the sand filter, forming iron hydroxide coatings on pipes, tank walls and probes contacting the filtrate.

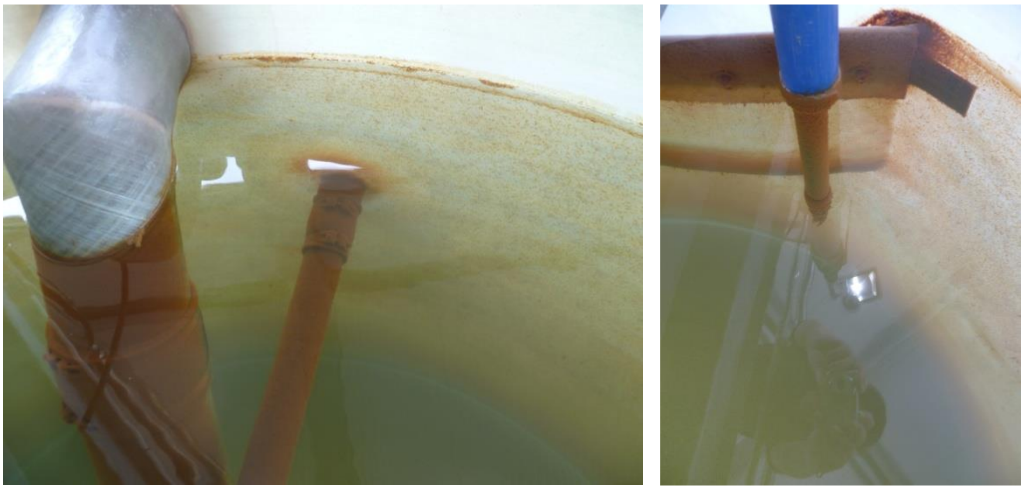

***Figure 2** Photographs of iron hydroxide coatings formed downstream the sand filter from the filtrate*

Monitoring of the treatment process revealed an extension in flocculation time from 15 min to 60 min with an increase in ferrous iron concentration in the coagulation basins from 5 to 25 mg/l. The ferrous concentrations in the coagulation basin occasional exceeded mine water inflow concentrations, indicating a reduction of the ferric iron added for coagulation. Reduced solutes of the mine water (e.g. dissolved methane) and iron reducing microbes may play a role in that.

The presence of ferrous iron during colloid formation and coagulation causes a mixed ferrous-ferric hydroxide formation, which is known to be less effective with respect to pollutant binding. Moreover, mixed ferrous-ferric hydroxides form sticky precipitates causing problems in sludge handling (MEND 1999), which were observed at plant operation as well. Iron hydroxide sorption of the reduced arsenite is generally inferior to that of the oxidized arsenate, too. Thus it was hypothesized, that both limited arsenic retention and unfavorable flocculation depend on an insufficient oxidation state during iron hydroxide colloid formation and coagulation.

Lab investigations for water treatment optimization

For technology optimization, oxidation of dissolved arsenite, ferrous iron and other reduced mine water solutes was tested in the lab using aeration (gassing with pressurized air; 2 hours) and hydrogen peroxide dosage (35% H_2O_2 dosage; 0.2 ml/l; reaction time 30 min). Subsequently, coagulation and flocculation (33% $FeClSO_4$; 195 µl/l; 23% $BaCl_2$; 81 µl/l) was tested at pre-oxidized and at original mine water (mixing time 30 min, settling time 70 min).

Fig. 3 shows pH, redox potential and ferrous iron concentrations of the mine water during pre-oxidation. H_2O_2 addition oxidizes the mine water faster and more extensive than aeration. While ferrous iron is still present after 60 min of aeration, no ferrous is detectable at H_2O_2 addition after 30 min. Moreover, the redox potential at H_2O_2 dosage (~470 mV) exceeds the average redox potential at aeration (~350 mV) by ~100 mV, and the pH stays constant at H_2O_2 addition instead of rising by CO_2 degassing at aeration.

The coagulation tests are discussed for dissolved iron and arsenic concentrations, since both are a measure for completeness of iron hydroxide colloid formation and coagulation. Low dissolved concentrations after coagulation indicate rapid flocculation and high pollutant retention in the treatment process.

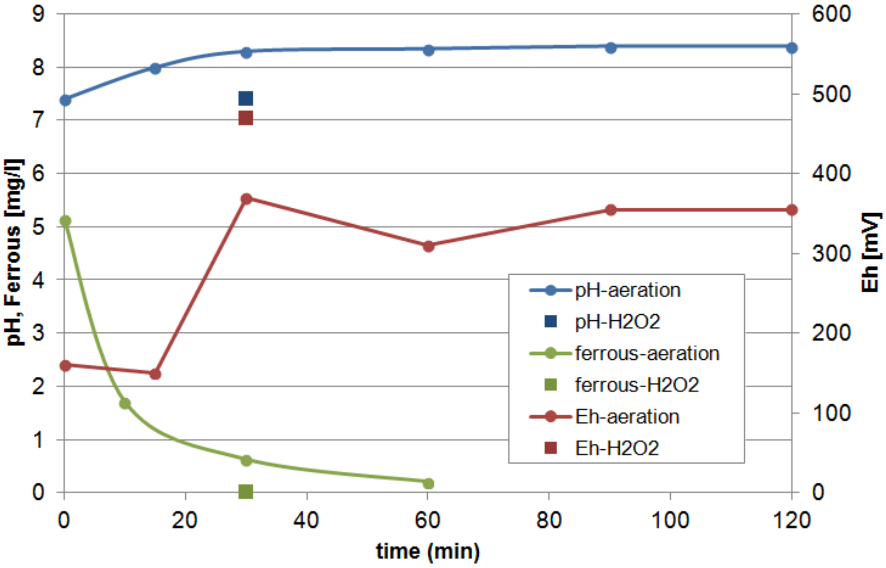

Figure 3 *pH, redox potential and ferrous concentration during pre-oxidation*

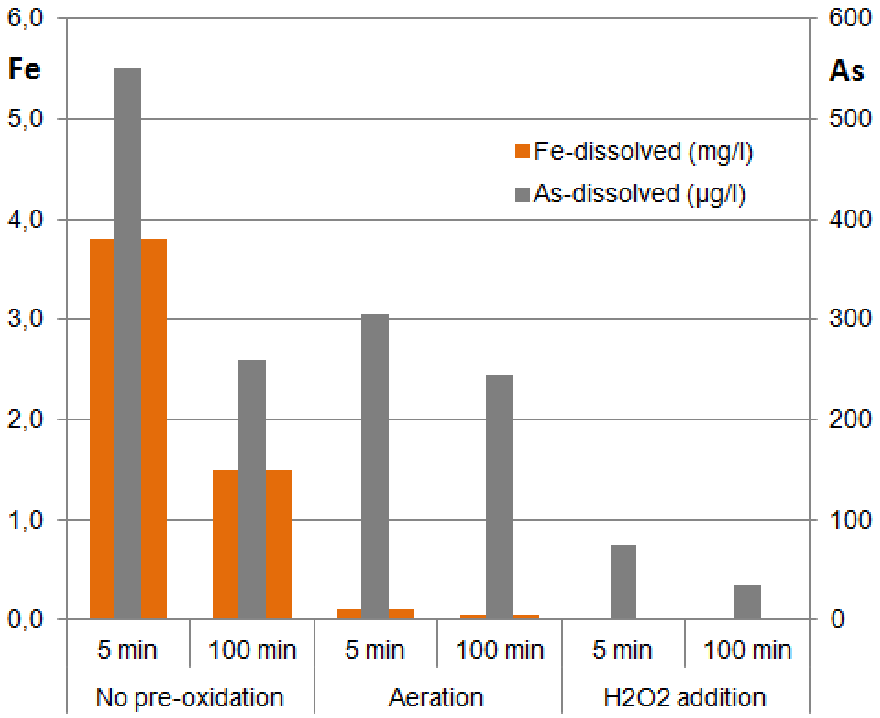

Figure 4 *Dissolved iron and arsenic after coagulation and flocculation at different oxidation states*

As depicted in Fig. 4, the dissolved arsenic concentration was below the effluent limit (100 µg/l) at H_2O_2 addition already after 5 min, while aeration left only little less arsenic dissolved after 100 min than coagulation without pre-oxidation (260 and 240 µg/l, respectively). Colloid formation and coagulation was rapid and complete only at the oxidation state reached by H_2O_2 addition. Obviously, the presence of reduced species and ferrous iron during coagulation and flocculation hampers the precipitation of iron hydroxide and the associated arsenic elimination in the treatment plant.

Field scale testing of treatment optimization

Field scale testing was performed by modification of the operation scheme of the treatment plant. After a period of baseline monitoring (~ 9 month), the effects of pH adjustment to pH 7 (stopping of NaOH dosage), pre-aeration of the mine water (change from pressure to gravity pipeline for mine water inlet) and H_2O_2 dosage (165 – 335 ml $H_2O_{2\ (30\%)}$ / m^3) on arsenic removal were tested. Table 2 indicates the duration and particular operation conditions of the single test periods. Fig. 5 depicts arsenic concentrations (average, min and max) of the plant effluents for each test period.

Table 2 *Field test periods and operation conditions*

No	Period	Modified operation conditions			
		Stopping NaOH dosage	Mine water pre-aeration	H_2O_2 dosage, ml/m^3	Sludge recirculation (partial)
1	01/2014-09/2014			Baseline monitoring	
2a	01/2015-02/2015	x			
3	03/2015-04/2015	x	x		
2b	06/2015-09/2015	x			
2c	10/2015	x		Baseline monitoring for period 4-6	
4	11/2015-01/2016	x		165	
5	03/2016-04/2016	x		165	x
6	05/2016	x		250-335	x

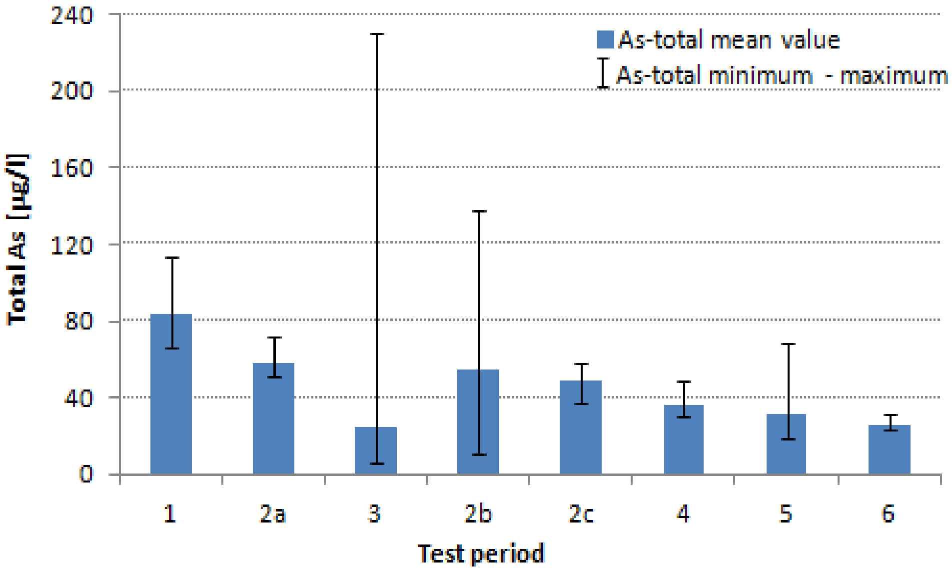

***Figure 5** Total arsenic concentrations in plant effluents (m-112; mean, minimum and maximum values for each of the individual test periods, see table 2)*

As compared to the original operation scheme, all tested modifications of operation conditions yielded a decrease in average total arsenic in the plant effluent.

Adjustment of pH from pH ~ 7.5 to pH ~ 7 (test period 2) decreased mean arsenic concentrations from [As] ~ 85 µg/l to [As] ~ 50 - 60 µg/l. The pH decrease favours the supposed arsenic retention mechanisms: scorodite formation (although totally amorphous at pH ~ 7) and anion sorption to iron hydroxides (increase in number of positive surface charge). In consequence, NaOH dosage was switched off and pH ~ 7 was retained for all subsequent test periods. The increase in data variation ($[As]_{max}$ ~ 130 µg/l) in test period 2b relates to effects of the previous tested mine water pre-aeration, were the decrease in average arsenic effluent concentration but also in data variation were most expressed ([As] ~ 25 µg/l; $[As]_{max}$ ~ 230 µg/l). At mine water pre-aeration in the inlet pipe (connecting the 3.5 km distance from the mine to the treatment plant), a partial oxidation of the mine water had resulted in in-pipe precipitation of arsenic rich iron hydroxide. This caused an expressed but unstable decrease in mean arsenic concentration. Sporadically, the precipitates were flushed out and overloaded the flocculation filter of the treatment plant, yielding arsenic break-through and test period break-off. A more stable decrease in mean arsenic effluent concentrations and low data variation could be achieved by H_2O_2 dosage. While partial sludge recirculation increased data variation in test period 5 ($[As]_{max}$ ~ 70 µg/l), the average effluent concentration of all H_2O_2 dosage test periods stayed below 40 µg/l. At highest H_2O_2 dosage rates (250-335 ml $H_2O_{2(30\%)}$ / m^3; test period 6) the average effluent concentration was as low as 25 µg/l, comparable to mine water pre-aeration but with significantly smaller data variation ($[As]_{max}$ ~ 30 µg/l).

The significant improvement in overall arsenic retention during the test phases with H_2O_2 dosage can be related to the decrease of dissolved arsenic concentrations in the effluent of the coagulation basin prior to sand filtration (m-241P). As shown in Fig. 6, H_2O_2 dosage caused a sudden decrease of dissolved arsenic concentrations in comparison to phase 2c values (As_{diss} ~ 300-400 µg/l). During the test periods 4-6 the mean of the dissolved arsenic concentrations was as low as $[As]_{diss}$ ~ 55 µg/l, i.e. well below the discharge limit of the plant at m-112. Likewise, the As_{diss}/As_{total} ratio of the reaction cell effluent decreased significantly, from 19% in test phase 2c to 4 % (period 4), 3 % (period 5) and 1% (period 6), respectively.

Obviously, advanced chemical oxidation can effectively improve arsenic retention by iron hydroxide precipitation on the field scale as well. The dominance of ferric and arsenate species promotes iron coagulation, adsorption and scorodite formation. Arsenic removal is best at vast iron coagulation, leaving low concentrations of dissolved iron in the effluent. This correlation of dissolved arsenic and iron was found in the reaction cell effluents and is depicted in Fig. 7, compiling data from the test periods 2c (baseline monitoring prior to H_2O_2 addition) and 4 – 6 (H_2O_2 addition at various dosage rates). Low concentrations of dissolved arsenic coincident with low concentrations of dissolved iron. This indicates extensive colloid and particle formation prior to flocculation filtration. Arsenic concentrations can be reliably reduced to values much below regulatory limits and incrustation of plant equipment downstream the sand filter can be prevented.

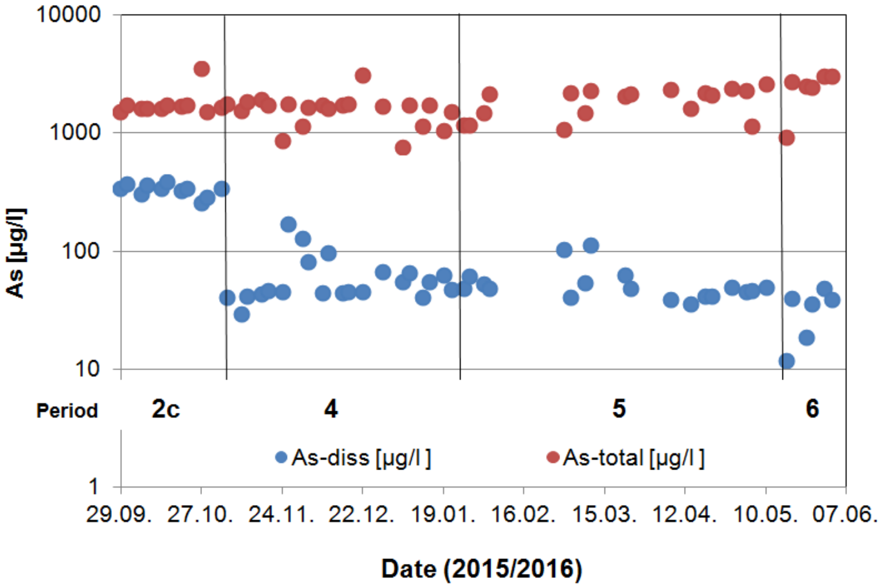

Figure 6 *Total and dissolved arsenic concentrations in reaction cell effluents (prior to filtration, m-241P) during test periods 2c (baseline monitoring prior to H_2O_2 dosage) and 4-6 (H_2O_2 dosage)*

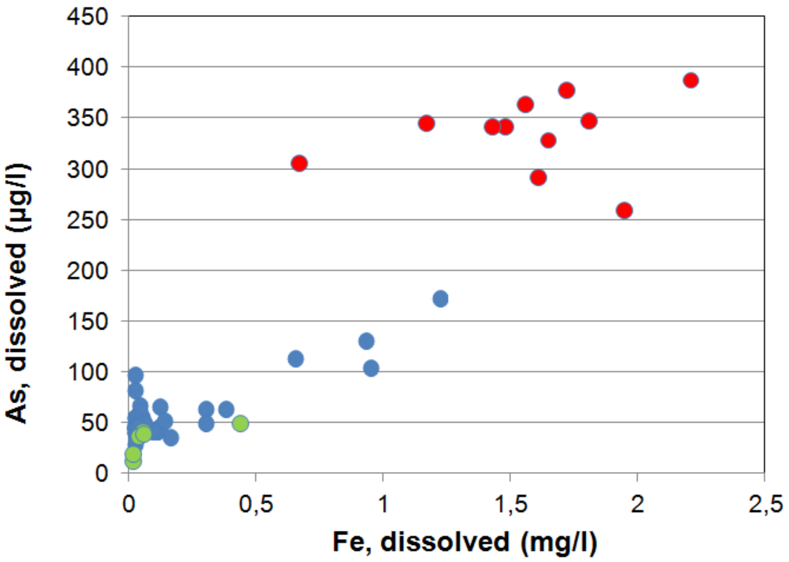

Figure 7 *Correlation of dissolved iron and arsenic concentrations in reaction cell effluents (m-241P) during test periods 2c (baseline monitoring prior to H_2O_2 dosage, red dots), 4-5 (H_2O_2 dosage, blue dots) and 6 (H_2O_2 dosage, green dots)*

Conclusions

The work clearly illustrates the optimization potential of water treatment operations by an approach based on chemical process analysis. The investigations carried out in lab and full scale revealed hydrogen peroxide pre-oxidation in combination with pH adjustment to pH ≤ 7 most effective in decreasing dissolved arsenic concentrations in the reduced mine water at Pöhla. The residual concentrations of dissolved arsenic in the coagulation cell effluent were diminished from 250-400 µg/l to < 50 µg/l by reducing the ferrous fraction of the total iron concentration from ~ 10 % to 1 - 2 %. Advanced chemical oxidation speeds up colloid coagulation preceding flocculation and results in a stable and substantially complete arsenic removal from reduced mine water. The findings of the study will be implemented into the regular long-term water treatment approach at the Pöhla mine site.

Acknowledgements

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Cadmium removal from real mine water by electrocoagulation

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Abstract

This study investigated Cd removal from real mine water by electrocoagulation and iron–stainless steel anode/cathode combinations as well as aluminum–stainless steel anode/cathode combinations. Parameters such as time, current density and the type of electrodes were investigated to optimize the electrocoagulation process. It was found that the current density has a direct effect on the cadmium removal. Specifically, Cd was removed better at 70 mA/cm^2 than at 10 mA/cm^2. In addition, the reaction time has a direct effect on the removal of Cd. By increasing the time, Cd was removed at higher removal rates compared to the beginning of the reaction.

On the other hand, it was understood that the type of electrodes has an influence on the removal of Cd. Specifically, Cd was removed much better by an iron–stainless steel anode/cathode combination than by an aluminum–stainless steel anode/cathode combination. The removal efficiency of the aluminum–stainless steel anode/cathode combination reached 82%, whereas the Cd removal efficiency by iron-stainless steel was 100% at 120 min of reaction and 70 mA/cm^2.

The best condition for Cd removal was therefore obtained by using an iron–stainless steel anode/cathode combination with a current density and reaction time of 70 mA/cm^2 and 120 min, respectively. Cd was removed by 100% with the aforementioned condition.

Key words: Electrocoagulation, Cd removal, real mine water

Introduction

Metal concentrations in water are considered hazardous as metals are not biodegradable (Vasudevan and Lakshmi, 2011). One of the hazardous metals in water courses is Cd (Vasudevan et al., 2010) as it is also considered as carcinogenic by the US Environmental Protection agency (Vasudevan and Lakshmi, 2011). It is released into water as a result of using phosphate fertilizers, pigments, alloys, welding and the pulp and mining industries (Vasudevan et al., 2010). The limitation for Cd in drinking water is set to 0.005 mgL^{-1} by the World Health Organization (WHO) (Vasudevan et al., 2010).

Cd in water can be removed by various methods, some of them being considered conventional such as electrochemical treatment, co-precipitation, reverse osmosis or coagulation (Vasudevan et al., 2010). Yet, physical and chemical treatment has several drawbacks. For example, chemical treatment of Cd is considered to be expensive and its sludge handling is problematic. On the other hand, physical methods are not always efficient and are expensive. Currently, electrocoagulation is known to be an effective method for removing Cd. It is a process which contains an anode and cathode, in which the anode dissolves in the water and water hydrolysis takes place (Vasudevan et al., 2010). One of the electrode combinations used in electrocoagulation are aluminum and iron, the latter being used as a sacrificial anode (Gatsios et al., 2015, Holt et al., 1999) and, in addition, it has been shown to be an effective treatment for reducing the chemical oxygen demand, oil and metal plating wastewater (Gatsios et al., 2015). Some of the advantages in electrocoagulation are its generally low cost, reduced sludge production and easy operate (Vasudevan et al., 2010).

The poly hydroxide and hydroxide complexes generated bond with the ions and deduce in coagulation (Vasudevan and Lakshmi, 2011). The following reactions display how electrocoagulation works on the anode and cathode (Liu et al., 2010).

Anode reaction:

$$\mathrm{M_{(s)}} \rightarrow \mathrm{M^{n+}_{(aq)}} + \mathrm{ne^-} \quad (1)$$

$$\mathrm{2H_2O_{(l)}} \rightarrow \mathrm{4H^+_{(aq)}} + \mathrm{O_{2(g)}} + \mathrm{4e^-} \quad (2)$$

Cathode reaction:

$$\mathrm{M^{n+}_{(aq)}} + \mathrm{ne^-} \rightarrow \mathrm{M_{(s)}} \quad (3)$$

$$\mathrm{2H_2O_{(l)}} + \mathrm{2e^-} \rightarrow \mathrm{2H_{2(g)}} + \mathrm{2OH^-} \quad (4)$$

The objective of this study was to investigate Cd removal on a laboratory scale from real mine water of the Pyhäsalmi mine, which is currently the deepest metal mine in Europe (Enqvist et al., 2005). The effect of current density, reaction time and type of electrode regarding the Cd removal was investigated.

Methods

The inter electrode distance was set to 0.5 cm to minimize the voltage drop. A direct current (GW INSTEK psp-405) with 0–5 A and 0–40 V, was applied for the experiments. Iron and aluminum were used as anodes, whereas stainless steel was used as cathode with the electrodes having dimension of 70 × 50 mm. The beaker was filled 500 mL of mine water in each experiment and the current density in each experiment was set to a predefined values. The water was stirred with a constant speed of 200 rpm via a magnetic stirrer (Figure 1).

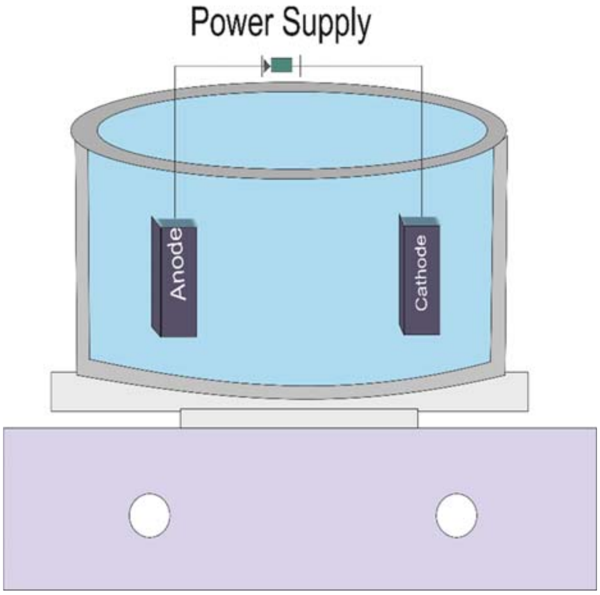


Figure 1. *Laboratory setup for electrocoagulation; monopolar electrode configuration, a stirrer and a DC electrical supply.*

The water was collected at the +500 m level in the Pyhäsalmi mine, which is located in Pyhäjärvi, Finland. All water samples were collected and stored in a freezer at a temperature of -20 °C and brought to ambient temperature immediately before each experiment. The redox-potential, electrical conductivity and pH were measured with Hach intelliCAL™ redox, electrical conductivity and pH probes connected to a Hach HQ40d (Table 1). All electrodes were rinsed before each experiment with 0.2 M HCl.

Table 1. *Cd concentration and other relevant parameters of the Pyhäsalmi mine water.*

Parameter	**Unit**	**Value**
pH (field)	–	2.86
Cd	mg/L	2.1
Electrical conductivity (field)	µS/cm	6968
Redox (corrected, field)	mV	467
Temperature (field)	°C	16.70

Cd concentrations were measured by ICP-OES (iCAP 6300, Thermo Electron Corporation) and the water samples filtered with a 25 mm syringe filter (0.2 µm cellulose acetate membrane), before each measurement. The Cd removal in each experiment was calculated using the following equation:

$$\text{Removal efficiency}, \% = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

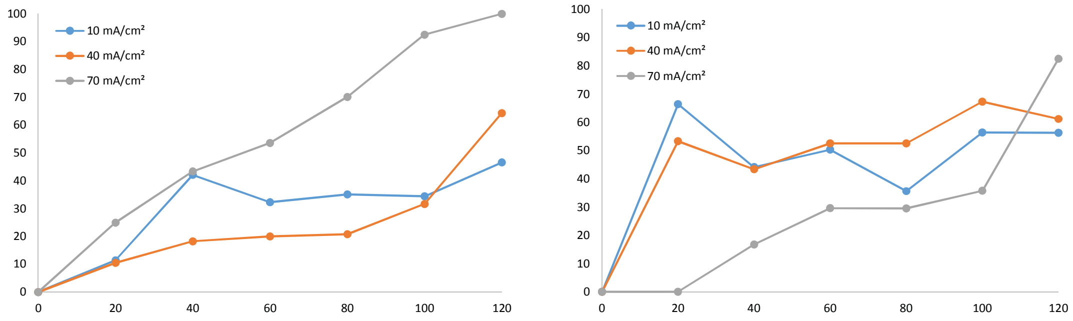
in which C_0 and C_t are the Cd concentration at 0 min and *t* min, subsequently.

It was shown that the current density has a direct effect on the Cd removal such that in increase in current density increases also the Cd removal. When the reaction time increases, the Cd removal efficiency also increases. This can be explained by the fact that with increasing time the release of the sacrificial anode as coagulant into water increases as well.

Cd removal was higher with the iron–stainless steel anode/cathode combination compared to the aluminum–stainless steel anode/cathode combination. It reached 46.6, 64.3 and 100% with the iron–stainless steel anode/cathode combination at 10, 40, 70 mA/cm^2, respectively. On the other hand, the aluminum–stainless steel anode/cathode combination removed 56.3, 61.2 and 82.4% Cd at 10, 40 and 70 mA/cm^2, respectively (Figure 2).

Cd removal reached its maximum at 70 mA/cm^2 and 120 min of reaction time with both aluminum and iron as anodes. It should be noted that the removal efficiency with an iron anode was better than with an aluminum anode.

The final Cd concentrations in the real mine water reached 1.85×10^{-5} mg/L and 0.01 mg/L with the iron–stainless steel anode/cathode combination and the aluminum-stainless steel anode/cathode combination, respectively. Therefore, Cd limits for drinking water can be met by using iron-stainless steel anode/cathode combinations.



(a)

(b)

Figure 2. *Effect of reaction time and the current density on the Cd removal by various electrode pairs, (a) iron–stainless steel and (b) aluminum–stainless steel.*

Conclusions

The results showed that a removal efficiency of 100% can be achieved by an iron–stainless steel anode/cathode combination with a current density of 70 mA/cm^2 and a reaction time of 120 min. It was found out that with increasing current density and reaction time, the Cd removal increases as well.

The final Cd concentrations in the mine water after removal were 1.85×10^{-5} mg/L and 0.01 mg/L with an iron–stainless steel and aluminum–stainless steel anode/cathode combination, respectively. It indicates that at least the Cd concentration in mine water can meet the standards for drinking water.

Acknowledgements

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Manganese removal from New Zealand coal mine drainage using limestone leaching beds

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Abstract

Limestone leaching beds can be utilised as passive treatment systems for oxidative removal of Mn(II) from mine drainage. Oxidation of Mn(II) by O_2 is kinetically inhibited at circumneutral pH, however it can be catalysed by Mn oxidising microorganisms and by mineral surfaces, particularly those of Mn oxides. Although limestone treatment can be effective, the mechanism of Mn removal is not well understood.

A series of six laboratory-scale reactors were built to determine the relative importance of microbial Mn oxidation and autocatalytic Mn oxidation in limestone leaching beds. Duplicate reactors were constructed using limestone, limestone with pyrolusite, and quartz (as a control). Acid mine drainage (AMD) containing 2 mg/L Mn, 0.3 mg/L Zn, and 0.08 mg/L Ni was collected from a stream on the West Coast of New Zealand. The ‘biotic’ set of reactors had AMD leaching through the rock bed, while AMD treated with biocide was percolated through the ‘abiotic’ reactors.

The limestone, and limestone with pyrolusite reactors removed Al and Mn from the AMD solution. Removal of Mn by limestone alone is minimal, and is enhanced by the presence of pyrolusite in a reactor. The most effective removal of Mn was achieved in the biotic limestone reactors, and microbial Mn (II) oxidation appears to be important for optimal removal of Mn from solution. Inoculating the limestone beds with pyrolusite boosted removal efficiency of the reactors. Pyrolusite addition to limestone beds could be considered if maximum Mn removal is required immediately, however once microbial communities are established any benefit will be negligible.

Keywords**:** coal mine drainage, limestone bed, manganese oxides

1. Introduction

Manganese (Mn) is a transition metal which occurs in several valence states in the environment. Mn is biochemically important as a trace element, but can become toxic and cause aesthetic effects in aquatic systems at high concentration. Therefore discharge of Mn to waterways is often regulated (ANZECC, 2000; Silva et al., 2010). Mn is a common component of acid mine drainage (AMD), and in AMD impacted streams on the West Coast of New Zealand, Mn concentrations range from 0.007 – 13 mg/L, up to four orders of magnitude above background levels (Pope, 2010).

Treatment of mine water for Mn removal can be performed via active or passive treatment systems. Active treatments typically utilize high pH and/or an oxidant to form solid $Mn(OH)_2$ or Mn(IV) oxides. Passive treatment systems include granite beds (Hedin et al., 2015), limestone beds (Tan et al., 2010), bacterially inoculated limestone beds , benthic and floating microbial and/or algal assemblages, and manganese removal aerated channels. The ‘Pyrolusite Process’ is a patented system developed by Vail and Riley (1995), where Mn bearing water flows through a Mn-oxidising bacteria inoculated limestone bed. In all of these systems, Mn removal is typically achieved through precipitation of sparingly soluble Mn oxides.

Oxidation of Mn(II) by O_2 is kinetically inhibited at circumneutral pH; however the reaction can be catalyzed by Mn oxidizing microorganisms, and by mineral surfaces (Diem and Stumm, 1984; Stumm and Morgan, 1996; Tebo et al., 2004). Bacteria and fungi species capable of Mn oxidation are widespread, and can accelerate oxidation rates in many environments (Spiro et al., 2009). Biotic Mn(II) oxidation may be caused by several processes: modification of pH and/or redox conditions, release of metabolites that chemically oxidise Mn(II), or production of polysaccharides or proteins that catalyse the reaction (Tebo et al., 2004). The primary products of microbial Mn(II) oxidation are poorly crystalline layered manganese oxides, with high surface area and Mn(IV) as the key Mn species. Mn oxidation can also be an autocatalytic process, and is abiotically catalyzed by Mn oxide surfaces. The surface hydroxyl groups on Mn oxide surfaces bind Mn(II) in inner sphere surface complexes ($(>SO)_2Mn$), which promote rapid oxidation (Diem and Stumm, 1984). As the reaction proceeds, the surface area of the Mn oxide increases, causing an increase in the heterogeneous reaction rate.

In this study an experiment was designed to assess the relative importance of abiotic, autocatalytic and biotic oxidation of Mn(II) in limestone leaching beds using acid mine drainage from the West Coast of New Zealand. Removal efficiencies of Mn and other contaminants are compared in reactors containing limestone, and limestone ‘seeded’ with pyrolusite to provide a Mn oxide surface for abiotic catalysis.

2. Materials and Methods

2.1. AMD collection and site description

The Island Block Coal Mine sits in the Victoria Range foothills on the West Coast of New Zealand. Coal from the Eocene Brunner Coal Measures sequence was intermittently extracted between 1962 and 2002. The coal is overlain by the Kaiata formation, consisting of marine mudstones and sandstones. Fanny Creek drains the eastern area of the mine, and is impacted by AMD drainage from a number of seeps in the waste rock. The AMD is derived from pyrite oxidation and mineral dissolution, similar to that in other Brunner Coal Measures deposits.

A comprehensive assessment of AMD characteristics was performed in the Fanny Creek catchment in 2008 (Mackenzie thesis). Drainage was typical of coal mines within the Brunner Coal measures, with low pH (2.5-4), elevated iron and aluminium concentrations, and high concentrations of trace elements (Pope et al. NZJGG 2010). For this study, AMD was collected from Fanny Creek on 3 occasions during the experiment, and stored in polyethylene containers. The first two batches of AMD were collected from the same location and had similar chemistry. An obstruction of the access track meant the final collection was from a different location in the creek, and metal concentrations were lower.

1.2 Experimental set-up

Six rectangular reactors were built using polymethyl methacrylate sheets, and polyvinyl chloride tubing (Fig. 1). The two control reactors were filled with 15.6 kg of 12-16 mm quartz pieces, and two limestone (LS) reactors were filled with 15.3 kg of 10 – 30 mm limestone chips. The final two limestone and pyrolusite (LS + PL) reactors were filled with 15.3 kg of 10 – 30 mm limestone chips, with 200 g of 5-13 mm pyrolusite grains mixed throughout. The ‘biotic’ set of reactors received AMD, and the ‘abiotic’ set received AMD treated with 1 mL/L biocide (B-AMD). The AMD percolated into one end of the reactors through two perforated pipes, and exited the other end of the reactor by the same method. The experiment began on the 28 August 2016. Flow rates for the first 3 weeks of operation varied between 2.5-4.5 mL/minute. From week 3 the target hydraulic residence time in the reactors was 2 days (1.5 – 2 mL/minute flow rate), and this was decreased to a one day residence time after 14 weeks of operation (2.3 – 4.2 mL/minute flow).

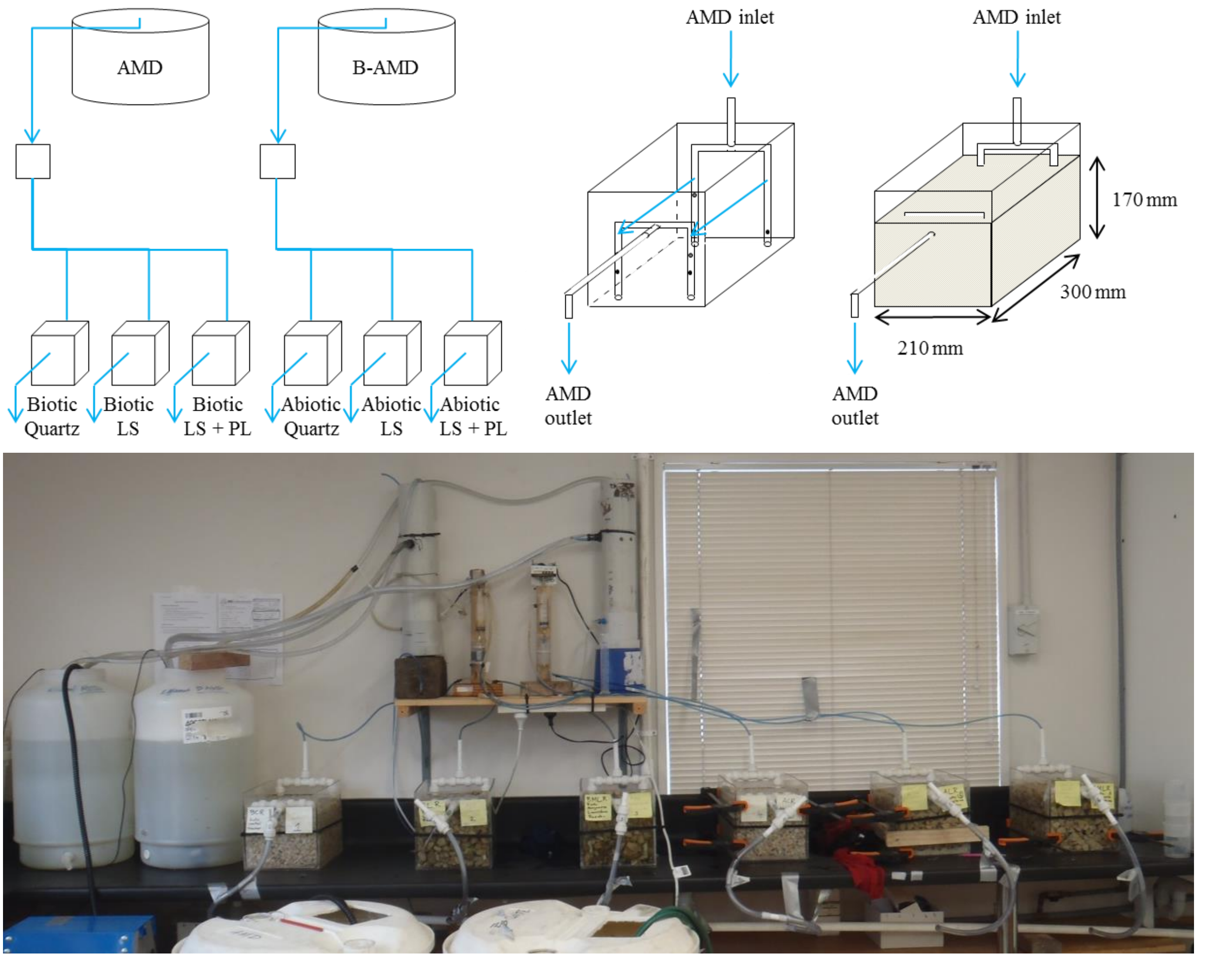

Figure 1 *Experimental set up. The reactors contain: A1. Quartz, A2. Limestone, A3. Limestone and pyrolusite, B1. Quartz, B2. Limestone, B3. Limestone and pyrolusite. Reactors 1-3 receive AMD, and reactors 4-6 receive bacteriocide treated AMD (B-AMD).*

1.3 Chemical analysis

Each week pH, dissolved oxygen and temperature were measured on the AMD and the reactor effluent, and samples were collected for alkalinity, dissolved metal, ammonia and major ion analysis. Meters used for measurements were calibrated on the day of use. Alkalinity was analysed by titration with 0.1 M HCl, metals were analysed by ICP-MS using the APHA method 3125 B. Major anions were analysed using the APHA ion chromatography method 4110 B.

Solubility modelling was performed using dissolved metal concentration data measured for the AMD and B-AMD solutions, together with the major ion data and pH measured in the reactors. These were entered into Visual MINTEQ 3.1 in order to predict which minerals may become saturated due to the changes in pH and major ion chemistry in the reactors.

3. Results and Discussion

3.1 Mine water chemistry

The four reactors containing limestone altered the pH, major ion and metal chemistry of the mine drainage water, while the quartz reactors had very little influence on the water chemistry. The influent water had pH of 4.3 – 4.9 and sulphate concentrations of 140 – 200 mg/L (Table 1). Metal concentrations were elevated, with Mn (2 mg/L), Ni (0.08 mg/L) and Zn (0.3 mg/L) concentrations exceeding trigger value guidelines for the protection of freshwater species (ANZECC, 2000). Concentrations of Fe were below 0.2 mg/L, and Al concentrations varied from 1.5 – 2.7 mg/L.

Water treated by the LS and LS + PL reactors had higher pH and alkalinity than the influent water. In the first three weeks of the experiment effluent pH was 6.9 – 7.2, after which the pH of the treated water remained between 7.3 and 7.8. Water pH was largely unchanged by the quartz reactors. The AMD and BAMD were oxygenated, and contained between 5 – 11 mg/L O_2. There was typically little difference between dissolved oxygen concentrations in the influent and effluent water of the reactors.

3.2 Biotic Mn removal

Manganese was removed from solution in both the LS and the LS + PL reactors (Fig. 2). No significant removal of metals occurred in the control quartz reactors. In the initial stages of the experiment, removal efficiencies were approximately 50 % in the biotic LS reactor, and 70 % in the biotic LS + PL reactor. After six weeks, Mn removal increased in both of the biotic reactors, to achieve nearly 100 % Mn removal by the ninth week of operation. The increased removal in the biotic reactors relative to the abiotic reactors is consistent with the presence of Mn oxidising microorganisms in the biotic reactors. The increase in removal efficiency in the biotic reactors after 6 weeks operation is likely due to growth of the population of organisms oxidising Mn(II). Both the biotic LS, and LS + PL reactors showed a slight decrease in removal efficiency when the flow rate was doubled, however this quickly recovered and it is likely this was due to a further increase in the population of Mn(II) oxidising organisms. There was a slight decrease in removal efficiency of the biotic LS + PL reactor in the final two weeks of the experiment, which is due to failure of the flow rate regulator.

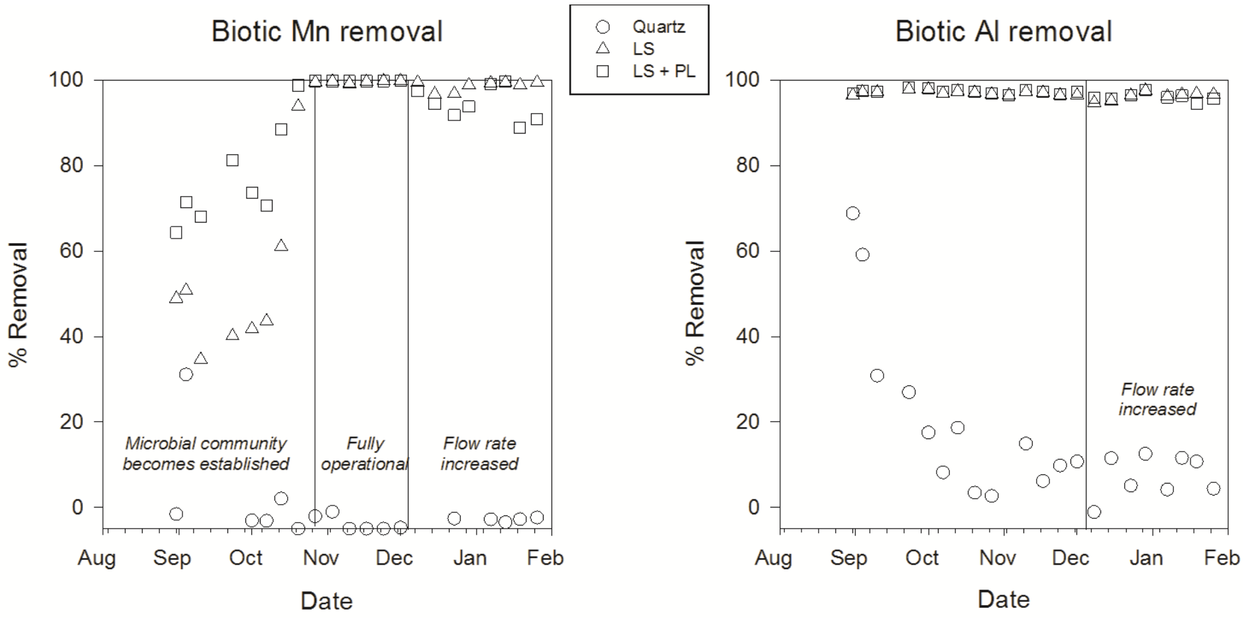

Figure 2 *The percent of influent Mn and Al that was removed from solution in the biotic reactors.*

The two biotic LS and LS + PL reactors became darker over the time period of the experiment (Fig. 3.). The black precipitates formed were interpreted to be Mn oxides. This precipitate is typically present as a coating on the limestone rocks, with some floc in the interstitial spaces between the limestone rocks. The macroscopic characteristics are consistent with manganese oxide coatings described in limestone leaching beds treating AMD (Tan et al., 2010), and the Mn oxides formed on granite beds (Hedin et al., 2015). However microscopic and mineralogical analysis is required to determine the minerals being formed. The areas of black precipitate were concentrated near the surface of the inlet end of the reactors, after the zone of white precipitate. The concentration of Mn oxide near the surface is likely due to preferential flow of AMD over the surface of the reactors. This is a function of the reactor design and could be altered so the inflow is at the base of the reactor, rather than several holes in the pipe at different lengths. It is also possible that dissolved oxygen concentrations near the reactor surface promote Mn oxidation, however the oxygen concentration in the outlet water is similar to the inlet concentration, an *in situ* oxygen profile would be required to investigate this.

3.3 Abiotic Mn Removal

Manganese removal was different in each of the four LS and LS + PL reactors, and also showed variations with time (Fig. 3.). The reactors that contained pyrolusite demonstrated increased Mn removal relative to the LS reactors in the initial stages of the experiment, and the biotic reactors showed more Mn removal than the abiotic reactors. The greater removal efficiency of the reactor containing pyrolusite is attributed to an abiotic, autocatalytic oxidation of Mn(II) on the surface of the pyrolusite grains.

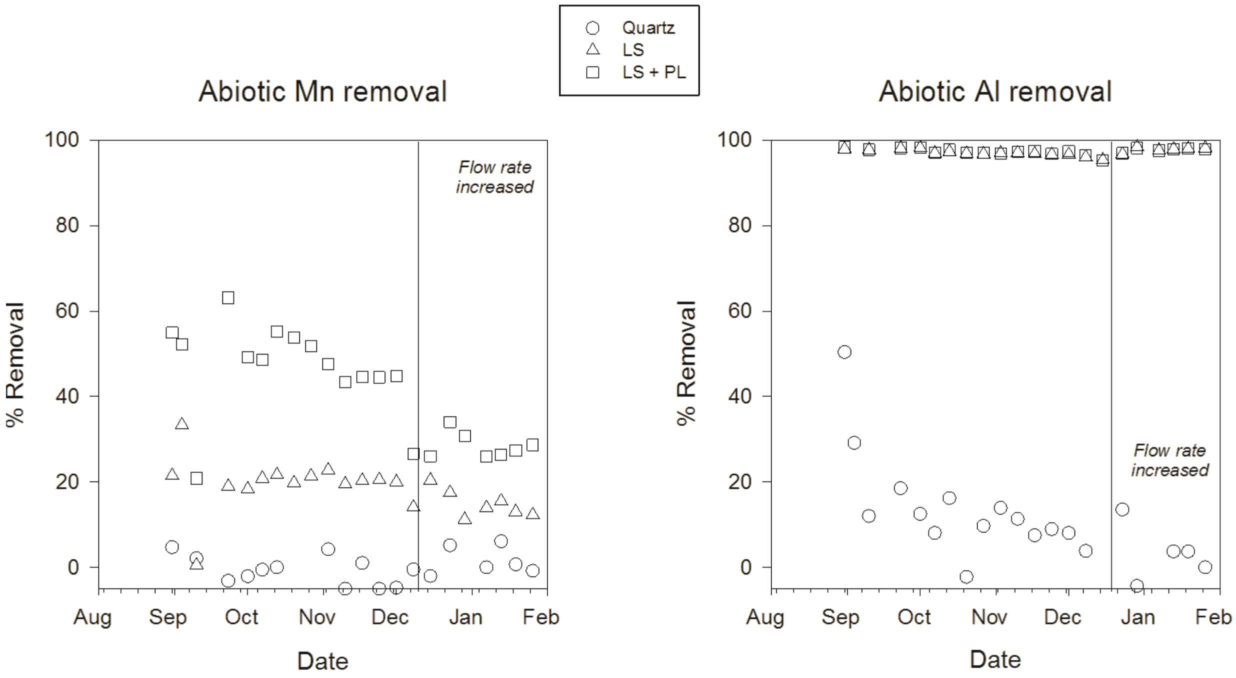

Figure 3 *The percent of influent Mn and Al that was removed from solution in the biotic reactors.*

The Mn removal efficiency of the abiotic LS reactor was fairly constant over the course of the experiment. Geochemical modelling suggests a slight oversaturation of the B-AMD with respect to rhodochrosite (a manganese carbonate) when treated with limestone. However; pyrolusite remains below saturation in these conditions. In spite of this, the black coatings on some of the limestone chips suggest Mn is being removed as an oxide. The removal that is occurring in the abiotic LS reactor may be a purely pH driven solubility effect. The nearly constant removal efficiency in this reactor despite flow rate changes supports this hypothesis. As the removal rates in these reactors did not increase over time, it is evident that Mn minerals forming *in situ* do not act as catalysts and enhance the rate of Mn removal. The % Mn removal achieved in the LS + PL reactor decreased when the flow rate was doubled. This effect of residence time on Mn removal in the abiotic LS + PL reactor suggests the rate of Mn oxidation by pyrolusite constrains removal efficiency. Therefore longer residence times, and perhaps a greater ratio of pyrolusite to limestone in the reactor may increase Mn removal in this system.

***Figure 4** Reactors after 19 weeks of operation. Flow direction is from left to right.*

3.4 Al Removal

From the first week of the experiment Al removal was close to 100 % in both the biotic and abiotic systems (Fig 2, 3). Solubility modeling demonstrated the solution becomes saturated with respect to several aluminum phases, including gibbsite, alunite, and amorphous $Al(OH)_3$. A white floc was observed near the inlet of the reactors from the initial weeks of the experiment, which spread further into the reactors over the course of the experiment (Fig 3). Precipitation of Al hydroxides, oxides, and hydroxyl sulfates is common in AMD solutions that become neutralized (Lottermoser, 2010; Pope and Trumm, 2014). The removal of Al by the reactors is therefore an example of metal removal due to pH driven solubility changes.

4.0 Conclusions

The reactors containing limestone were effective in raising the pH of the AMD solutions, and removing Al and Mn from solution. It is likely that Mn is being removed as an oxide, which is supported by black precipitates forming in the reactors. The addition of pyrolusite enhanced removal of Mn from solution, however it appears that Mn oxides forming in the abiotic limestone reactor do not further catalyse Mn oxidation. Microbial oxidation is the major process that removes Mn(II) from solution in limestone leaching bed treatment systems, and the population of Mn oxidising organisms can grow to accommodate increased Mn loads. The enhanced removal due to inclusion of pyrolusite in the biotic reactors was minor once microbial populations developed in the limestone reactor. The reactors were not run to failure, however a maximum rate of Mn(II) oxidation by microbes in the system could be measured in this way. Further research will identify the Mn minerals that are forming in the reactors and identify the microbial communities that have developed.

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Development of a low-tech treatment for neutral mine water – a case study

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Abstract

Lovisagruvan is a Pb-Zn-Ag mine in mid-south Sweden, with a yearly production of some 40 000 tons. There are four main levels in the mine: 55, 105, 145 and 190 m below ground. Water is continously pumped at a rate of 5 m^3/h, passing sedimentation pools at each of the four main levels in the mine and finally one above ground. A modified backfill mining is used and in order to visually separate the ore from the waste rock limestone is used as a separating layer. Limestone addition in combination with non-acid producing mineralisation generates a pH-neutral mine water. For many years the mine has had problems with high levels of zinc and lead in the mine water released to recipient. The primary contaminants, lead and zinc, were mainly found as particles or associated to particles. With a combination of several measures including a sandfilter and $FeSO_4$ addition suspended matter was reduced 93 %, lead 91 % and zinc 71 %.

Key words: sand filter, sedimentation, iron hydroxides, lead, zinc

Introduction

Lovisagruvan is a mine located in mid Sweden where sulfide ore (Pb-Zn-Ag) has been mined since 2004. The ore consists almost only of galena (PbS) and sphalerite (ZnS). Every year around 40 000 tons of rock (containing 50 % ore) is mined. Ore is being crushed at the mine site prior to being transported for enrichment off site. There is thus no tailings produced at the mine site. No acid producing minerals are found in the mine and original mine water is therefore near neutral. During the mining operation crushed lime stone is used to separate ore and waste rock when loading the ore on mine trucks. This results in a near neutral or slightly alkaline mine water. Water is pumped up from the mine at a rate of 5 m^3/h and is first collected in four sedimentation pools underground (at 190 m, 145 m, 105 m and 55 m below the surface) before it is pumped to a sedimentation pool above ground with a three days turnaround time. Before 2013, surface water from the sedimentation pool above ground was then released to the recipient. Mine water pumped from Lovisagruvan has a near neutral to slightly alkaline pH (7-8) and is mainly contaminated with lead (530 µg/L) and zinc (1.4 mg/L). Investigations prior to 2011 had shown that the water treatment facility at that time did not lower the heavy metal content enough and it was clear that the water needed further treatment. Filtration studies on the mine water had also shown that the major part of the contaminants in the water were associated to particles (mainly as sulphides). The particulate fraction was in early stages of water treatment development around 76 and 82 % for lead and zinc, respectively. Later, more lead and zinc have been found in the dissolved fraction.

Material and methods

Stepwise development

In order to improve the water quality a stepwise approach was used. Steps are summarized in tab. 1.

Step 1 and 2 – 2011

In spring 2011 a more extensive sampling program than what earlier had been present was initiated. This included thorough analysis of parameters, physical and chemical, with potential of having negative impact on the mine water quality. After some months of frequent sampling and measuring of water quality in the sedimentation pool above ground, a pattern of high metal concentrations was found, clearly coinciding with week days when the primary crusher was active. Hence, the first action taken, in spring 2011, was to install a roof on the sedimentation pool above ground in order to keep metal containing dust from entering the pool. Lastly, the primary crusher was also moved from the proximity of the sedimentation pool in autumn 2011.

Table 1 *Changes done to the dewatering and water treatment facility at the Lovisagruvan mine.*

Step	Time	Performed change
1	2011 Spring	Installation of roof on the sedimentation pool
2	2011 Autumn	Moving of the primary crusher
3	2013 October	Sand filter installed
4	2014 March	Change of filter sand
5	2014 October	Pumping between underground pools changed in order to minimize resuspension
6	2014 October	Addition of $FeSO_4$ started
7	2015 Spring	Addition of NaOH started

Step 3 – 2012 & 2013

With metal concentrations still exceeding recommended levels it was proposed to install a passive sand filter based on a nearby magnetite tailings material. Long term tests using the magnetite tailings were performed primarily to study removal of particulate contaminants from the mine water (Fahlqvist et al. 2012). Water from the mine was pumped from the sedimentation pool above ground into a 1 m^3 container and transported to the laboratory. Water was pumped from the container to the columns at a rate of approximately 20 L/day. Total volumes through the columns were 1 300-1 600 L.

Initially the filtration increased the pH but as more water passed the values decreased to about the same as for the untreated mine water (pH 8.04).

Both zinc and lead concentrations decreased when passing through the columns, indicating that physical filtration was the dominating process. Lead concentrations were lowered with 97.5 % and zinc with 99.7 % (Fig. **1**). Trace metal removal was higher in all columns compared to filtration through polycarbonate filters with an exact pore size. This indicated that also some adsorption occurred in the columns.

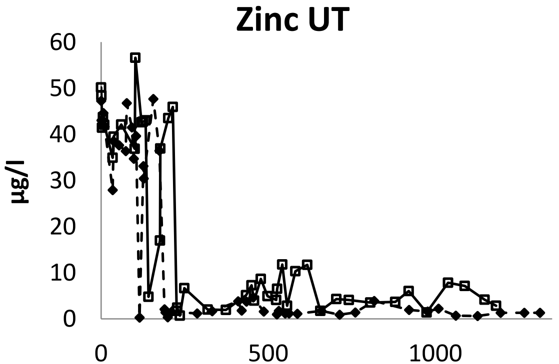


Figure 1a *Zn in water filtered through the magnetite filter (Zn concentration in ingoing water: 690 µg/L).*

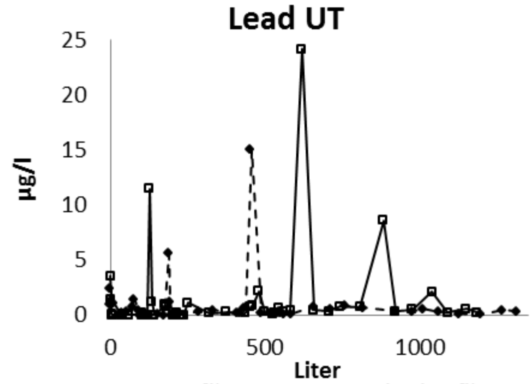


Figure 1b *Pb in water filtered through the magnetite filter (Pb concentration in ingoing water: 370 µg/L).*

In addition to column testing of the magnetite tailings from Stråssa, also 1 m^3-filters were built on site at Lovisagruvan. These filters were in operation during one year and showed positive results, indicating the magnetite tailings would be a good choice for full-scale trials. Therefore, from the positive results from both the pilot scale test and the column test (Fahlqvist et al. 2012) it was decided to construct a full scale filter to remove particulate metals from the mine water using the magnetite tailings.

In October 2013, a full-scale filter was ready to be taken in operation. The filter basin was divided into two subfilters in order to be able to run different filter materials and change the filter media without having to shut the filter down or by pass it. Volume for treatment in each subfilter was around 45 m^3.

Step 4 – Spring 2014

In full scale it was, however, quickly noted that the grain size distribution of the magnetite tailings made the filters to clog due to the presence of small grain sizes. It was decided to change to a graded natural filter sand instead to improve the hydraulic properties of the filter.

Step 5 – Autumn 2014

As a result of water quality measurements in the underground sedimentation pools it became apparent that metal concentrations increased from the lowest to the highest underground level, as a result of resuspended contaminants in water entering the 145 level through gravity. Therefore, pumping between underground pools changed in order to minimize resuspension (Fig. **3**).

Step 6 – October 2014

In order to increase the amount of adsorption surfaces in the sand filter (Benjamin et al. 1996) it was decided to start adding $FeSO_4$ solution to the pool 55 m below the surface. A very simple dosing system was designed based on an intermediate bulk container (IBC) and a small dosing pump. $FeSO_4$ solution in the IBC is prepared 1-2 times each month.

Addition of $FeSO_4$, however, made the pH to drop from around 8.1 to around 7.8, thus increasing the zinc concentrations.

Step 7 – Spring 2015

In order to increase pH to around original levels it was decided to start adding NaOH to the pool 55 m below surface. Experiments in the laboratory were therefore set up, with the purpose of optimizing the amount of $FeSO_4$ and NaOH to be added to the mine water in order to lower concentrations of primarily zinc (Fig. **2**).

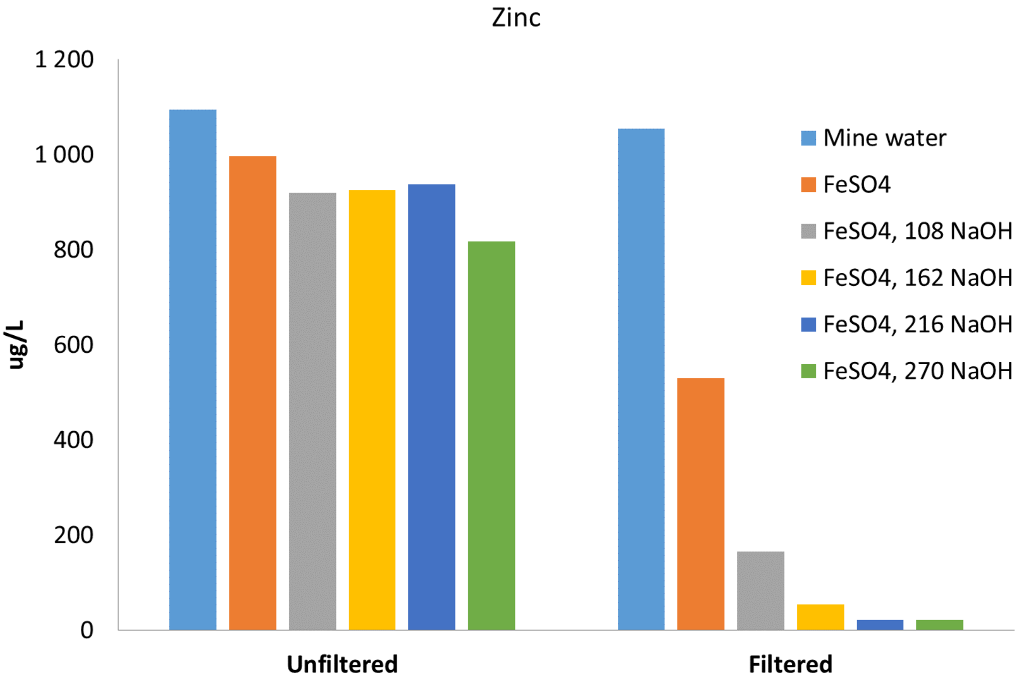


Figure 2 *Optimization of $FeSO_4$ and NaOH addition to mine water at the pool 55 m below surface.*

An outline of the mine water treatment presently working at Lovisagruvan is presented in Fig. **3**. Water is pumped through four sedimentation pools below ground, and water that may contain resuspended contaminants at level 145 is re-circulated down to level 190. Addition of $FeSO_4$ and NaOH is performed at level 55 meters below ground. The sedimentation pool above ground is followed by a passive sand filter. Contaminated sand from the filter as well as iron(oxy)hydroxide sludge are backfilled in the mine.

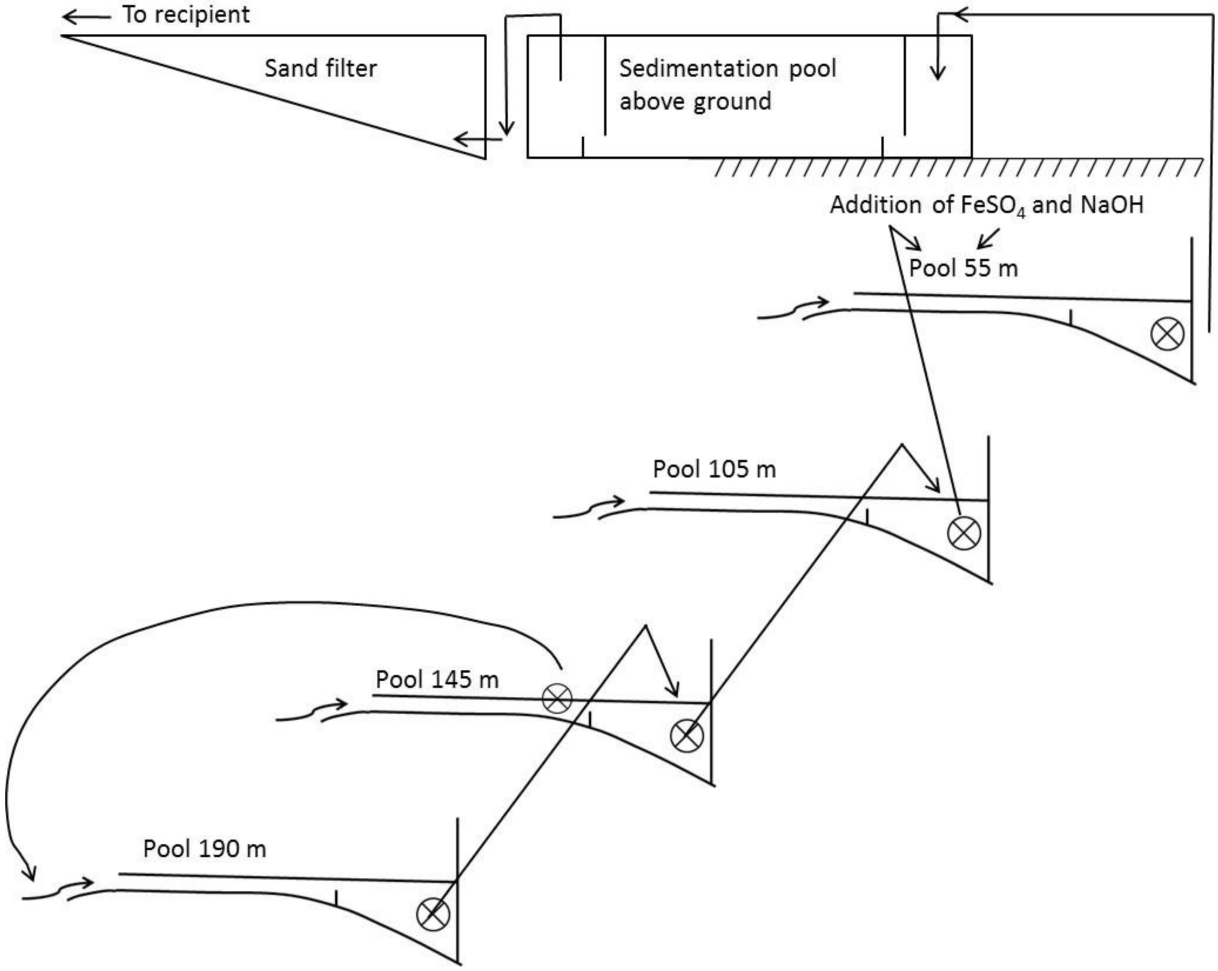
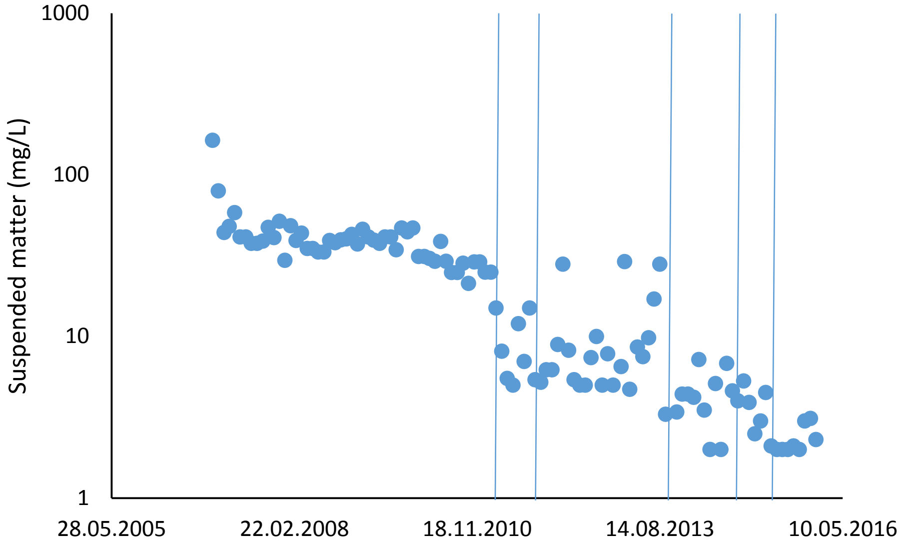


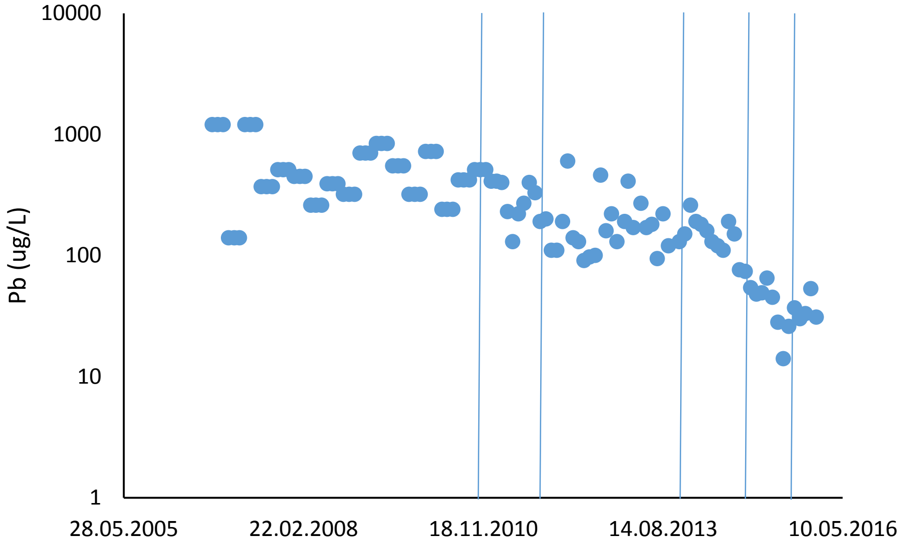
Figure 3 *Principal layout of the dewatering and water treatment systems at Lovisagruvan, Sweden.*

Results and discussion

Concentrations of suspended matter, lead and zinc from the mine are shown in Fig. **4**. It is obvious that shielding the above ground sedimentation pool from the primary crusher (Step 1 and Step 2) reduced the concentrations of primarily suspended matter, but also reduced the concentrations of lead and zinc. Prior to shielding the sedimentation pool the average concentration of suspended matter was 40 mg/L compared to on average below 9 mg/L after (tab. 2). Lead and zinc concentrations also decreased significantly as would be expected if the deposition of ore particles to the sedimentation pool is reduced.

Passive treatment in Step 3, intended to use gravity to separate particles with lead and zinc followed by a sand filter for further removal. This step reduced the suspended matter with around 50 %, while the metal concentrations only decreased with around 25 % (tab. 2). At the end of October 2014 (Step 6) iron sulfate ($FeSO_4$) started to be added in the upper most sedimentation pool below ground (55 m). The goal was to achieve iron(oxy)hydroxide surfaces for sorption of metals. As precipitation of iron hydroxide is an acid producing reaction, pH decreased slightly during Step 6 (from around 8.2 to around 7.8). Concentrations of lead decreased significantly due to increased sorption onto formed iron hydroxides, but for zinc, being more pH-sensitive, concentrations increased slightly during this step. This phenomena has been observed earlier for zinc in mining water at around pH 7 (Bäckström and Sartz 2011). In order to increase sorption of especially zinc, sodium hydroxide was added together with the iron sulfate in the spring of 2015 (Step 7) – bringing concentrations of lead and zinc to acceptable levels.





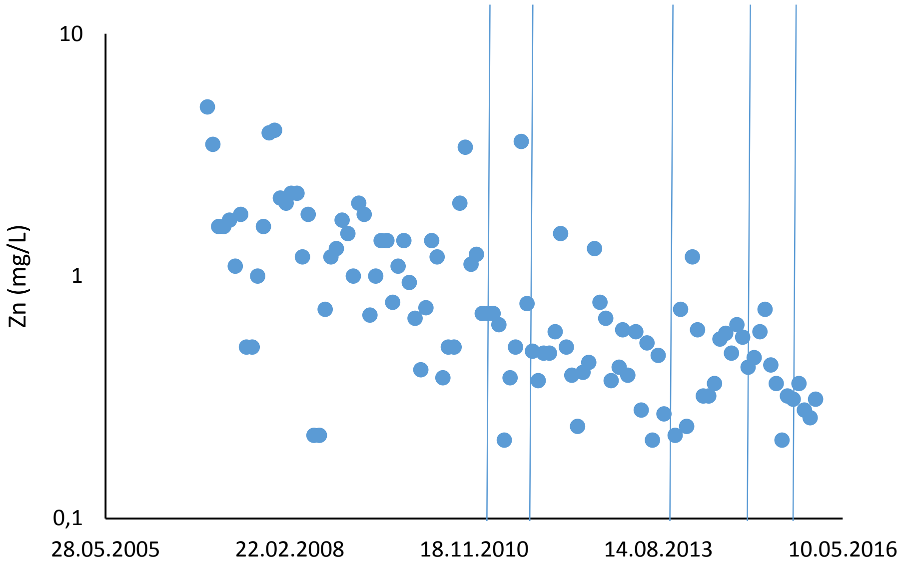


Figure 4 *Suspended matter (mg/L), lead (µg/L) and zinc (mg/L) concentrations during development of the water treatment (2006-2015) at Lovisagruvan, Sweden. Blue lines indicate Step 1, Step 2, Step 3, Step 5/6 and Step 7.*

Table 2 *Average suspended matter, lead and zinc concentrations during different periods of the water treatment development.*

Period		Suspended matter (mg/L)	Pb (µg/L)	Zn (mg/L)
Prior to Step 1	n 52	40	530	1.4
Between Step 1-Step 3	n 30	9.5	210	0.63
Between Step 3-Step 6	n 10	4.3	160	0.51
After Step 6	n 17	3.0	50	0.42

Conclusions

A stepwise approach towards mining water contamination using simple techniques reduced the concentrations of suspended matter 93 %, lead 91 % and zinc 71 %. This low-tech system has proven to be a good solution for Lovisagruvan. It is easy to handle and can without difficulty be managed by one of the mine workers. It is very robust and it is easy to find and fix any problems that may occur.

Acknowledgements

Thanks to Lovisagruvan AB for giving us the opportunity to present the case.

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Nitrate reduction in real mine water using zero-valent iron (ZVI) and iron waste

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Abstract

Nitrate is present in blasting agents used by the mining industry and thus can contaminate mine water. Despite several methodologies that have been applied for the removal of nitrate, many approaches produce harmful by-products such as nitrite, and other technologies have disadvantages, such as the high energetic costs and high biomass production.

In this study, the three iron sources (ZVI) iron nanoparticles, iron powder and iron waste from a mold industry were used for the reduction of nitrates from mine water. By performing a pH and iron dosages optimization with iron powder, pH 2 showed to be the only pH capable of reducing nitrate from a range of 2 to 4. The use of 4 g/L and 20 g/L of iron nanoparticles and iron powder, respectively, reduced nitrate completely in 180 and 270 min. The iron waste tested reduced 53% and 44% for washed and unwashed iron surface of the waste, respectively, showing that the waste does not have many impurities that could affect the experiment. In spite of the surface area being determinant for choosing the load of iron and for showing the kinetics of the reaction, it proved that the type of by-product formed at the end of the chemical reduction of nitrate is not relevant. The main by-product generated was NH_4^+ and < 7% of NO_2^- was produced.

The iron waste showed to be an interesting source of iron for this environmental application. This is true not only from an economical point of view but as a greener approach since a waste is used as a raw material instead of promoting the production of other materials for mine water remediation.

Key words: nitrate, zero-valent iron, iron waste, real mine water

Introduction

Eutrophication and Methemoglobinemia are some of the main concerns related to the existence of nitrogenous compounds in water (Rocca et al., 2007). Mine water has been polluted with nitrogenous species because the mining industry blasting agents composed of ammonium nitrate fuel oil (ANFO). Part of the detonated explosives is leached into the water, increasing the concentrations of nitrate, NO_3^-, and ammonia or ammonium, NH_3/NH_4^+ (Gusek and Figuera, 2009). Around 300 mg/L of NO_3^- can be found in mine waters; nevertheless there is a lack of regulations regarding mine water discharge into water courses (Häyrynen et al., 2009).

Nitrate removal technologies include biological approaches (Koren et al., 2000), ion exchange resins (Hekmatzadeh et al., 2013), membrane processes (Häyrynen et al., 2009) and more recently electrochemical methods (Govindan et al., 2015). However, these methods still have some drawbacks like the elevated biomass production in the biological methods, high costs and membrane fouling in membrane processes. The main difficulty regarding the electrochemical approach is related to the production of by-products such as nitrite, NO_2^-, with a high toxicity associated and some ammonia, NH_3.

Iron in the metallic form, Fe^0, very well known as zero-valent iron (ZVI), can be employed for the removal of various contaminants such as metals, dyes or chlorinated compounds. Permeable reactive barriers (PRBs) are used for *in-situ* treatments with high efficiencies for pollutants removal. ZVI can be synthesized by chemical precipitation with $NaBH_4$ or by using polyphenols from prolyphenol rich media (e.g. tea extracts), between several other methodologies. This technology is simple and effective for several applications due to high reactivity in reducing species, like NO_3^-.

The aim of the present study was to use three types of ZVI for the NO_3^- reduction of mine water: iron nanoparticles, iron powder and an iron waste from a mold industry. Thus, it will be ascertained if a waste can be used for the depollution of mine water contaminated with NO_3^-.

Methods

Samples were taken from a phosphate mine located in the center of Finland. The water was analyzed on site regarding pH (intelliCAL™ pHC101 probe), redox potential (intelliCAL™ REDOX MTC101 probe) and electrical conductivity (intelliCAL™ CDC401 probe); all measured with a Hach HQ40d handheld device. Other parameters were measured in a commercial laboratory, Ramboll Analytics (Table 1). Three types of ZVI were used for NO_3^- reduction: commercial iron nanoparticles used as a slurry (Nanofer Star product; Fe^n) from NanoIron, s.r.o.; iron powder, -325 mesh (Fe^p) and iron waste from a mold industry (Fe^w). Parameters such as pH and ZVI dosage were optimized using Fe^p as a first approach. Thus, the experiments were performed in a 500 mL closed reactor under stirring conditions with an incubator shaker (IKA KS 4000 I control) where mine water was previously degassed with N_2. Initial pH ranges tested were 2, 3 and 4, and Fe^p was tested in different dosages (0.8 g – 8 g), during 3 h of reaction time, where samples were taken during time and filtered (cellulose acetate membrane, 0.2 μm). The other two types of ZVI were used as a final step for comparison purposes.

The three sources of iron were analyzed for their BET surface area (Brunauer-Emmett-Teller specific surface area) by a Micromeritics, Gemini V device. Iron nanoparticles were observed by transmission electron microscopy (TEM), with a HT7700 120 kV High-Contrast/High-Resolution Digital TEM. The nanoparticles were sonicated for 30 min after the addition of ethanol and 1-buthanol before being placed in the TEM grid.

Table 1 *Parameters analyzed in the mine water (October 2014). Values measured in mg/L and redox potential was corrected to the SHE. EC: electrical conductivity.*

Parameter	Result	Parameter	Result	Parameter	Result
pH_{field}	7.80	Mg^{2+}	19	Hg	< 0.0001
EC (μS/cm)	1057	Ca^{2+}	100	Co	0.00077
Redox (mV)	427	K^+	65	Cr	< 0.001
Fe_{Total}	0.036	Na^+	76	Cu	< 0.001
N_{Total}	36	Cl	30	Pb	< 0.0005
NH_4^+	0.00645	F	1.10	Mn	0.015
NO_3^-	160	Al	< 0.01	Ni	< 0.001
NO_2^-	0.067	As	< 0.001	Si	5.60
PO_4^{3-}	0.030	Ba	0.091	Zn	< 0.005
SO_4^{2-}	200	Cs	< 0.001	U	0.0068

pH optimization

An initial pH range of 2 – 4 was chosen to react with Fe^p, since it has been proven that acidic cleaning of the ZVI surface avoids an oxide layer to be formed around the metallic Fe^0-core. When the pH increases, the oxide coating formed is no longer dissolved and the shell of oxides will remain on the surface of ZVI, decreasing the efficiency of the chemical reduction (Huang and Zhang, 2004; Yang and Lee, 2005). After the pH adjustment, this parameter was not controlled any more. The pH showed to be a critical parameter, since the reduction of NO_3^- requires very acid conditions of pH 2 (Figure 1) in order to obtain a decrease of NO_3^- from 160 mg/L to 86.5 mg/L during the firsts 5 min of reaction. After 180 min, the efficiency of NO_3^--reduction reached 0.4 mg/L (99.7% of reduction). However, at the initial pH values of 3 and 4, the effect of pH on the NO_3^--reduction was almost negligible. This result might possibly be associated with the fast increase of pH during the reaction, due to the production of OH^--ions (Eq. 1), also promoting the formation of FeO in the surface of the ZVI (Choe et al., 2004; Yang and Lee, 2005), since the pH increased up to 7.3 and 9.0 when the initial one was at 3 and 4, respectively.

$$4\,Fe^0 + NO_3^- + 7\,H_2O \rightarrow 4\,Fe^{2+} + NH_4^+ + 10\,OH^- \qquad (1)$$

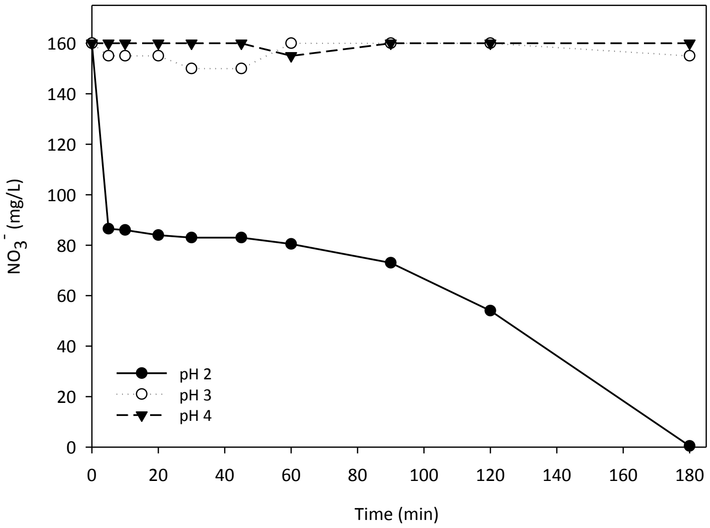

Figure 1 *Influence of pH in nitrate reduction in mine water (4 g/L of Fe^p, pH range tested: 2, 3 and 4).*

Optimization of the ZVI dosage

Dosages of 2, 4, 10 and 20 g/L of Fe^p were used for the NO_3^--reduction in mine water for 270 min (Figure 2). The use of higher dosages of ZVI in an acid medium at pH 2 showed to have lower NO_3^--concentrations at the end of the reduction reaction. An almost complete reduction (99.9% of NO_3^--reduction) was obtained with 10 g/L after 180 min and 20 g/L after 270 min. On the contrary, with 2 g/L, less ZVI was accessible for the chemical reduction, leading to 34.0 mg/L of NO_3^- (78.8% of NO_3^--reduction).

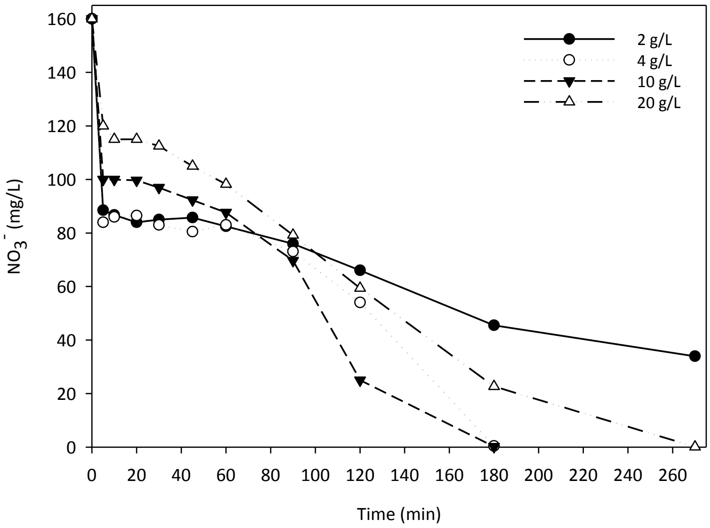

Figure 2 *Influence of the Fe^p dosage in mine water at pH 2.*

Fe^n and Fe^w as alternative metallic iron sources

Fe^n morphology was observed by TEM (Figure 3a), where the nanoparticles showed to be rearranged in chains with spherical clusters, with a diameter range of 73.2 – 169.0 nm. The average diameter of Fe^n was 119.4 nm, but despite the high aggregation of the nanoparticles, several studies seem to indicate that it does not decrease their reactivity as the high porosity is not affected (Hwang et al., 2011). Fe^n proved to have a higher surface area (27.7 m^2/g) when compared with Fe^p (0.3 m^2/g). Thus, the dosage used for the NO_3^--reduction at pH 2 for 180 min with Fe^n was lower (2 and 4 g/L) than the one used with Fe^p (Figure 3b). Using 2 g/L and 4 g/L of Fe^n is enough to obtain concentrations of NO_3^- of 73.0 mg/L and 2.60 mg/L, respectively, in 90 min. At 180 min, all NO_3^- was completely reduced with 2 and 4 g/L of Fe^n.

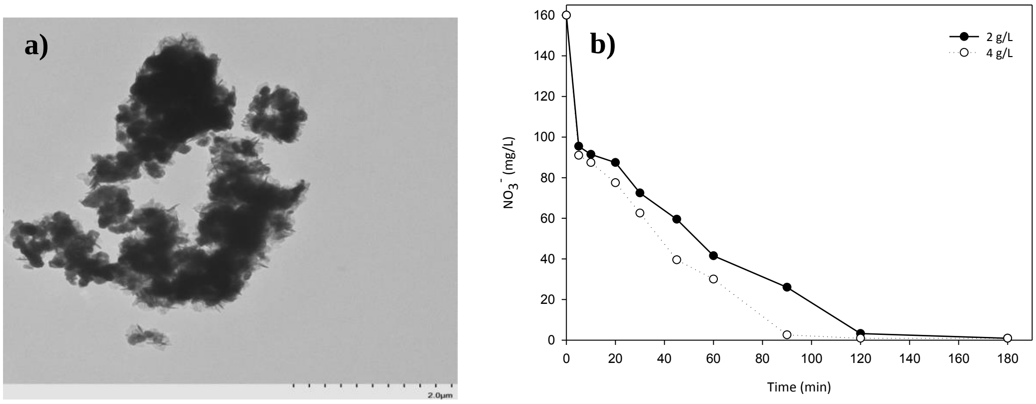

Figure 3 *Iron nanoparticles, Fe^n: a) TEM image; b) NO_3^- reduction with Fe^n (2 and 4 g/L, pH 2).*

The same reaction was performed with Fe^w; this time with higher dosages of ZVI due to the low surface area (≈ 0 m^2/g): 4, 10 and 20 g/L at pH 2 for 48 h, both with washed and unwashed Fe^w (Figure 4). After 1440 min (24 h) reaction time, 20 g/L was the best dosage of unwashed Fe^w achieved 95.0 mg/L of NO_3^-. Similar results were obtained at 2880 min (48 h), with 93.5 mg/L of NO_3^- (41.6% of reduction), indicating that the reaction kinetic is slower compared to Fe^n or Fe^p. By doing a surface washing with oxalic acid (0.2 M), the surface of the Fe^w did not appear to have major impurities that prejudiced the chemical reduction since the value obtained with the surface washing, was 75.3 mg/L of NO_3^-, representing a 52.9% reduction (11.3% of difference).

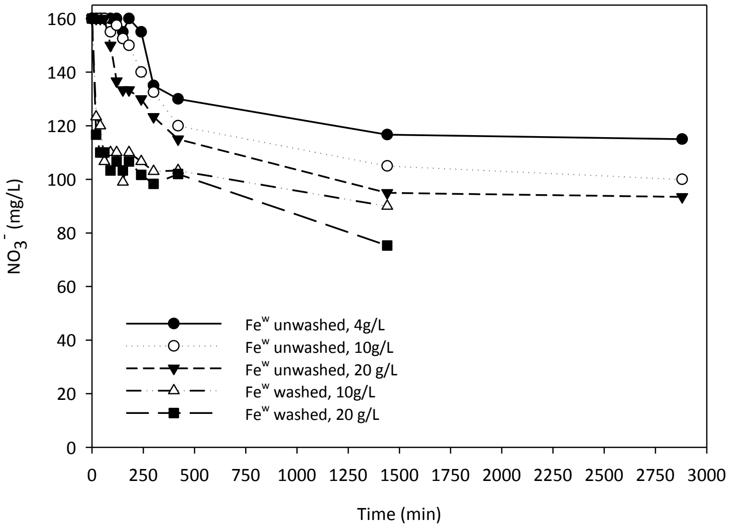

Figure 4 *Use of iron waste (Fe^w) on NO_3^- reduction in different dosages at pH 2.*

Nitrogen species analysis

During the NO_3^--reduction reaction with the three types of iron sources, the samples were analyzed regarding the production of total nitrogen (TN) and by-products in terms of NH_4^+ and NO_2^-. The N_2 (g) produced was estimated by a mass balance (Figure 5). Independently of the type of iron source used, the main by-product was NH_4^+, and the NO_2^- concentrations were negligible (< 7% of N_2 content; < 2.4 mg N/L of NO_2^-). The concentrations of N_2 estimated showed to be low, with a maximum of 13% (4.6 mg N/L), indicating that the production of N_2 and the by-products did not depend on the typology of the iron source used. This does not comply with the studies reported by Choe et al. (2000). These authors suggest that the size of the iron source is determinant to ascertain if N_2 or NH_4^+ will be produced. They believe that nanoparticles and iron powder will produce, N_2 (g) and NH_4^+ at the end of the chemical reductions of NO_3^-, respectively. Yet, this could not be verified in the present study (Figure 5a and 5b), where practically only NH_4^+ was formed with Fe^n and Fe^p, where a maximum of N_2 (g) produced was around 12% for both Fe^n and Fe^p (4.4 mg N/L and 4.6 mg N/L, respectively). Similar results were observed with Fe^w unwashed (Figure 5c) or washed (Figure 5d), and once again the surface cleaning showed not to be relevant. The maximum of N_2 (g) generated was 14.5% (5.2 mg N/L).

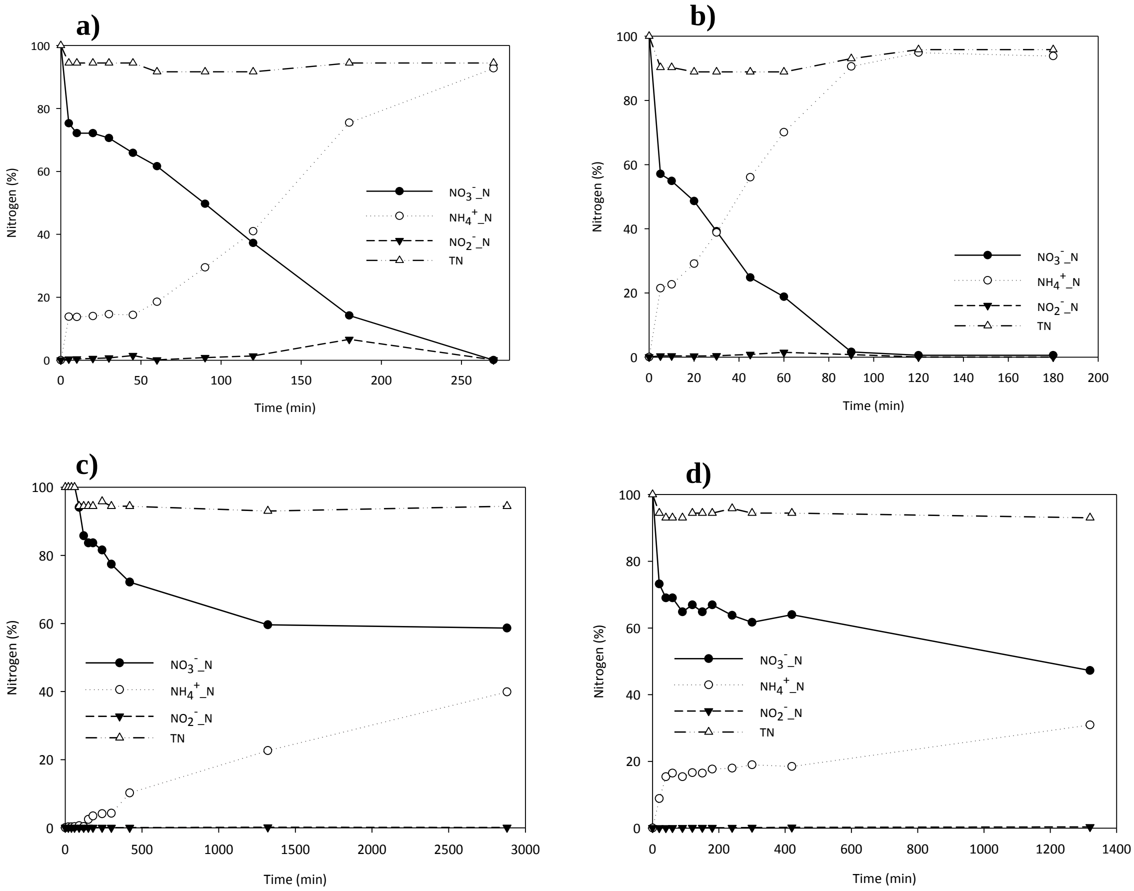

Figure 5 *Nitrogen species during NO_3^- reduction with the three iron sources at pH 2: a) Fe^p (20 g/L); b) Fe^n (4 g/L); c) unwashed Fe^w (20 g/L); d) washed Fe^w (20 g/L).*

Conclusions

Zero-valent iron was used for nitrate reduction in real mine water by comparing three types of iron sources: iron nanoparticles, iron powder and iron waste. The reduction of nitrate was possible at a very acid medium with pH 2, but no alterations on the nitrate levels were observed at pH 3 or 4 possibly due to a rapid formation of iron oxides, avoiding the contact of the metallic core (Fe^0) with the pollutant. The dosages of iron needed for the chemical reduction were investigated, where higher loads of iron can reduce more NO_3^- from the water, depending only on the surface area of each type of iron.

Iron nanoparticles (4 g/L) with a surface area of 27.7 m^2/g, were the most effective in less time, having a complete reduction of nitrate in 180 min. On the other hand, iron powder (20 g/L), with a surface area of 0.3 m^2/g, had a complete nitrate reduction in 270 min. The iron waste (20 g/L) had lower efficiency results and kinetics due to the extremely low surface area around 0 m^2/g. However, in two days, a maximum of 53% of reduction was obtained with washed waste particles, which brings economic benefits by using a waste as a raw material for this kind of environmental applications.

Nitrogenous species produced during the reactions were investigated, where it was concluded that the main by-product is NH_4^+ and the production of by-products is independent of the typology of the iron source used.

The nitrate reduction studied with an iron waste is a good option to be tested in an acid mine water since the optimum pH tested was pH 2. Further studies need to concentrate on reducing the reaction time as the relatively high reaction times are not yet feasible for an industrial use of this methodology.

Acknowledgements

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FAMDT - A new Approach for flexible AMD Treatment

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Abstract

The treatment of acid mining drainage (AMD) affected surface water is a worldwide challenge. Corresponding to this, the aquatic ecosystems in Lusatia has suffered from high loads of iron hydroxide sludge, which can be traced back to the inflow of ferrous groundwater into the surface waters. Due to the centralized location of the existing state of the art water treatment plants, these cannot contribute adequately to solve the widely spread problem of the region. Therefore, decentralized solutions at strategically important strain hot spots are required. Against this background flexible acid mining drainage treatment (FAMDT) was developed, which offers a new approach in technical AMD treatment. FAMDT forms a kind of modular construction kit for the building of treatment plants. Its modular character gives a number of benefits. Differently equipped transport containers encase the various process technologies. This allows easy adjustment to the specific site conditions or in case of temporarily changing boundary conditions. Thus, FAMDT is suitable for a markedly wide range of construction sites. The high flexibility allows a manifold reuse of the modular components. For the treatment of ferrous waters with FAMDT three construction sites have been projected in Lusatia already. The first realized FAMDT plant will be „Burgneudorf". Its commissioning is scheduled for the year 2017.

Key words: FAMD, iron hydroxide, sludge, modular, water treatment

Introduction

The treatment of AMD affected waters is a worldwide challenge. Especially mining regions require appropriate solutions to solve the environmental problems caused by AMD (Kurtz et al 2009). Lusatia, located in the east of Germany, is one of the world's greatest lignite mining region. Decades of open cast mining have substantially affected the hydrogeology of the catchment area. Here, especially the inflow of ferrous groundwater into the water courses has become an obvious issue.

Starting just a few years ago, the aquatic ecosystems have suffered from high loads of iron hydroxide sludge. Although iron hydroxide shows no acute toxicity, it harms the environment by clogging the sediment interspace and sticking the gills of fishes. To ensure the hydraulic discharge, the river beds have to be excavated periodically and the sludge needs to be deposited. This procedure is incurring high river maintenance costs.

According to the state of the art, these loaded waters need to be collected and transferred through pipes to central water treatment plants. The treatment capacity of the central water treatment plants is determined by the quantity and quality of the incoming water. It is strictly fixed due to the physical structure of the plants (Bilek et al 2013). In case of later adjustments high expenditures incur.

The construction of central plants for the treatment of AMD loaded waters is determined by serious cuts to land demand, ownership structure and infrastructure. Thus, this treatment option induces high expenditures of costs and time.

The waters, that have to be treated, are characterized by high spatial and temporal variability in regard to their quantity and quality. To achieve a significant reduction of the iron burden, new technologies are required. For this purpose the LUG Engineering GmbH has developed FAMDT. FAMDT is following a new approach in the design of AMD treatment plants.

FAMDT features the following benefits:

- High application flexibility

- Wide range of treatment capacity
- Easy to adapt to changing boundary conditions
- Compact building space
- Short time demand for building, mounting and dismounting
- Reusability of the modular components

Figure 1&2 *Ochre color of AMD affected streams in Lusatia, pictures by LUG.*

State of the Art

State of the art water treatment plants in the region are large and stationary technical objects. Those plants require high efforts for planning, permit procedure and building. Furthermore the construction design defines a treatment capacity corresponding with only a relatively small margin of the influent flows. In case of changing influent flows high expenditures are needed for the adaption of the plants.

Figure 3&4 *Central water treatment plants in Lusatia „Rainitza“ and „Am Wolkenberg“, pictures by Peter Radke LMBV and Vattenfall EM.*

Likewise, water treatment systems based on standardized containers are state of the art. They are characterized by the installation of all essential process steps within a single container. Due to the fixed dimensions of the casing this induces unfavorable limitations of the treatment capacity.

To improve the capacity of those systems a number of containers have to be operated parallel. Therefore the number of containers is necessarily determined by the limiting process step. This means, that most of the installed process steps are overdimensioned, so that the whole plant threatens to run inefficient.

FAMDT

FAMDT is a further development of the widely used stationary treatment plants as well as of container based plants. It uses the proven and tested process technologies of aeration, flocculation and sedimentation. These process technologies are commonly used in plants for the treatment of AMD affected waters - but FAMDT puts them together in a new approach.

Every particular process technology performs in different equipped transport containers. This forms a kind of modular construction kit characterized by a maximum of flexibility. Depending on the specific requirements of a construction site or in case of changing influent flows it offers the opportunity to add, to remove or to combine modular components. This ensures an easy adaption on changing boundary conditions. So FAMDT is suitable for a markedly wide range of construction sites. The high flexibility allows the manifold reuse of the modular components on different sites.

The high grade of prefabrication ensures short time demands for mounting, dismounting and modification. This helps to save efforts in time and costs. FAMDT is applied for patent under the registration number DE 10 2015 106 823.0.

A Construction Kit of Modular Components

1 Reaction container

The reaction container encases a number of aerators following the principle of airlift pumps or ejectors. The arrangement of the aerators allows carrying out several process technologies simultaneously:

- Input of fine air bubbles for the complete oxidation of the solute iron
- Mixing of flocking agent (e.g. lime hydrate) to adjust an optimal pH value for the flocculation
- Creating turbulences in order to avoid undesirable depositions

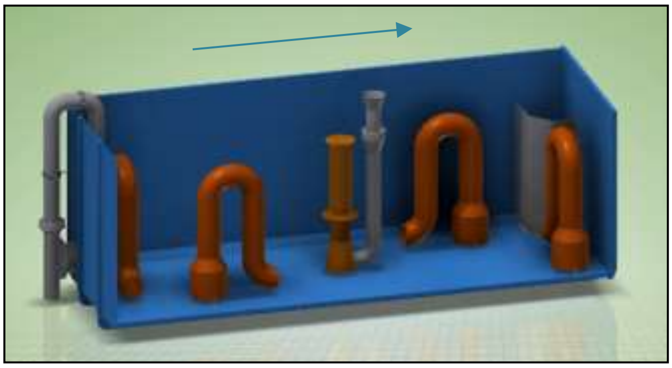

Figure 5 *Reaction container with airlift-aerators.*

The aerators are specially designed for operating within the reaction basin. Besides their function as aerators they allow to delete a disperser that is commonly used as an addition unit for the flocking agent. Furthermore they substitute stirring units. This multifunction offers some benefits:

- Highly efficient oxygen input
- Absence of mechanical construction elements
- Minimized wearing elements
- High operational safety

2 Flocculation container

In the first sector of the flocculation container the addition and mixing in of flocculation aid (e.g. polymer) is carried out. A highspeed vertical stirring device ensures over-all mixing.

The second sector is constructed for the ripening of the iron hydroxide flocks. For this a slow spinning horizontal paddle supports the agglomeration of the flocks. Furthermore this paddle lifts the flocks nondestructively into the transfer line to the subsequent sedimentation container.

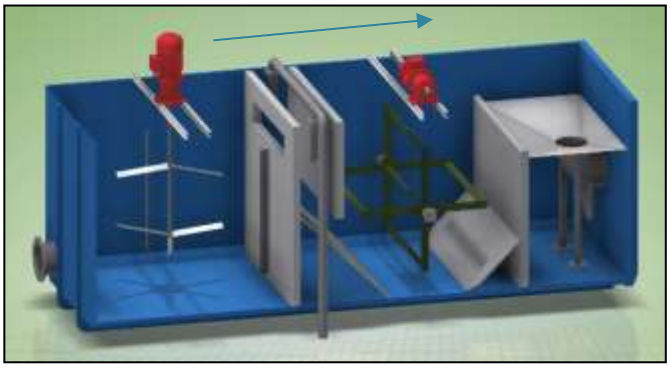

Figure 6 *Flocculation container with basins for mixing and for flock ripening.*

3 Sedimentation container

The sedimentation container is arranged with baffle plates for high efficient separation of the beforehand generated iron hydroxide flocks.

In the upper container the clear water discharges through a dented sill. In the lower part the sludge is taken off by pumps through a pipe system.

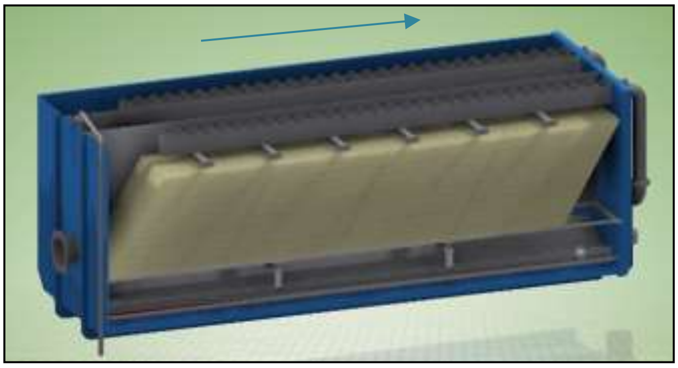

Figure 7 *Sedimentation container with baffle plates.*

Sludge Recirculation

A part of the extracted sludge from the sedimentation container recirculates back to the flocculation container. There it works as an initial nucleus and supports the formation of preferably large flocks. This helps to save flocculent aid, enhances the degree of efficiency and increases the dry substance content of the finally separated sludge.

Sludge Treatment

The treatment of the sludge takes place by thickening and if necessary by additional pressing. This improves the sludge quality with view to transportation and to dumping. Therewith the options for feedstock utilization of the high purity iron sludge improve significantly.

Flexibility

The intended use of FAMDT is the treatment of AMD affected waters. For this its strong point is high flexibility. The approach allows treating influent streams with a wide range of iron concentrations between 50 and 1,500 mg L^{-1}. The adaption to a volume flow of 5 to 500 L sec^{-1} is easy to be done and it can deal with oxygen free groundwater as well as with fully oxidized surface waters with oxygen demands from 0 to 230 mg L^{-1}.

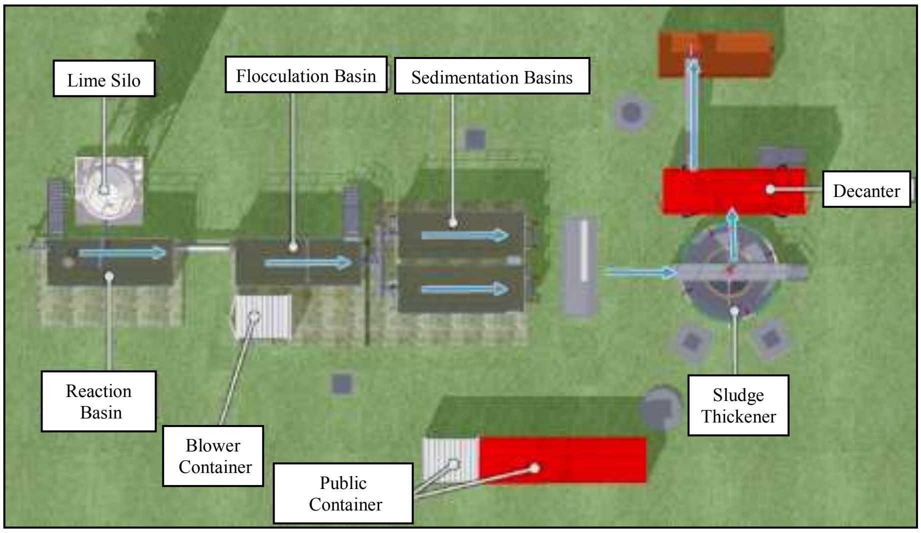

Figure 7 *Floor plan for a plant with a treatment capacity of 25 L sec^{-1} respectively 90 m^3 h^{-1}.*

Examples

For the treatment of ferrous waters with FAMDT three construction sites have been projected already. The waters to be treated vary especially with view to the iron concentrations.

First realized FAMDT plant will be „Burgneudorf". It is going to be put to operation in the year 2017. According to the existing permission, this plant has to show a cleaning capacity of not less than 90 % of the average incoming iron (Kochan & Bilek 2016).

Table 1 *Main parameters of the influent flows of three already projected FAMDT plants in Lusatia.*

Site		Burgneudorf	Neustadt	Ruhlmühle
Influent Flow		Well Bar	Trench	Creek
pH Value		5.3	3.5	4.8
El. Conductivity	µS cm^{-1}	600 - 800	1800	1300
Fe total	mg L^{-1}	60 - 120	365	208
Flow Rate	L sec^{-1}	100	25 - 50	100

Acknowledgements

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Use of alkaline mine waste as treatment for acid drainage

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Abstract

The environmental impact of industrial drainages on South Africa affects surface- and groundwater in a country already stricken by the extreme scarcity of water resources. Ba-Phalaborwa municipality of Limpopo province is a clear example of this environmental impact. There is an industrial area, with two mines and a fertilizer industry, allocated between the town and Kruger National park. In this study, several options have been researched to improve the environmental impact of that area and to reduce the risk of environmental damage to Kruger National park.

The main aim of this experimental study was to investigate the possibility of treating the extremely acidic drainage produced in this area with the alkaline rocks (mainly carbonatite) disposed in the waste rock dumps and tailings of the mines. Thus, the quality of their water would be improved and, at the same time, the volume of the waste rock dump and/or tailings material within the mine facilities will be reduced.

The experiments showed a clear improvement of the acidic water with the carbonatite from dump: pH increased from 1.4 to 4.3; total dissolved solids (TDS), electrical conductivity (EC) and salinity (Sal) decreased up to 68%, sulfate dropped 28%, total iron decreased 99.6%. The experiments with tailing material showed similar results; TDS, EC and Sal decreased between 51 and 65% and total iron was 96% removed. The main difference between the treatment with dump and with tailing is about the sulphate; the tailing removed up to 53.4% of sulfate, which is 30% more than the removal produced by waste rock dump.

This is the first study about using carbonatite as a water treatment. The results obtained from the batch experiments encourage a deep study about the use of this mine waste in a future treatment plant.

Key words: Acid drainage, batch experiment, carbonatite, tailing, Water treatment, Kruger National Park.

Introduction

The Phalaborwa Industrial Complex (PIC) is allocated in the central Lowveld of Limpopo province. It includes two mines and a fertilizer industry. Due to its proximity to the Kruger National Park (KNP), the area is especially sensitive to the environmental impact that PIC may cause to the surrounding area, with the ground- and surface water the main concern. There are numerous watercourses on PIC; northern courses drain into Loole Creek (seasonal tributary of Selati River), Eastern course drain to Tshutshi Spruit (seasonal tributary of Olifants River), and southern watercourses drain directly into the Selati River and Olifants River. Both rivers also catch groundwater which flows radially from PIC, mainly in the south and east sectors. According to Department of Environmental Affairs “Olifants river is negatively impacted by poor quality of water as a result of mining activities at Phalaborwa” “from the Selati Confluence to Downstream border in the Kruger National Park” (DEA 2009).

Climatology is also an important environmental factor to be considered, since it directly and indirectly influence the quality of the water. Temperature, precipitation and evaporation affect the physicochemical characteristics of the surface water stored in the dams within the PIC and, therefore the characteristics of the water that infiltrates into the aquifers. These parameters may affect a water treatment system and should also be considered during its design.

The area experiences subtropical conditions, with dry winters and wet summers. The temperature is warm to hot; in summer the daily temperatures range from 18 to 30° C while in winter it ranges from 10 to 23 °C. The average rainfall is 480mm per annum, but it varies from 250 to 700mm. The number of rain days is about 65 days per annum. January use to be the rainiest month and most of the rainfalls occurs in the form of heavy showers accompanied by electrical storms. The average evaporation is 2074 mm per annum. The wind blows at medium speed at about 1.1 - 3.5 m/s, predominantly from south-southeast. The area is under calm conditions 29% of the time. (DEA 2009).

The aim of this study is to approach an affordable solution for the fertilizer industry, whose process water lies in several dams allocated within the facility. This is at the expense of climatic condition that may decrease its volume and increase the concentration of pollutants by evaporation during climatic water deficit periods, or contrary wise during water excess periods. Treating this water up to the quality level that can be re-used for the plant process, employees, irrigation, etc. would be the best option from an economic and environmental point of view. Conventional water treatment was not an affordable option in the past due to the extremely high cost necessary to treat water of these specific characteristics. Therefore, the present study focuses in searching an affordable pre-treatment that increases the quality of the water up to level that can be successfully treated by a conventional industrial water treatment system.

The water is extremely acidic and hence needs large amounts of alkaline material to achieve the desired neutral stage. Within the PIC area there are large volume of carbonatite piled in the waste rock dumps and tailings of the mines facilities. Several experiments have been performed to test the carbonatite as reagent that could be used to increase the quality of the water up to desired level. Due the proximity of this material and its waste-character, it is the material of choice for this experiment. The success of the results could make a significant improvement in the environmental impact of the PIC to the surrounding area and an important decrease of the environmental risk that PIC represents for KNP. The success of the present research could entail a drastic decrease of the volume of dumps and/or tailings of the mines as well as decreasing the risk of spillages to ground- and surface water bodies.

The reagents used in this study come from the dump and tailing and contains the mined and processed carbonatites and foskorite rocks from the Palabora Complex (PC). PC is an intercontinental plug that was emplaced at 2060 Ma into granite basement of the Archean Kaapvaal craton (Wu et al. 2011). This complex is mainly formed by carbonatite, foskorite, syenite and pyroxenite (Giebel, Gauert & Costin 2016) been carbonatite the most interesting rock in this study due to its high concentration of carbonates (mainly calcite), which has high acid consumption potential. The PC has the unique carbonatites in the world that hosts minable Cu ore. Carbonatites with low concentration of Cu (among other metals) are deposited in the waste rock (WR) dumps while those with high concentrations are crushed, milled and the Cu-rich fraction is separated from the host rock, mostly carbonatite, which is then deposited on the tailings (Roux et al. 1989).

Methodology

Two sets of solid samples (mainly carbonatite) were collected from a WR dump and a tailing. A portion of each sample (100 g) was grinded to powder size. Water samples from the dam, which collects drainage produced by the fertilizer industry (FI) have been treated with carbonatite from the dump and tailing in six different experiments:

- Experiment D1(Dump 1): five falcon tubes were filled with 40 mL of subsamples from FI and 1 g of carbonatite from dump (ratio 1:40 w/v) and placed in a rotor at 30 rpm (Figure 1 left). Each subsample was removed after 2, 4, 6, 12 and 24 hours from the rotor, respectively. Physicochemical parameters (pH, EC, T and TDS) were measured from each subsample. Then they were centrifuged at 3000 rpm for 20 min at 5°C to separate the solid products from the solution. The supernatant of each subsample was collected with a sterile syringe and filtrated with 0.45 µm syringe filter of cellulose acetate. Sulphate and total iron were analysed with spectrophotometer HACH DR 3900. The supernatant extracted from each subsample was acidified and stored till its analysis by ICP.

- Experiment D2 (Dump 2): The methodology was the same than in experiment D1. Only the amount of carbonatite was increased up to 2g (ratio 2:40 w/v).
- Experiment D3 (Dump 3): The methodology was the same than in experiment D1. Only the amount of carbonatite was increased up to 3g (ratio 3:40 w/v).
- Experiment D4 (Dump 4): 250 mL flask was filled with 200mL wastewater from the fertilizer industry and 20 g of carbonatite from the dump (ratio 4:40 w/v). The flask was agitated horizontally at 160 rpm for 24 hours in a shaking incubator (Figure 1 right). pH, EC, T and TDS were measured directly from the flask after 2, 4, 6, 12 and 24 hours of agitation. At the end of the experiment the solution was centrifuged, filtrated and analysed as described above (experiment D1).
- Experiment T1 (Tailing 1): five subsamples were filled with 40 mL of wastewater from the fertilizer industry and 1 g of carbonatite from the tailing (ratio 1:40 w/v). The methodology was the same than in experiment D1 and the contact time for each subsample was 2, 4, 6, 12 and 24h, respectively.
- Experiment T3 (Tailing 3): The experiment T1 was repeated with 3 g of tailing (ratio 3:40 w/v). The same protocol was repeated.

Figure 1 *Pictures of batch experiments with 50 mL falcon tubes in the rotor (left) and 250 mL flask in the shaking incubator (right).*

Analytical procedures.

The physicochemical parameters of the FI sample (previous treatment) were analysed on site, also each subsample was analysed immediately at the end of each designated time. This was to avoid any possible change on the hydro-geochemical characteristics of each subsample due to gas leakage or any further reaction, i.e. precipitation, which may occur over time. The following parameters were measured by YSI ProDSS multi-parameter; temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS). Each subsample was then filtered with teflon filters 0.45 µm (cellulose acetate). The spectrophotometer Hach DR 3900 Benchtop was used to determine the concentration of sulfates and iron; the analyses were performed as described in USEPA Sulfaver 4 Method 8051 (equivalent to USEPA375) and USEPA Ferrover Method 8008, respectively. After filtration, pH, EC and TDS of the samples from the experiment D1 were measured again. The aim of this double check was to elucidate possible benefices of including a filtration system in the possible upscaling of the water treatment system. The sample from FI and the subsamples from each experiment were stored at 4 °C for further ICP-OES analyses.

Results

The quality of the water that is in contact with the carbonatite from the dump and the tailing improved over time. The pH increased from 1.4 to 2.3, 4.1, 4.2, 4.3, 3.0 and 3.1 after 24 hours of contact time in experiments D1, D2, D3, D4, T1 and T3, respectively, while EC and TDS decreased between 23 and 65 %. The best removal rate of EC and TDS were obtained in the experiment D2 and D3 with an average of 60 and 65 %, respectively. However the experiment D1 shows similar improvement after filtration on both parameters, increasing more than twice of the initial removal rate, probably due to the removal of suspended solids whose size were bigger than 0.45 µm. The drop of values from parameters such as TDS and EC, obtained from filtered solution, suggested that a filtration system could be an alternative as a post-treatment. According to the HACH analysis the concentration of sulphate, decreased between 14.4 and 53.4% in all the experiments (the maximum removal was achieved on experiment T3) with the exception of experiment D2, in which sulphate concentration increased slightly (Table 1). The majority of the sulphate was removed within 2 to 4 hours of contact time. The removal of iron oscillated between 96.3 and 99.6% in all the experiments and the majority of the removal was again within 2 to 4 hours of contact time (Figure 2).

Table 1 *pH and removal of EC, TDS, Sulfates and Iron measured immediately after 24 hours of contact time.*

	Parameters	**D1**	**D1 filtered**	**D2**	**D3**	**D4**	**T1**	**T3**
	pH	2.3	2.4	4.1	4.2	4.3	3	3.1
Removal (%)	**EC**	23	56.1	60.1	59.5	25.4	56	51
	TDS	25.7	58.9	65	64.4	33.6	48.9	59.5
	Sulfates	14.4		-2.5	21.2	28	18.6	53.4
	Fe total	96.3		99.5	99.6	96.3	99.5	96.4

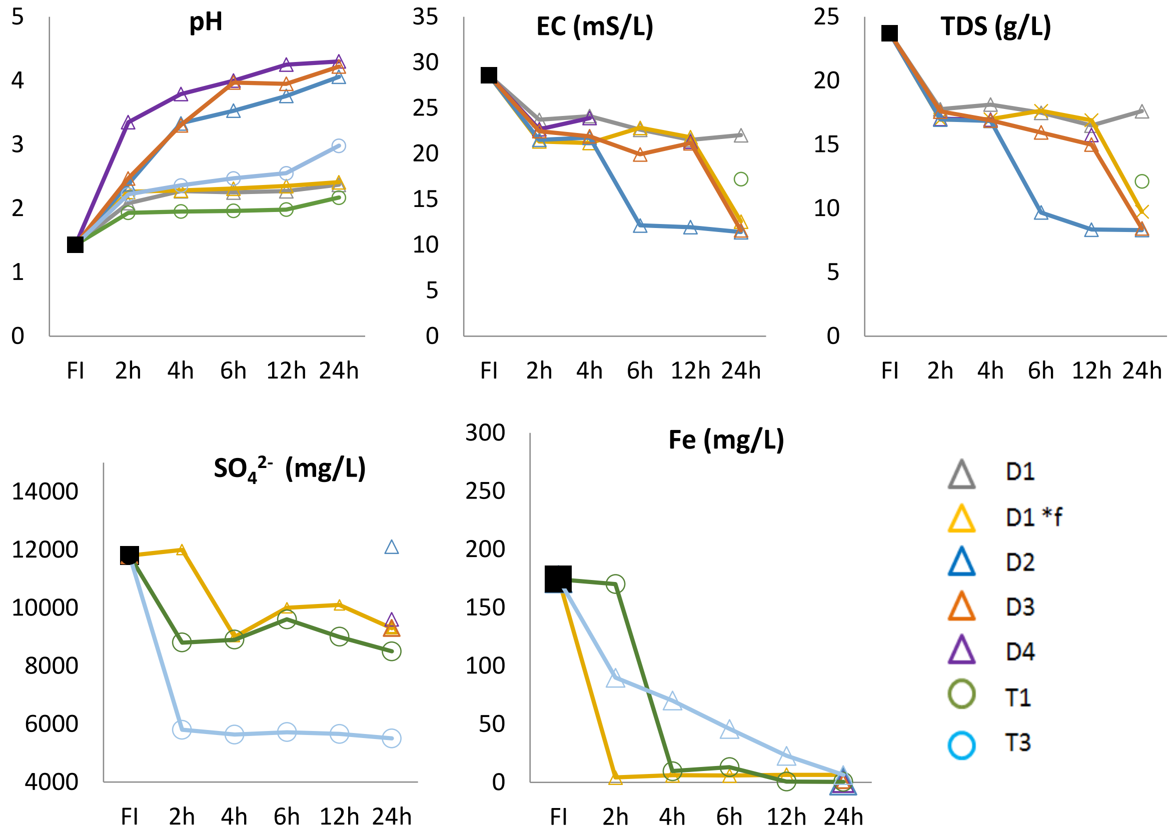


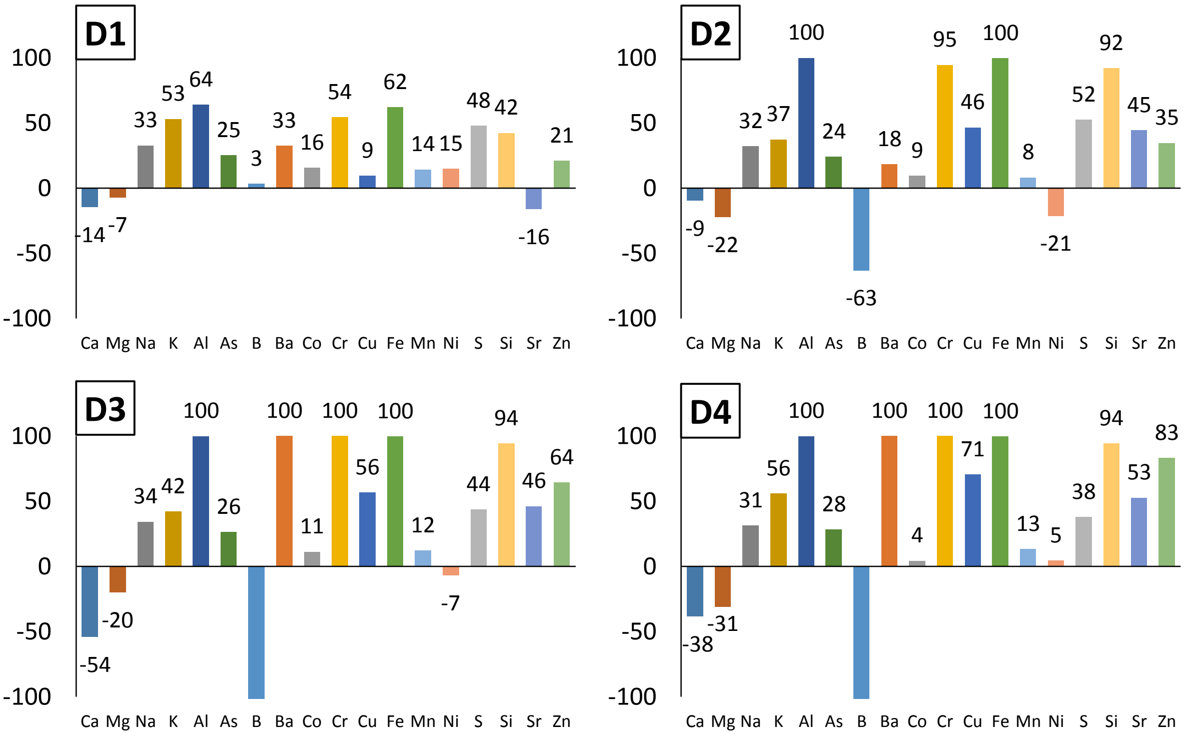
Figure 2 *Temporal evolution of pH (top- left), EC (top-middle), TDS (top-right), sulfates (bottom-left) and total iron (bottom-right) for each experiment; D1 (grey), D1 filtered (yellow), D2 (dark blue), D3 (orange), D4 (purple), T1 (green) and T3 (Clear Blue)*

ICP-MS results

According to the ICP analyses, the concentration of most of the cations and anions present in the water decreased in all the experiments performed with carbonite and tailing (figure 3); Na, K, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, SO_4^{-2}, Si and Zn. However the concentration of Ca increased in all the experiments, probably due to the dilution of $CaCO_3$ present in the carbonatites. Mg also increased, but only in the experiments with dump material; the experiments with tailing show removal of about 20%. Sr, B and Ni did not follow a clear pattern; the concentration of Sr decreased by about 50% during the experiments D2, D3 and D4, but increased between 4 and 36% in the rest. B increased about 80% throughout the experiments D2, D3, D4 and T3, but decreased 3 and 7% in experiments D1 and T1, respectively. The concentration of Ni increased in experiments D2 and D3 (21 and 7%, respectively). The differences on the removal ratio of Sr, B and Ni were probably related to the presence of those elements in the reactive material used, which might be dissolved by the acidic water.

As can be seen in the graphics below, 1 gram of carbonatite (ratio w (g): v (mL) 1:40) was not enough to achieve the maximum quality that the water can achieve through these treatments. When the amount of reactive material was increased (i.e. experiment D2, ratio 2:40), there was a clear improvement of the quality of the water. However, according to the results, the ratio 3:40 (experiments D3 and T3) was considered as the optimum ratio since there was a clear improvement with respect to the ratio 2:40, but there was no clear improvement of the experiment with ratio 4:40 (experiment D4) with respect to 3:40.

In experiments D3 and T3 (both 3g of reagent) most of the elements (Na, Al, As, Ba, Cr, Fe, Mn and Si) had the same ratio of removal (about 34, 100, 27, 100, 100, 99, 14 and 93 % on average, respectively, with a standard deviation of 0.9). However the dump material is more effective in the removal of Cu, Sr and Zn, but the increase of Ca was lower in all the experiments with dump material than in those with the same ratio reagent/water of tailing. It increased the concentration of Mg, B and Ni, probably because these elements were present in the carbonatite. Therefore the removal induced by the tailing material was better for those elements, as well as for Co and specially sulphate.



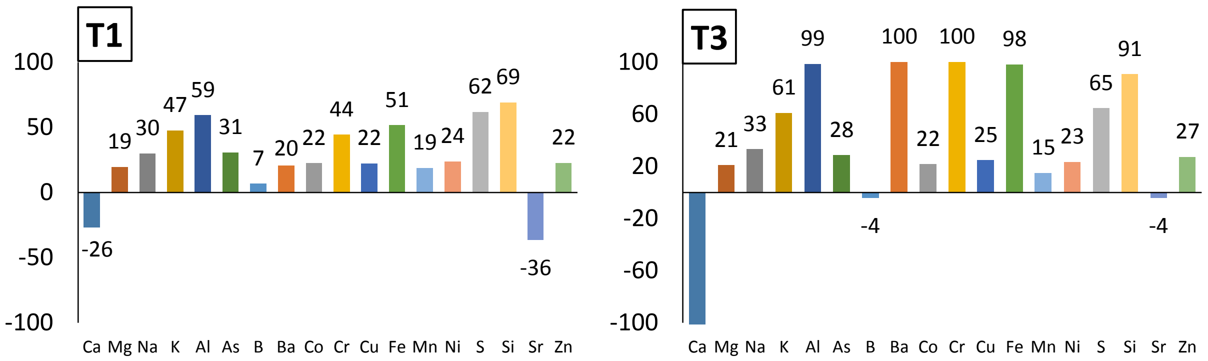


Figure 3 *Percentage of removal (positive) and increasing (negative) of all the elements analysed in the samples (Cd, Mo and Pb were always below detection limit)after 24 hours of contact time.*

Conclusions

According to the results, the quality of the water improved with carbonatite from both dump and tailing material. The improvement can be observed within two hours, but they keep improving over time and reached the highest quality at 24 hours. The lowest percentages of removal were obtained in experiments with ratio 1:40 (in both cases dump and tailing). The experiment with ratio 2:40 got a higher removal and the experiments with ratios 3:40 and 4:40 gave the best results. Therefore the ratio 3:40 would be the recommended ratio since it was the most efficient. By comparing the experiments D1 with T1 and D3 with T3, it can be concluded that the tailing produced better removal rates than the dump material, especially for sulphate.

For all these reasons, a treatment of FI water with carbonatite from the tailing with a ratio w/v of 3:40 would be recommended and further research will be performed to optimize a possible water treatment system with this material as main reagent in a 3:40 ratio. This water treatment would improve the characteristics of the water from the FI. At the same time it will reduce the volume of tailing from the mine.Therefore, the environmental impact on Palabora Industrial Complex and thus Kruger National Park would be reduced considerably.

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A compact Passive Treatment Process for AMD Using Rice Husk and Rice Bran

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Abstract

An energy and cost saving biological passive treatment system for acid mine drainage (AMD) developed by Japan Oil, Gas and Metals National Corporation (JOGMEC) is a vertical flow anaerobic process that utilizes sulfate-reducing bacteria(SRB) with rice husk and limestone as the substrate and rice bran as the organic resource of SRB. In addition to this sulfate reducing process, an aerobic process of iron oxidation and removal that utilizes iron-oxidizing bacteria is applied to treat high iron content AMD. Iron scale from the aqueduct of drainage treatment facilities has been used as source of the iron-oxidizing bacteria. This passive treatment process is called “JOGMEC Process”.

In Japan, flat areas that can be used for mine drainage treatment are limited due to geographic conditions. Therefore, it is necessary to introduce a compact passive treatment system with a higher flow rate (shorter hydraulic retention time (HRT)) compared to the other conventional anaerobic processes that utilize SRB. Then, the laboratory tests have been carried out under short HRT conditions about 25 ~ 50 hours.

Since 2014, bench-scale tests have been carried out at an abandoned mine site in Japan. Concentrations of dissolved metals in AMD of the mine are 35-40 mg/L iron (mainly ferrous ion), 18 mg/L zinc, and 8 mg/L copper, respectively, and the value of pH is 3.5. As the AMD contains high concentration of iron, it is firstly removed with the aerobic process of iron oxidation and removal, and then the other metals have been removed with the anaerobic process in the subsequent stage. The results of bench-scale tests show that the metals have been continuously removed for about 300 days under a flow rate of 80 mL/min (the nominal HRT in anaerobic process: 50 hours). During the test term, atmospheric temperature dropped to around -15°C in the winter, and the temperature inside of the reactor of the anaerobic process dropped to around 5°C. The performance of metals removal has been stable even in the lowest temperature during the test term. At present, the metals removal has stably continued for about half a year under challenging conditions that a flow rate has been set to 160 mL/min (the nominal HRT in anaerobic process: 25 hours).

Since rice bran, which contains high amount of carbon as sugar, protein and lipid, would be easily decomposed by bacteria, it seems that much organic acids have supplied to SRB and the metals removal has stably continued under short HRT and low temperature conditions. The results suggest that “JOGMEC Process” is able to treat AMD under shorter HRT compared to the conventional biological processes.

Key words: AMD, Passive Treatment, Sulfate Reducing Bacteria

Introduction

Japan Oil, Gas and Metals National Corporation(JOGMEC) has conducted researches on the passive treatment for mine drainage since 2007, and has focused on treatment methods in which metal ions would be removed as sulfides using sulfate reducing bacteria (SRB). For neutral pH mine drainage, field tests have been carried out using an anaerobic bioreactor filled with “rice husk” as an organic carbon source. The successful removal of metal ions had continued for approximately 1100 days under the appropriate conditions (retention time: 50 h, water temperature: over 15 °C).

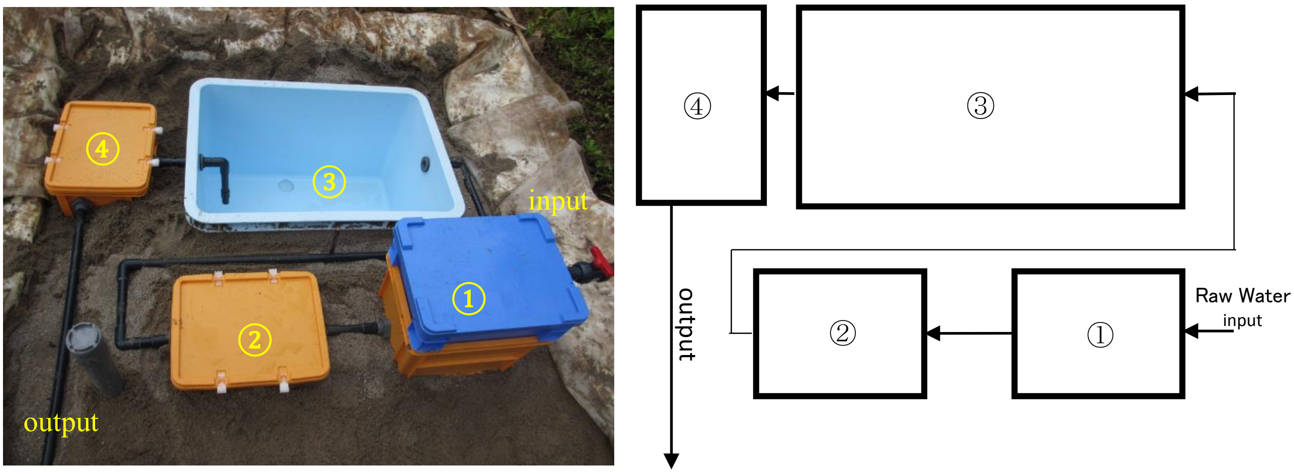
Further, the field test has been carried out using the anaerobic bioreactor filled with “rice bran” in addition to “rice husk” for acid mine drainage since 2014. Continuous removal of metals for more than 300 days has been confirmed with the retention time of 50 hours under natural environment where the atmospheric temperature in the winter reached to around -10 °C.

As mentioned above, the “JOGMEC process” which utilizes the SRB growth inside the anaerobic bioreactor filled with rice husk and rice bran to remove metal ions as sulfides has been proven to have enough capability for long term treatment of acid mine drainage with a retention time of about 50 hours. In addition, the analyses on metal precipitates, bacterial flora, and so on, in the bioreactor have revealed various aspects of the reaction mechanisms related to removal of metal ions with hydrogen sulfide ions originated by the reduction with SRB. As the retention time of 50 hours is one third to one fifth shorter compared to those in general test cases, the treatment equipment could be downsized. However further advance in efficiency of the process would be needed to increase applicability to treatment systems for mine drainage in Japan. Thus, it is under investigation to aim at realizing the process with a retention time of 25 hours since 2015.

Methods

(1)Equipment

A test field of about 3 m square in area and 1 m in height was prepared in abandoned mine site in Akita prefecture, northern part of Japan. Each bioreactor was installed in the field surrounded by soil walls. Mound was layered within the field to simulate land burial. There are sequentially placed an “aerobic iron oxidation-removal bioreactor (iron oxidation bioreactor)” which oxidizes ferrous ions to ferric ions and precipitates as oxy-hydroxide and an “anaerobic bioreactor” which utilizes SRB to precipitate metal ions as sulfides. Fig. 1 shows an arrangement of an iron oxidation bioreactor and an anaerobic bioreactor used in this test.



(a) a picture of test apparatus (b) a plain view of test apparatus

***Fig.1** Test Apparatus*

① : iron oxidation bioreactor, ②④ : tank for obtaining samples、③anaerobic bioreactor

(2)Structure and contents of the bioreactors

Dimensions of the iron oxidation bioreactor and the anaerobic bioreactor were 422 mm × 320 mm × 300 mm and 1006 mm × 703 mm × 603 mm respectively. As the ion oxidation bioreactor requires air supply to activate aerobic iron-oxidizing bacteria, a tank with numerous drainage holes on the bottom surface is stacked upon the iron oxidation bioreactor and the raw water has been introducing to the upper tank at first and then dropped down on iron oxidation bioreactor through contact with the air. The iron oxidation bioreactor is filled with approx. 20 kg in wet weight of iron-scales that have been precipitating on the aqueduct for mine drainage.

The anaerobic bioreactor is filled with the following materials. Soil collected from the surface layer around the mine site was used as "a resource of bacteria "including SRB. Rice husk was used as "a base material" of the bioreactor and as "a nutrient" for bacteria. Furthermore, rice bran and green tea leaves were added as "easily decomposable organic matters", which is decomposed by bacteria more easily than rice husk. It was shown by the analysis that rice bran in particular contains much protein, lipid and starch and green tea leaves contain much protein, so they would be easily decomposable by bacteria. It is assumed that low-molecular substances will be provided to SRB. Limestone (3 to 20 mm in size) was used as structural material for "securing cavities" and for buffering the pH value. The initial weight of those filling materials were 25.5 kg of rice husk, 24.5 kg of rice bran, 8.5 kg of green tea leaves, 102 g of soil, and 10.2 kg of limestone. Rice husk, green tea leaves, and soil were steered evenly and filled in the column so that they were distributed evenly in the whole reactor but rice bran was filled intensively in the upper portion. A total of 250 L of mine water could be filled into the bioreactor as raw water after the reactor had been filled with those contents. Further 5 kg of rice bran was added to make a total weight of 29.5 kg in May 2015 when the flow rate of the water was doubled.

(3)Experiments

・Acclimation of SRB

Before filling the bioreactor, rice husk, green tea leaves, limestone, and soil were mixed in a separate vessel and water sealed with the mine water as sulfate ion source and SRB were acclimated for approx. 2 weeks. Then, the contents were filled into the bioreactor and SRB were further acclimated within the bioreactor up to 5 days. When ORP value of the water filled in the bioreactor became approx. -200 to -300 mV, SRB were thought to be active and mine water has been fed to the bioreactor. Feeding was started in August 2014.

・Quality of treated water

The pH value of drainage is 3.5 and the concentrations of iron, zinc, copper, cadmium, and sulfate ions are around 40 mg/L, 15 to 18 mg/L, 3 to 10 mg/L, 0.06 mg/L, and 300 to 350 mg/L respectively. They have not showed fluctuation so much throughout the year.

・Analysis of items

Samples of the treated water from the bioreactor were collected periodically. Analysis items included temperature, pH, ORP, metal ions concentrations (iron, copper, cadmium, and so on), sulfate ion concentration, sulfide ion concentration, and COD. Concentrations of metal ion were determined using ICP and sulfate ion was determined using ion chromatography. Sulfide ion concentration was colorimetrically measured as hydrogen-sulfide ion and COD value determined titration method.

・Flow rate

Flow rate was maintained at 80 mL/min since August 2014 to May 2015. As the water volume of the anaerobic bioreactor is 250 L, the retention time is 50 hours. The flow rate was increased to 160 mL/min to reduce retention time to 25 hours since May 2015. Time period with retention time of 50 hours was 275 days and that with retention time of 25 hours was 263 days at the end of January 2016.

・Temperature conditions

Neither of the bioreactors was subjected to temperature control except the use of minimal heat insulating material (glass wool) for frost protection of water channel for the raw water. Equipment had not been protected with a roof so that tests were conducted in the condition similar to natural environment, thus they were covered with snow (around 70 to 80 cm in thickness) in the winter.

Results

(1) Inflow rate to the equipment

Fig.2 shows the changes in flow rate of the test equipment (flow rate was measured for the treated water). As the pre-determined flow rate (80 mL/min or 160 mL/min) was kept almost for the test term, it seemed that a natural flow of the water was maintained generally. Decreases in the flow rate were observed on 150th day (at the beginning of January in 2015) and on 400th day (at the beginning of October in 2015) after the start of the experiment. The former was caused by clogging of rice bran within a channel which conducted the raw water to the anaerobic bioreactor and the flow rate was recovered after the removal of it. The latter was caused by iron scales that had been precipitated on the bottom of the tank that was stacked upon the iron oxidation bioreactor. After the removal of scales which had blocked drainage holes of the tank, the flow rate was recovered.

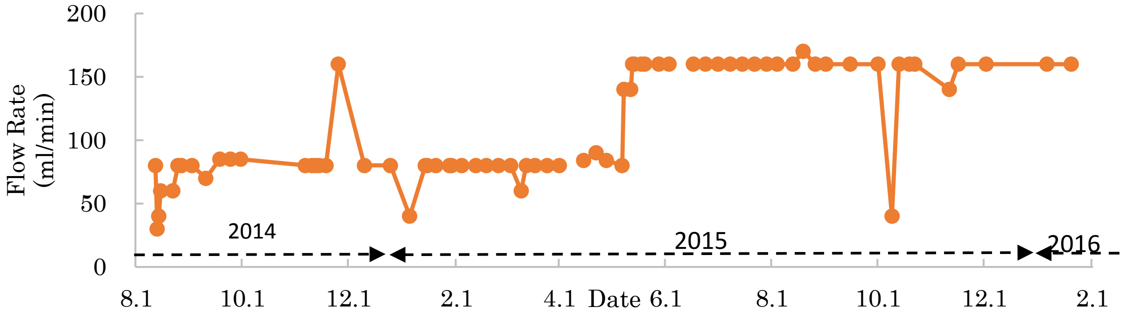


Fig. 2 *Changes in flow rate*

(2) Changes in temperature in the anaerobic bioreactor

Fig.3 shows temperature changes in the inside of anaerobic bioreactor as well as those in the raw water and in the outside air. The temperature inside the bioreactor was measured at the center portion. Fig.3 shows that the mine water used in this test have been flowing in at a constant temperature (12 to 14 °C) throughout the year.

Regarding the temperature change in the anaerobic bioreactor, it was above 20 °C at the initial stage of the experiment and decreased gradually to 5 °C in December 2014 as the atmospheric temperature decreased. After the flow rate was doubled in May 2015, the temperature variation in the inside of the bioreactor became small and the temperature was stabilized at around 10 °C in December 2015. This is thought to be caused by the increased flow rate in twice, which made the temperature inside the bioreactor less affected by that in the atmosphere. In terms of temperature, the environment inside the bioreactor with the retention time of 25 hours exhibited less variability and was estimated to be more suitable for maintaining microflora and activity of bacterial groups.

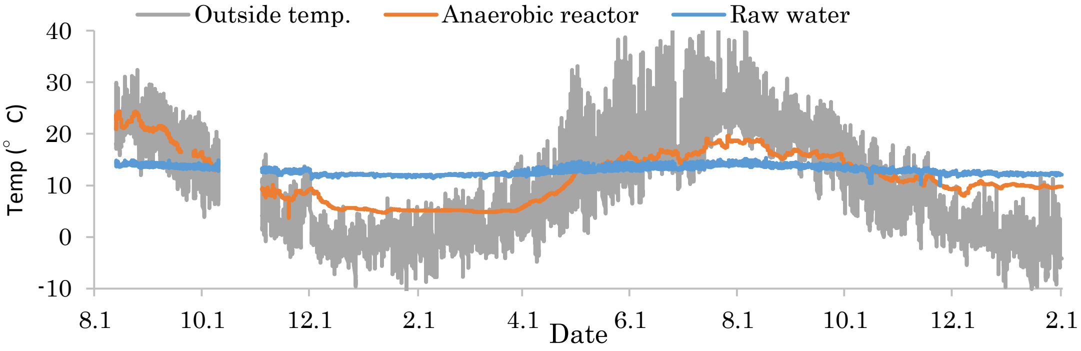
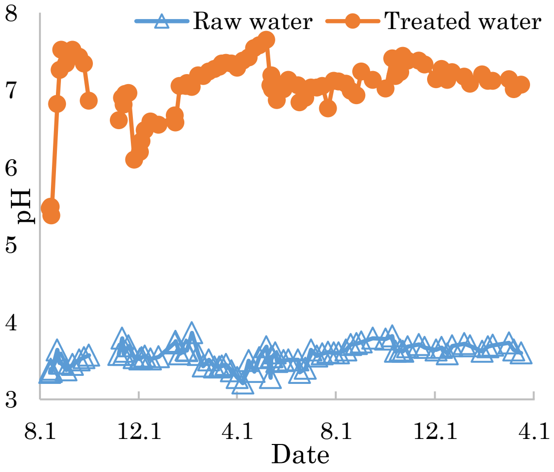


Fig. 3 *Changes in temperature*

(3) Changes in pH and ORP values in the treated water

Figs.4 and 5 show the changes in pH values and ORP values respectively. These show that pH values in the raw water were maintained around 3.5 throughout the year. For the treated water, the pH value increased to over 6 and had become stable below the regulation standard except the initial stage of water feeding. ORP values were also maintained below -200 mV except the initial stage, suggesting a stable reductive atmosphere was formed inside the anaerobic bioreactor. Both the pH and the ORP remained stable without showing instabilities under the retention time of 25 hours. The stable pH was thought to be maintained by continuous neutralization effect due to limestones filling the inside of the bioreactor and the ORP was thought to be stabilized by continuous sulfate ion reduction by the SRB inside the bioreactor. It is suggested that the retention time of 25 hours induced stable expressions for both measures.



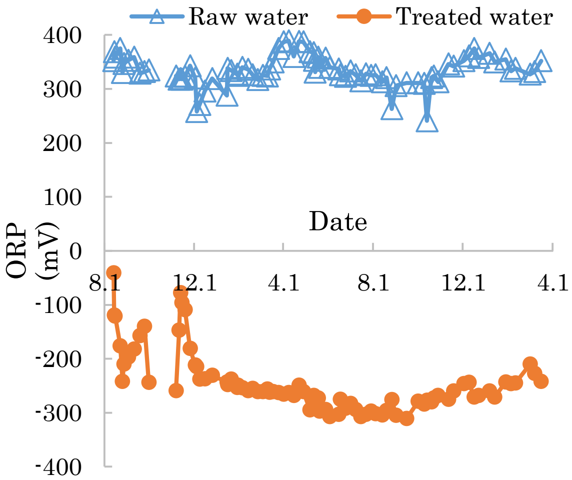


Fig. 4 *Changes in pH values*

Fig. 5 *Changes in ORP values*

(4) Changes in sulfate ions in the treated water

Changes in the sulfate ion concentration in the raw water are compared to those in the treated water in Fig.6. The concentration of sulfate ion in the bioreactor decreased immediately after the start of water feed and was kept at stable decreased level in the winter season. A decrease in ion concentration was approx. 150 mg/L. Soon after the increase in flow rate in May 2015, the concentration of sulfate ion was shown a temporary increase, and then began to decrease again. A decrease in ion concentration was over 200 mg/L in the summer season. Since October 2015, the concentration of sulfate ion in the treated water tended to increase. After that, however, the deference between the sulfate ion concentration in the raw water and that in the treated water was stably kept during the winter. This showed that the reduction by SRB adequately lasted even in the winter. Compared to the trend in the winter season with the retention time of 50 hours, decrease in sulfate ion in the bioreactor with retention time of 25 hours was small but the amount of reduction was approx. 100 mg/L and maintained stably in the winter season. Along with the results shown in Fig.5, continuous and stable reduction of sulfate ions by SRB is suggested

(5) Changes in the concentration of metal ions in the treated water

Fig.7 shows the changes in the concentration of iron, zinc, and cadmium in the treated water. Slightly higher concentrations, especially higher iron concentration, were observed immediately after both the start and the interruption of the test, but all of metal ion concentrations were at an appropriate lower level thereafter. Mean metal ions concentrations throughout the test period were 1.26 mg/L for iron, 0.16 mg/L for zinc, and 0.002 mg/L for cadmium.

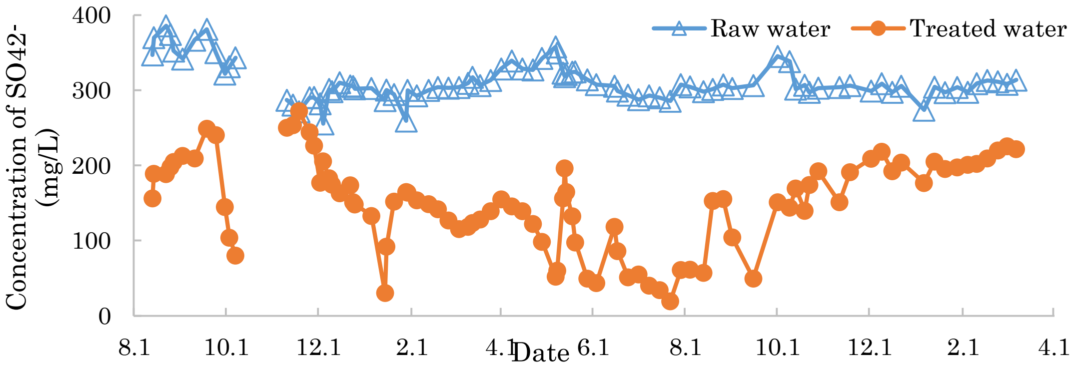


***Fig. 6** Changes in concentrations of sulfate ion*

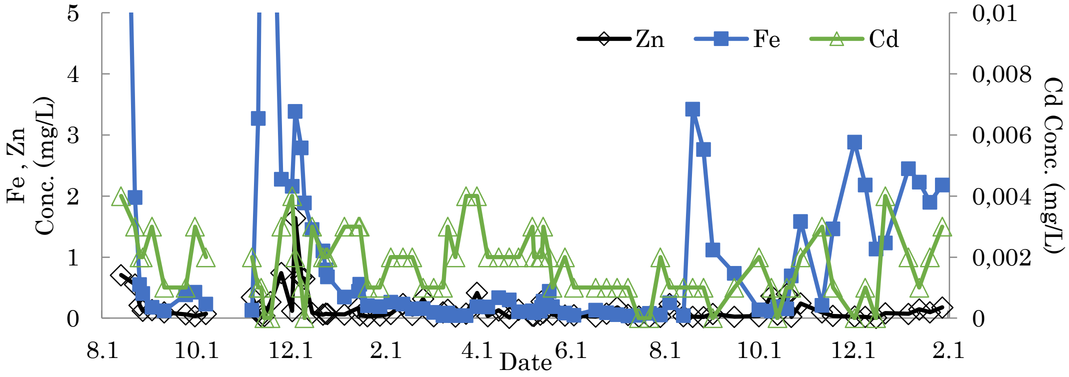


***Fig. 7** Changes in concentrations of Zn, Fe and Cd*

Discussion

・Treatment performance for metal ions with the retention time of 25 hours

Based on the results shown in Figs. 5 to 7, it can be estimated that the sulfate ion in the raw water has been reduced by SRB, and hydrogen sulfide ion has been produced, and metal ions have been precipitated as sulfides, and then metal sulfides have been collected by the rice husk. Although decrease in concentration of sulfate ion with the retention time of 25 hours have been smaller than that with the retention time of 50 hours, the concentration of metal ions has been reduced to the similar level in the treated water in the both cases. Thus, these treatment performances for metal ions have been thought to be about same.

Fig.3 shows that the temperature fluctuation in the bioreactor with the retention time of 25 hours was as small as around 10 °C even in the winter season, in which condition activities of bacteria groups including SRB to reduce sulfate ion could be more effectively maintained. In spite of increased load with doubled flow rate, a suitable environment for bacteria groups might be provided in terms of temperature. Increased flow rate imposes load to the bioreactor from the viewpoint of the increase of volume to be treated, while it reduces load related with the temperature fluctuation. This may be suggestive to design more efficient and compact processes.

When the flow rate was doubled, rice bran was refilled to the bioreactor. Therefore the low molecular organic carbons provided to SRB also increased. This might contribute to enhance the capability of metal treatment. So, rice bran added could supply sufficient amount of low molecular organic carbons to the SRB to reduce sulfate ion efficiently and stably even with the retention time of 25 hours. Here, only rice bran was added and tested. The production/supplying area of green tea leaves are limited compared to that of rice bran in Japan, and so only rice bran was refilled in terms of availability. In consequence, in case of rice bran significant effect could be obtained as described above, and then, rice bran seems to have good aptitude as the easily decomposable organic matter in this process.

The results suggest that the structure of the bioreactor, filling content, and filling volume used in this experiment with the retention time of 25 hours could successfully treat AMD. As for the continuity of the treatment, it has run stably over 250 days so far and further stable processing would be anticipated for a long-term stability.

Conclusions

During the field test on the JOGMEC process utilizing the activity of the SRB to treat AMD, the stable metal removal with the retention time of 25 hours continues currently. Therefore, it could be said that more effective metal removal would be realized compared to the conventional process. Firstly, the seasonal fluctuation of temperature in the bioreactor has resultantly become smaller due to the increase of flow rate of water through the reactor. Secondly, appropriate refilling of rice bran which supplies low molecular organic carbons has adequately improved the activity of bacteria including SRB. Thus, the compactification of the JOGMEC process could be expected and the applicability to AMD treatment would be extended in Japan.

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Microbial Iron Retention in the Groundwater upstream to a River

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Abstract

High iron and sulphate concentrations are observed in several surface waters of the Lusatian mining district. Especially iron affects the freshwater fauna (fish, insect larvae) and aquatic plants by lowered pH or high turbidity. Both iron and sulphate are mobilized from iron sulfides like pyrite and marcasite, which are decomposed under oxic conditions. These conditions appear in the underground of large areas after lowering the groundwater table to enable the opencast lignite mining. To develop a treatment technology, we built a pilot plant at the location "Ruhlmühle" (north Saxony) in 2014, where an iron hot spot (about 400 to 550 mg/L Fe) in groundwater was detected. At the pilot plant, groundwater is extracted by 3 wells, mixed with glycerin and re-infiltrated. The infiltration line consists of 30 lances and has a width of about 100 m. The infiltrated glycerin serves as a carbon source for sulphate-reducing bacteria (SRB). Although the microbes operated under the difficult starting conditions (pH-value of about four), it took a longer time than expected to rise the pH above five by bacterial metabolism. Under these conditions, the iron could precipitate as iron sulfide, generating additional alkalinity. Up to now, the iron concentration has been reduced to about 200 to 300 mg/L. Sulphate and electrical conductivity have decreased (SO_4 from about 1100 mg/L to about 500 mg/L) too, and the neutralization potential has risen from between -15 to -20 mmol/L to above -10 mmol/L. We expect a further decrease of the iron concentrations down to 30 mg/L during the continued operation.

Key words: groundwater, remediation, pyrite oxidation, iron hydroxides, iron sulfides, glycerin, glycerol

Introduction

Pyrite and marcasite oxidation is a common consequence of opencast lignite mining. However, the oxidation of iron sulfides is not only restricted to the mine dumps but it also occurs in the adjacent areas with lowered groundwater tables. As a consequence, some rivers of the Lusatian mining district, e. g. the rivers Spree, Schwarze Elster and most of their tributaries contain high and visible iron concentrations. If reduced iron from the groundwater is transformed into iron hydroxides in an oxygen rich environment like a river, it has severe negative effects for the water biocenosis (e.g. lowered pH, high turbidity). Therefore, a reduction of the iron mass flow is necessary.

Study area - subsurface conditions

The groundwater treatment is located southwest of river Spree near the small town Neustadt in the North of Saxonia in a FFH reserve area. The treated groundwater flows almost perpendicular to an abandoned river course ("Altarm"). The "Altarm" flows into river Spree downstream outside of the study.

Geological, the area is characterized by the glacial trough structure "Spreewitzer Rinne". Quaternary deposits in the study area consist of fine to coarse sands or gravel with thin silty or clayey layers, partly with a high share of lignite. Glaciofluvial variations in water discharge and flow direction formed small-scale heterogeneous sediment structures (Hildmann et al. 2016). The sediments have a porosity of about 30 % and an average hydraulic conductivity of $6.6 \cdot 10^{-4}$ m/s. The longitudinal dispersivity is approximately 0.2 m.

The lower limit of these aquifer forms glacial till. This zone of low hydraulic-conductivity rises from 25 m to 15 m below the terrain surface downslope the first row of observation wells. The thickness of the aquifer decreases, which corresponds to faster groundwater flow in the surroundings of the second and third row of observation wells.

Knowledge about the subsurface is exclusively based on the information of drillings and sediment analysis. Some suppositions have been defined and specified by the hydraulic modeling and were confirmed by the results of a tracer experiment.

A tracer experiment with sulfur hexafluoride (SF_6) was conducted from November 2014 to march 2016. Tracer was injected into six DSI-lances in the middle of the infiltration line. It was detected at the first row of observation wells after 35 days (distance: 20 - 25 meters), at the second row after 100 days (distance: 85 - 95 meters) and at the third row after more than 235 days (distance: 185 - 205 meters). Based on these data, we calculated flow rates between 0.45 - 0.6 m/d in the surroundings of the first row of observation wells and 0.7 - 0.95 m/d further in the downgradient area.

Groundwater level has risen steadily in consequence of the termination of lignite mining in the past. A considerable acid and salt input into the aquifer was triggered due to the ascending groundwater. However, the level remained relatively stable since the beginning of this experiment. The current water table fluctuates between 8.0 and 8.3 meters below ground in the area of the first row of observation wells. Hence, there is a thick unsaturated layer with a high potential of acid inflow into the aquifer.

Untreated groundwater in this investigation area is characterized by pH-conditions lower than four, an electrical conductivity of about 1800 µS/cm, iron concentrations > 400 mg/L, and sulphate concentrations between 1100 - 1500 mg/L. Caused by the high acid content, iron and manganese concentrations, neutralization potentials are below -15 mmol/L (Schöpke et al. 2015).

Method

The project started in 2014 to evaluate reduction potential of the iron mass flow while passing an active subsurface zone. A carbon source (glycerin = glycerol) is infiltrated into the subsurface to enhance the biochemical reduction sulphate in the aquifer (fig. 1). Anaerobic sulphate-reducing bacteria (SRB) use the oxygen of sulphate for oxidation of the organic matter. As a consequence, sulfide and solute iron(II) precipitate as iron-monosulfides within the aquifer and the transport into the surface water is reduced.

The following chemical equation describes the process:

$$Fe^{2+} + SO_4^{2-} + \frac{4}{7}C_3H_8O_3 \rightarrow FeS \downarrow + \frac{12}{7}CO_2 + \frac{16}{7}H_2O$$

The groundwater treatment is only conducted in the saturated zone with anoxic, reducing conditions and operates in accordance with the water approval of the mining authority of the Free State of Saxony.

The pilot system plant (fig. 1) is composed of pumping wells for extracting a part of the groundwater, a container for the dosage unit plus system control and 30 injection lances (DSI-lances) for infiltration of a water-glycerin-mixture for treatment. Depending on the monitoring results, additional nutrients can be supplied for the metabolism of microorganisms (phosphate, nitrogen).

The technical process of groundwater extraction, dosage and re-infiltration operates automatically. The plant operates as a closed system without oxygen input.

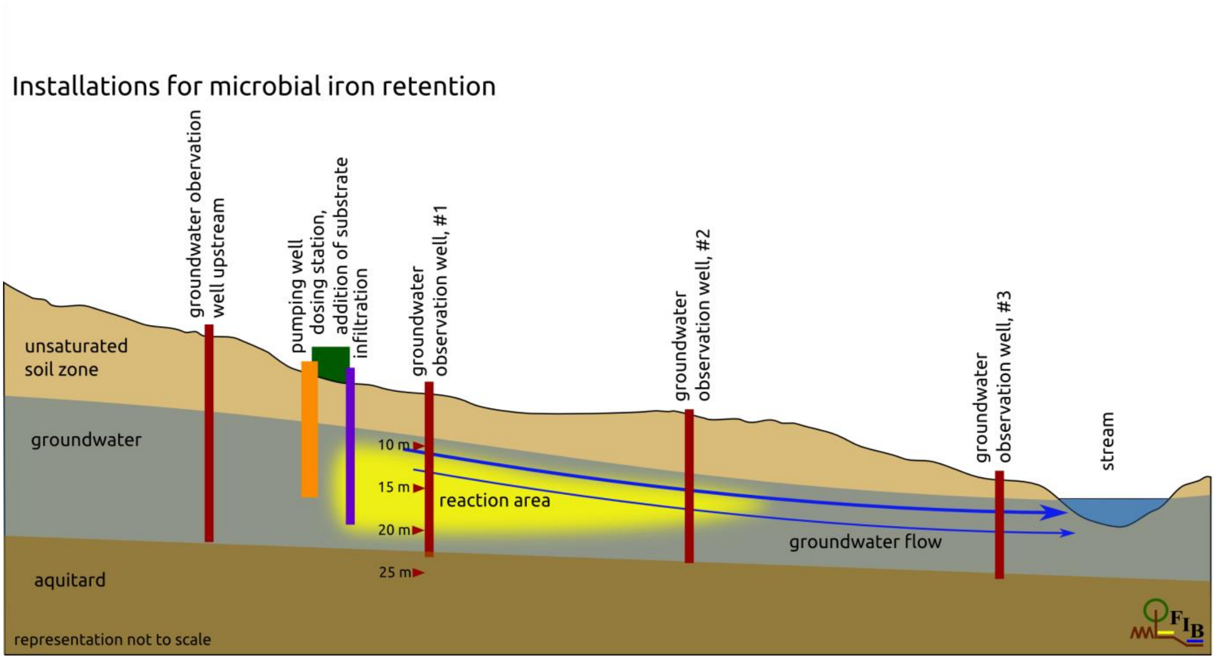

Figure 1 Vertical section through the test area.

The active subsurface zone is positioned in a line of about 100 meters length and captures a 9 meters thick part of the aquifer. Treatment is discontinuous: infiltration cycles alternate with undisturbed groundwater flow, which enhances the mixing of treated and untreated water. 18 observation wells (in 3 rows perpendicular to the groundwater flow direction) are used for monitoring.

Results

System operation

48.680 m³ of groundwater was extracted during 23 infiltration cycles from December 2014 to April 2016, charged with 16.500 liter of glycerin and 3.580 liter of phosphate solution and re-infiltrated.

The quantities of glycerin and phosphate are dosed based on the monitoring results. Especially in the beginning, the dosage was rather low to avoid unmetabolized outflow. Currently, 6 L/h of glycerin and 6 g/h of phosphate are infiltrated.

The sulphate-reducing bacteria currently use a large proportion of the natural nitrogen reserve for their metabolism. Another part is adsorbed on the rock matrix. Therefore, an additional infiltration of nitrogen is necessary in the near future.

The technical installations have operated reliably. During installation of the plant, the exact automatic measurement of the infiltrated glycerin volume was a challenge. This problem was solved by the subsequent integration of a water pressure device and temperature sensor with a feedback to the stored program control (SPC).

Groundwater treatment

The low pH-conditions retarded the iron(II) precipitation at the beginning of the treatment process. However, the rate of SRB increases slowly and through their metabolism the pH rose to values above pH 5 (fig. 2).

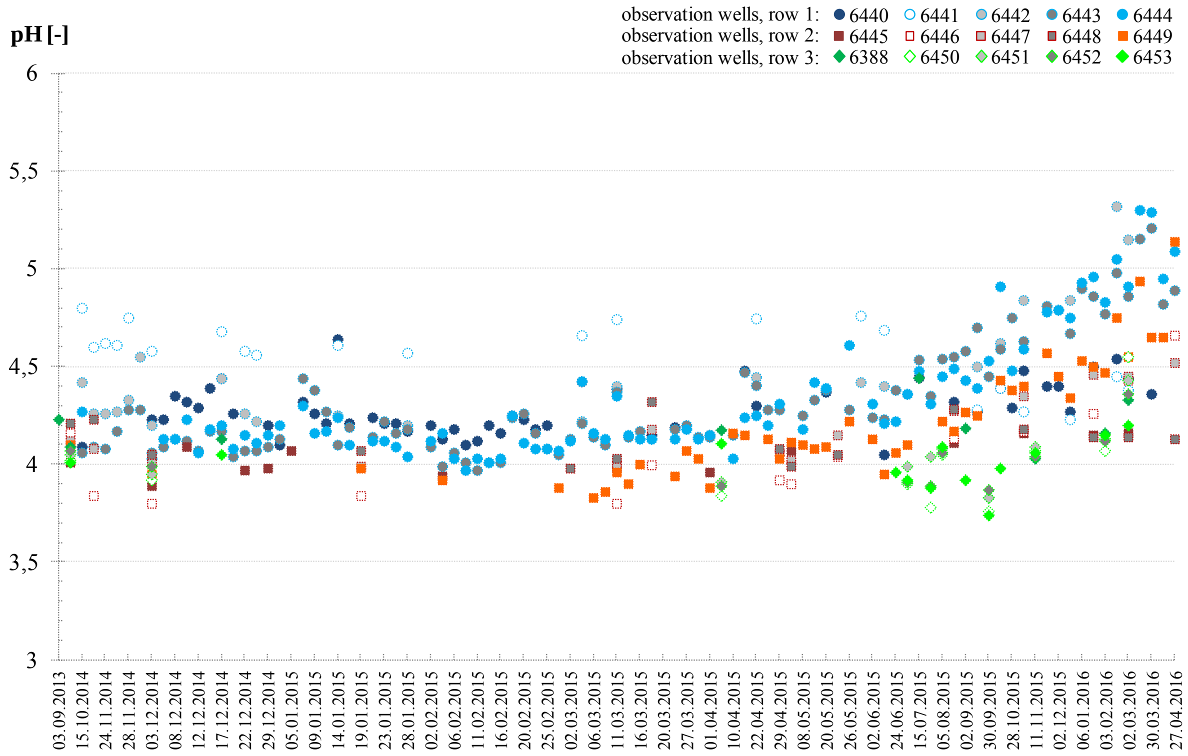

Figure 2 *Development of pH- conditions in the downgradient area of the pilot plant.*

After 16 months of treatment, the pH values enabled the removal of iron from groundwater by sulfide precipitation in a relevant degree. Electrical conductivity decreased depending on concentrations of iron and sulphate, and also calcium and aluminum decreased significantly.

Acid load in groundwater decreased at low level analogous to improved pH conditions. This effect was detected in the observation wells directly downstream to the infiltration line first and arrived at the second and third row in the beginning of the year 2016.

The best remediation successes were observed at the measuring points 6443, 6444, 6449 and 6451. The iron concentrations decreased by 32 - 61 % from concentrations of 420 to 560 mg/L to values between 195 to 330 mg/L in this monitoring area. This indicates that iron is precipitated in the subsurface. The sulphate concentrations in the aforementioned observation wells changed from values of 1120 to 1455 mg/L to values between 480 to 900 mg/L, which corresponds to a reduction of 38 - 57 %. Depending on the acid potential, decreasing iron (II), aluminum and manganese concentrations increased the neutralization potential by 8.1 - 10.9 mmol/L. This represents an improvement of 39 - 58 %. The concentrations of calcium dropped from values around 100 mg/L to values around 70 mg/L. Aluminum decreased from average concentrations of 25 mg/L to 3,5 mg/L.

In the following, the developments in the observation well 6444 are described in detail. Groundwater at this measuring point showed iron concentrations of 500 mg/L, sulphate concentrations of 1100 mg/L and a neutralization potential of -16 mmol/L at the beginning of the study. The iron concentrations could be reduced to below 200 mg/L (fig. 3), the sulphate concentrations decreased to 480 mg/L (fig. 4) by the groundwater treatment up to now.

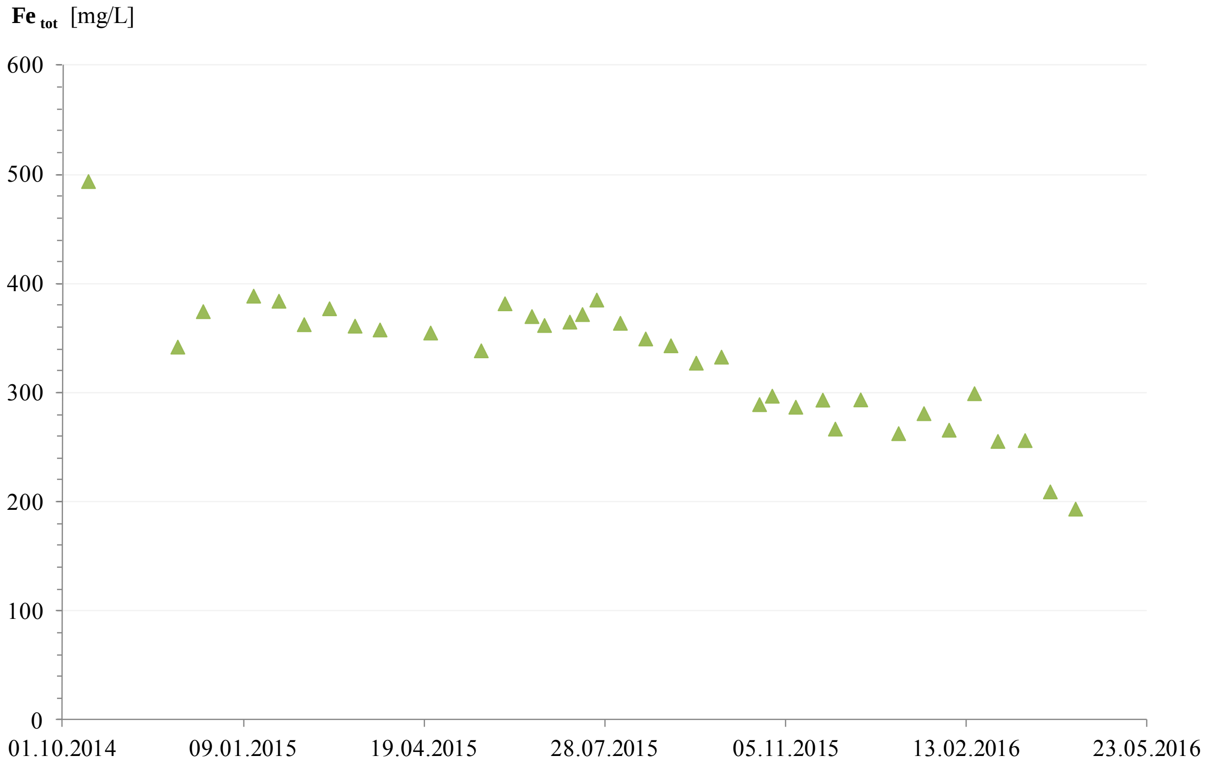

Figure 3 *Decrease of iron concentrations at groundwater observation well 6444.*

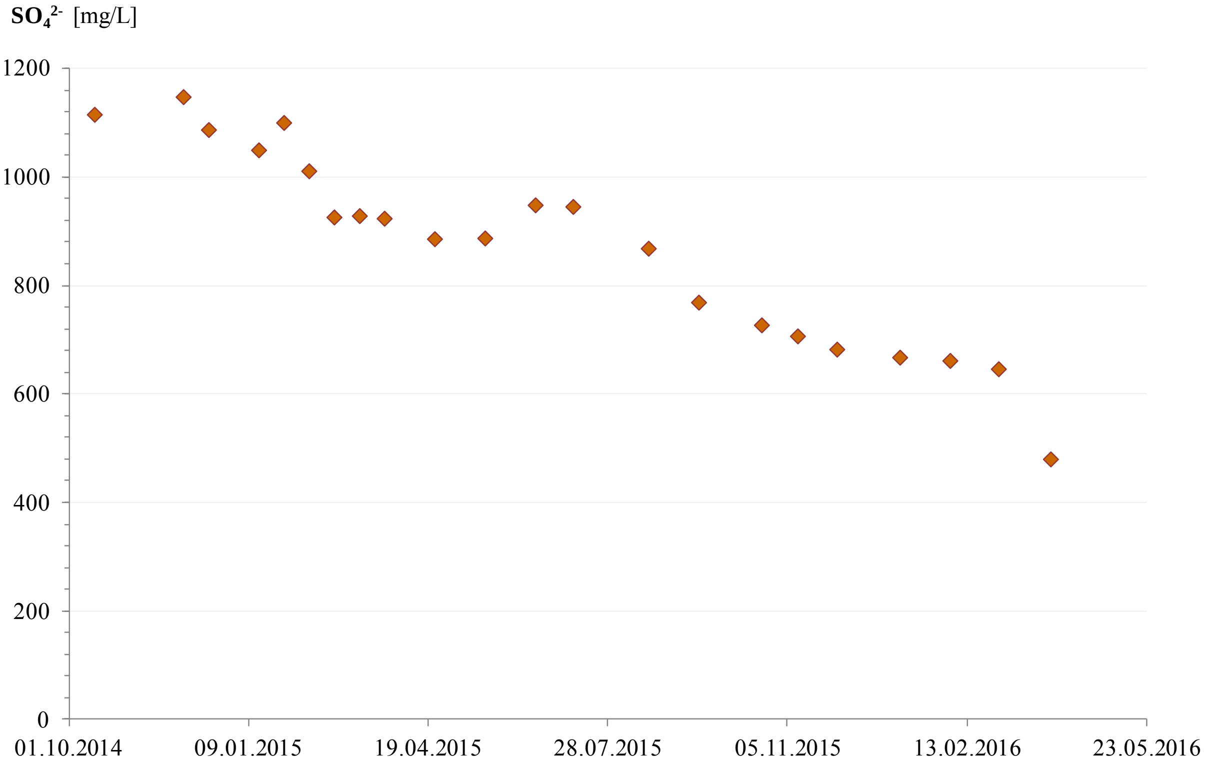

Figure 4 *Decrease of sulphate concentrations at groundwater observation well 6444.*

Evangelou (1995 in Schöpke et al. 2011) defined the neutralization potential (NP) as a measure of the acidity of water, particularly for acid mine drainage. Schöpke et al. (2011) simplified the formula as follows:

$$\mathrm{NP} \approx \mathrm{K}_{\mathrm{S}4,3} - 3\mathrm{c}_{\mathrm{AL}3+} - 2c_{Fe2+} - 2\mathrm{c}_{\mathrm{Mn}2+}$$

A neutralization effect results from precipitating again the reaction products of the pyrite oxidation, particularly iron. In the area of the observation well 6444 the neutralization potential improved by 9.2 mmol/L during the groundwater treatment (fig. 5).

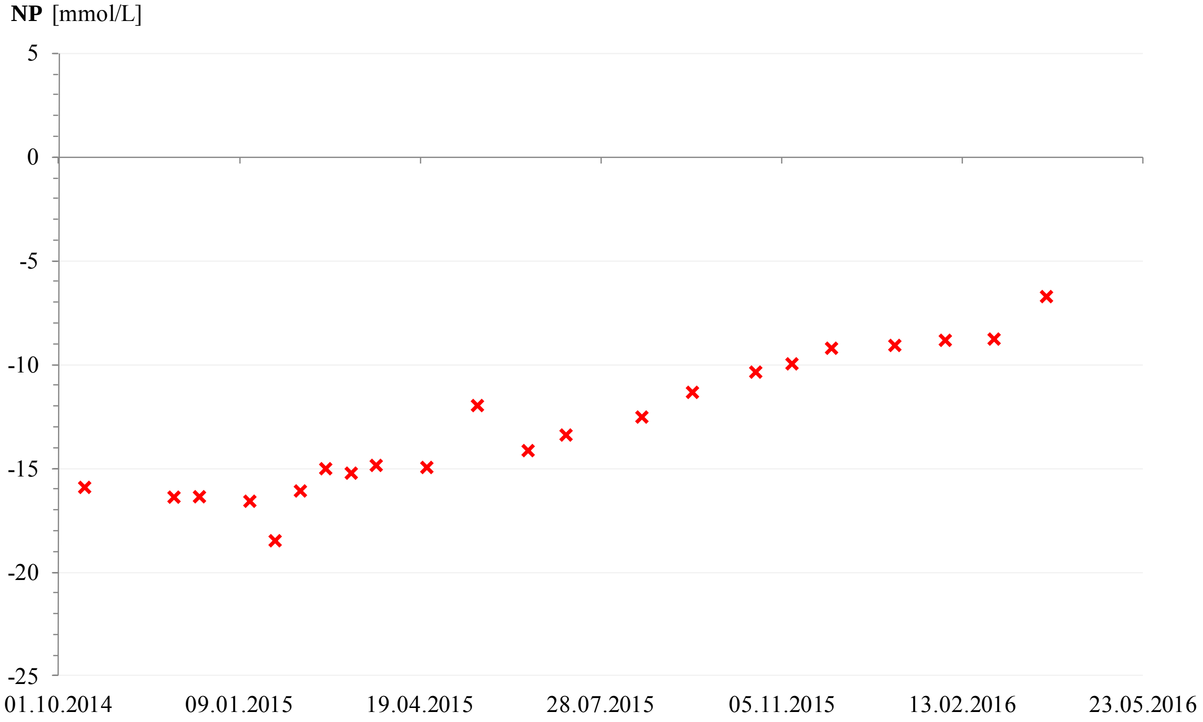

***Figure 5** Increase of neutralization potential at groundwater observation well 6444.*

Reaction area

Not all observation wells are affected equally. No changes could be detected at the measuring points 6440, 6445, 6448 and 6388. A possible reason is that the measuring points 6440, 6445 and 6388 do not receive the treated groundwater (fig. 6). An improvement of groundwater quality is detectable at all other observation wells. These results of the operation monitoring correlate with the results of the tracer experiment.

The best results could be observed at the measuring points 6443, 6444, 6449 and 6451. It can be assumed that the reaction zone further expands during the continued groundwater treatment. Additionally, through diffusion, dispersion and retardation in the flow path an increasing mixing of untreated and treated groundwater can be achieved.

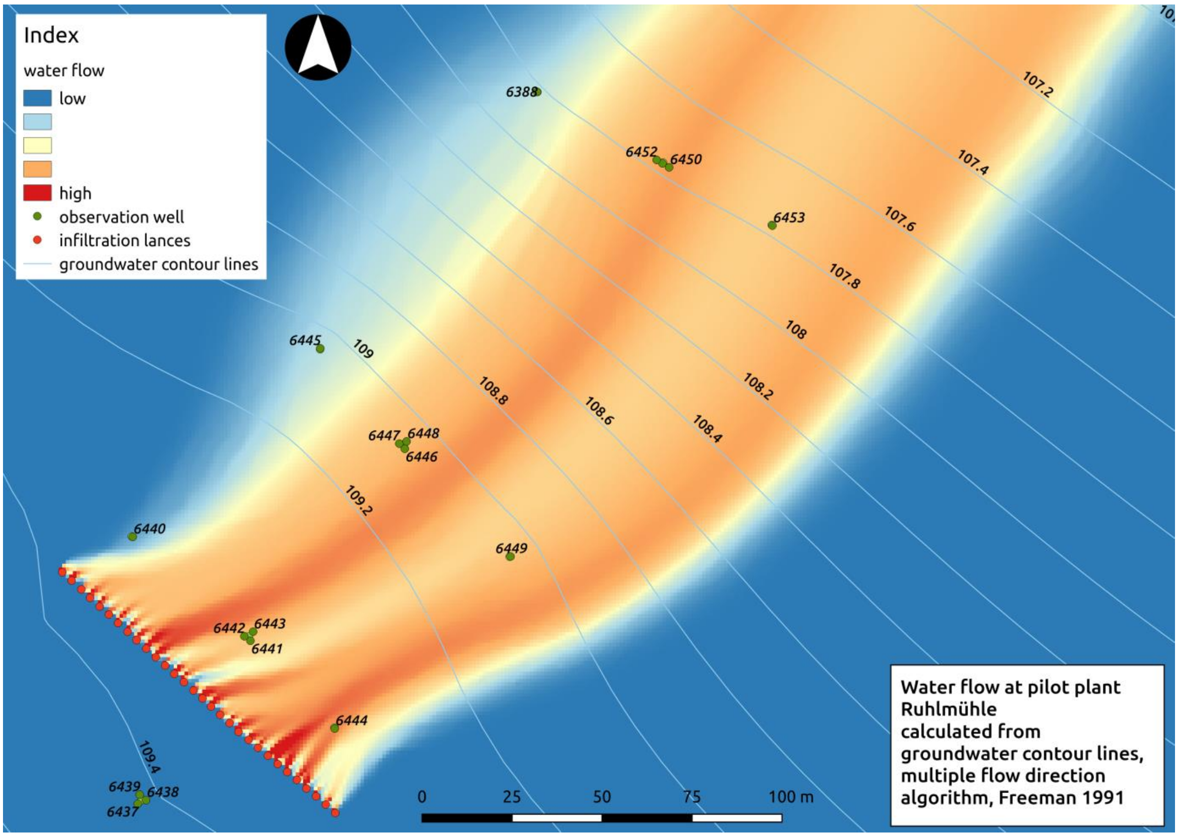

Figure 6 *Water flow at pilot plant Ruhlmühle. Shown is the direction of water flow from the infiltration lances to the stream, derived from the groundwater contour lines.*

Discussion

Sulfate reducing bacteria were stimulated with the infiltration of glycerin, while very low pH values of the groundwater indicate difficult living conditions. Experimental work of Tuttle et al. (1969) and Johnson et al. (1993) showed that SRB are able to reproduce even at pH 2.9, but not at lower pH. Our results indicate the growth of SRB about three month after stimulation by the occurrence of sulfide at the field scale, too. Even if their growth is delayed, stimulation of SRB seems to be a robust process.

Compared to a former pilot plant (Gast et al. 2010, Schöpke et al. 2013), the whole process was scaled up for the use as remediation technology. Extraction of water, dosing and infiltration is fully automated and worked reliably.

Other approaches use the process of sulfate reduction, too. Water treatment within tubes with sand could be used (example Hainer See), but all water need to be extracted, performance in winter is low and the remaining iron sulfide has to be deposed. Autotrophic sulfate reduction supports the microbes with hydrogen instead of a carbon source (Bilek et al 2007, Bilek 2012). In this case, control of the multi-level process in artificial reactors, with removal of iron sulfide and partially with pH control by CO_2 fumigation, is much more costly.

Reduced iron could be precipitated by aeration, both if oxygen is brought into the underground (as done for iron removal for drinking water pumping wells) and if the water is extracted. However, the underground may be clogged or iron hydroxide sludge has to be removed, and sulfate remains untreated. Iron precipitation without sulfate reduction is provoked during neutralization of mining lakes (Grünewald et al 2012), with remaining high sulfate concentrations at the lake outflow. Bilek (2012) gives an overview about further approaches.

In comparison, the pilot plant Ruhlmühle has some important advances. The process could reduce both iron and sulfate concentrations, and the precipitated iron sulfide remains in the subsurface.

Conclusions

Low pH-values about four of the upstream groundwater are regarded as difficult for SRB. However, the SRB have been capable to use the infiltrated glycerin for their metabolism, as indicated by sulfide formation and decreasing sulphate concentrations. Low pH-values inhibit the precipitation of iron and sulfide as iron(mono)sulfide. During the operation of the pilot plant, pH-values rose slowly due to sulphate reduction, and finally the precipitation of iron sulfide get started, as decreasing concentrations of iron indicates. Coupled to this process, pH-values rises up to 5 and accelerate the precipitation process. Nevertheless, the process needed about 16 months to show significantly decreasing iron concentrations and will still take some time, until iron concentrations < 100 mg/l are reached.

Although the process took a long time to start, the operation of the pilot plant shows already achievements of remediation. Retention of iron and sulphate in the underground are an important advantage of the process, because there are no remaining disposals. The aquifer provides constantly reduced conditions avoiding recurrent iron mobilization. Experiences from an earlier project show that the pore volume will not block, also because the iron sulfide is much smaller then iron hydroxide, which is often causes problems in wells.

In summary, the process is suitable to treat groundwater with high iron and sulphate concentrations, so called hot spots. Hot spots upstream of rivers and lakes in former mining areas are the result of the heterogeneity of the pyrite and marcasite deposits. Efforts are still needed to reduce the environmental costs of the process, for instance by identifying alternation carbon sources.

Acknowledgements

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Sulfate Reducing Bioreactor Longevity Estimates based on Substrate Characterization and Initial Carbon Release

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Abstract

Sulfate reducing bioreactors have the potential to provide treatment of mining influenced water (MIW) with low operation and maintenance requirements. However, there is a lack of validated design guidance on the specifications of the organic substrate to ensure longevity of bioreactors for metals removal. Current design criteria are based on an assumed rate of carbon release coupled to sulfate reduction from a generic substrate. Linking the specifications of the organic substrate mixtures to the rate and extent of carbon release is a first step in improving design guidance.

Three 18-liter columns were filled with one of three organic materials: woodchips, sawdust or alfalfa hay, and operated for 500 days with a MIW containing Zn ≈ 170 mg/L, Sulfate ≈ 5000 mg/L with a pH ≈ 6. The composition of organic materials was characterized using sequential chemical extractions to operationally define carbohydrate, cellulose and lignin like fractions. The carbon released by the substrate was calculated using the effluent carbon concentration and flow plus estimated carbon utilized for sulfate removal. The potential longevity was estimated based the calculated bioavailablility of the individual substrate components, the carbon released after 1.2 year of operation and two scenarios for future effluent carbon and sulfate reduction rate.

Half of the bioavailable carbon in all columns was utilized in the first 1.2 years of operation and primarily was related to effluent carbon. The estimated longevity of the columns was influenced by the effluent carbon assumption. The high value of effluent carbon used (500 mg/L as COD) was the average measured value at 1.2 years from all the columns. Zero effluent carbon was used to set a theoretical maximum longevity assuming a sulfate reduction rate of 0.3 mol/m^3/d. Our data supports a conservative estimate of SRBR substrate longevity in the 2 to 5 year range.

Key words: Treatment, Anaerobic, Bioavailability

Introduction

Mining influenced water (MIW) may contain heavy metals, metalloids, and sulfate due to the production of sulfuric acid from sulfide existing in ore bodies under aerobic condition. Physicochemical treatment processes are typically used to treat MIW by alkaline addition. Anaerobic biological treatment of MIW using sulfate-reducing bacteria (SRB) to biogenically produce sulfide is an attractive treatment alternative. Metal sulfide sludges are less voluminous that hydroxide sludges produced by alkaline treatment. Biological sulfate reduction requires the addition of a suitable electron donor, which may be provided by a range of organic materials.

Biological sulfate reduction may be implemented in a passive configuration that requires low levels of operation and maintenance. Passive treatment processes are ideal for closed mine sites characterized by remoteness and lack of accessibility for low MIW flow and projected long-term treatment duration. To date, diverse natural organic substrates such as hay, woodchips, sawdust, alfalfa, manure, walnut shells, and corn stover, have been used as the source of electrons for the biological sulfate reduction (Bless et al. 2008, Doshi 2006). The relatively low bioavailability and degradation rate of natural organic substrates will control the design and thus the treatment efficiency and rate in passive biological treatment system.

The number of passive biological MIW treatment systems in operation is still limited and the design is usually based on short-term experiments with a black box approach. The scope of this paper focuses on the evaluation of expected longevity of sulfate reducing bioreactors based on substrate bioavailability, effluent carbon and sulfate removal rates.

Methods

The sulfate reducing bioreactor columns were fed MIW collected from an inactive mine site. MIW collected from the site was stored in a 2,500 gal capacity non-transparent polyethylene tank to maintain the influent quality and to prevent algae growth during reactor operation. The key characteristics of the influent MIW were: pH ≈ 6; sulfate ≈ 5,000 mg/L; zinc ≈ 167 mg/L. PVC column reactors with an operating volume of 18-liters with height and inner diameter (ID) of 1.32 m and 0.15 m, respectively, were used to evaluate the carbon release and sulfate reduction.

The columns were packed with a single substrate or mixtures of ponderosa pine woodchip, pine sawdust, alfalfa hay, as electron sources and limestone as an alkalinity source. The packed height of the mixture of organic substrate and limestone was ≈ 1 m. The mass of substrate and limestone used in each column is shown in Table 1.

Table 1. *Substrate compositions in SRBR Columns*

Reactor ID	Organic material 70% by weight, g	Limestone 30% by weight, g
Hay	2,450	1,070
Saw dust	4,370	1,870
Wood chip	2,790	1,150

Ponderosa pine woodchip and sawdust were obtained from a lumber mill in New Mexico, USA. Locally grown alfalfa hay was purchased from a feed store in Arizona, USA. Limestone aggregate was from a limestone quarry in Arizona.

Each column was filled with MIW and liquid was recirculated from bottom to top of reactor at ~15 L/day for 1 month followed by inoculation with ≈ 500 mL of a sulfate reducing mixed culture. Column liquid was subsequently recirculated for 1 month. Column operation was then changed to continuous down-flow mode with an initial flow rate of 0.4 L/day, flow rate varied between 0.1 and 1.6 L/day over the 500 days of operation. Additional details about the experimental system may be found in Landkamer et al. (2013).

Effluent organic carbon was measured using a Shimadzu TOC analyzer. COD and sulfate concentrations were measured by the HACH methods. Anaerobic bioassays (modified from Owen et al. 1979) were conducted to estimate the bioavailable fraction of the substrates. The biodegradable component was defined as the difference between the initial and final mass of the organic substrate evaluated. The bioavailability of the substrate was also calculated based on lignin fraction using a modification of the Chandler et al. (1980) and Van Soest (1967) methods. Operationally defined organic fractions of organic substrate were estimated by sequential extraction in hot water (TAPPI Method 207 om-88) followed by acid (National Renewal Energy Laboratory, Chemical and Analytical Testing Laboratory Analytical Procedure - Determination of Acid-Insoluble Lignin in Biomass, 1995).

The amount of carbon released from the organic substrate in the column was estimated by the cumulative amount of effluent organic carbon and the calculated organic carbon needed to support the measured sulfate reduction. Units of chemical oxygen demand (COD) were used to evaluate organic matter consumption. Organic carbon (OC) concentration was converted to COD units by a factor of 2.67 g COD/g OC. A ratio of 70.4 g COD/mmol sulfate removed was used to convert sulfate to COD units. The ratio is based on the amount of COD needed for sulfate reduction and cell growth.

Results and Discussion

The results presented herein focus on estimating organic carbon release and prediction of the bioreactor column longevity. Information on metal removal and microbiology is presented in Landkamer et al. (2013). The initial organic carbon content of the substrate was based on the measued COD of the solid phase organic substrate and a conversion factor of 2.67 g COD/g C. The amount of solid phase organic mass degraded in the anaerobic bioassay was comparable to the value calculated from the operationally defined composition and the Chandler and Van Soest equations. The estimated total carbon, initial bioavailable carbon and remaining bioavailable carbon at 1.2 years is presented in Table 1. The longevity of the substrate is presented relative to the fraction of bioavailable carbon remaining with time for hay, sawdust and woodchip in Figures 1, 2 and 3, respectively. The fraction of bioavailable carbon released versus time in the first 1.2 years is based on the cummulative amount of effluent carbon and the estimated carbon consumption associated with the measured sulfate reduction. The high value of effluent carbon used (500 mg/L as COD) in predicting longevity, was the average measured value at 1.2 years from all the columns. Zero effluent carbon was used to set a theoretical maximum longevity assuming a sulfate reduction rate of 0.3 mol/m^3/d.

Table 2. *Estimated total and bioavailable organics in columns*

Reactor ID	Initial organic carbon, grams	Estimated initial bioavailable organic carbon, grams	Estimated bioavailable organic carbon remaining at 1.2 years, grams
Hay	1080	550	260
Saw dust	2110	105	50
Wood chip	1370	70	35

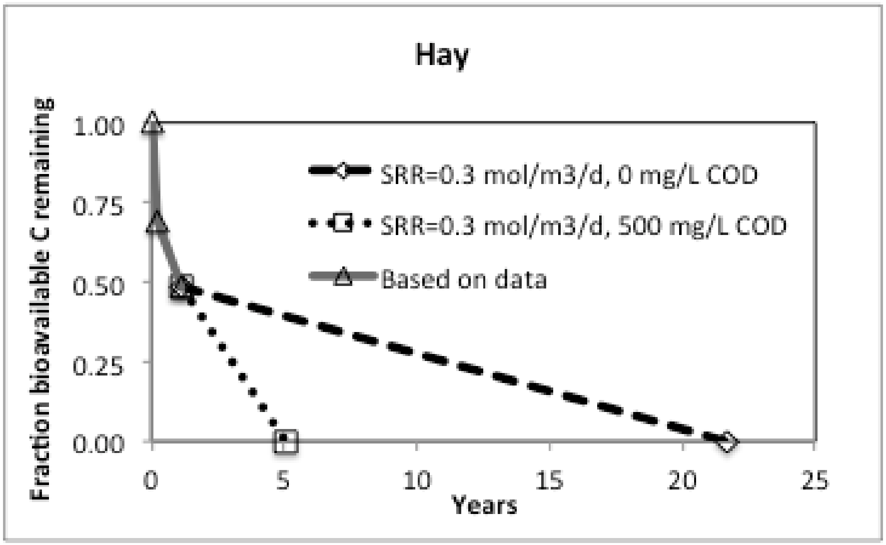

Figure 1 *Estimated bioavailable carbon utilized through 1.2 years and predicted bioavailable carbon remaining with time for hay under two scenarios of effluent carbon concentration and sulfate reduction rate.*

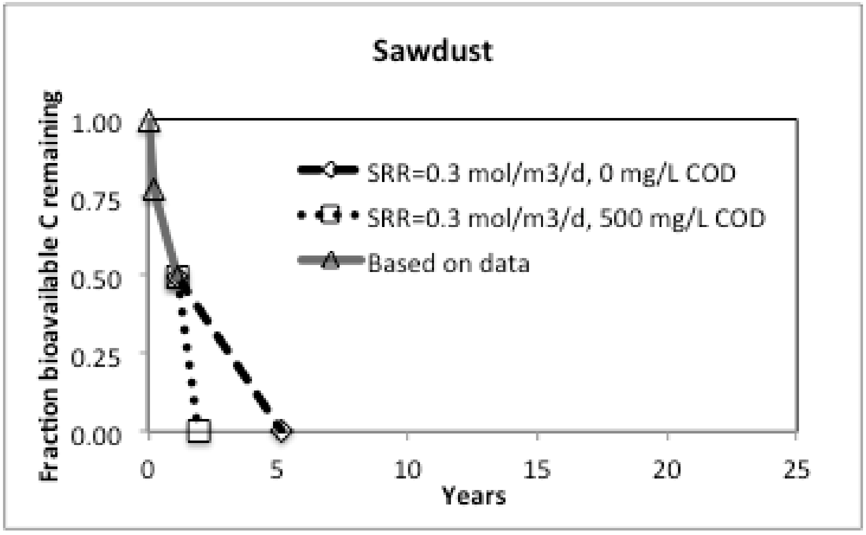

***Figure 2** Estimated bioavailable carbon utilized through 1.2 years and predicted bioavailable carbon remaining with time for sawdust under two scenarios of effluent carbon concentration and sulfate reduction rate*

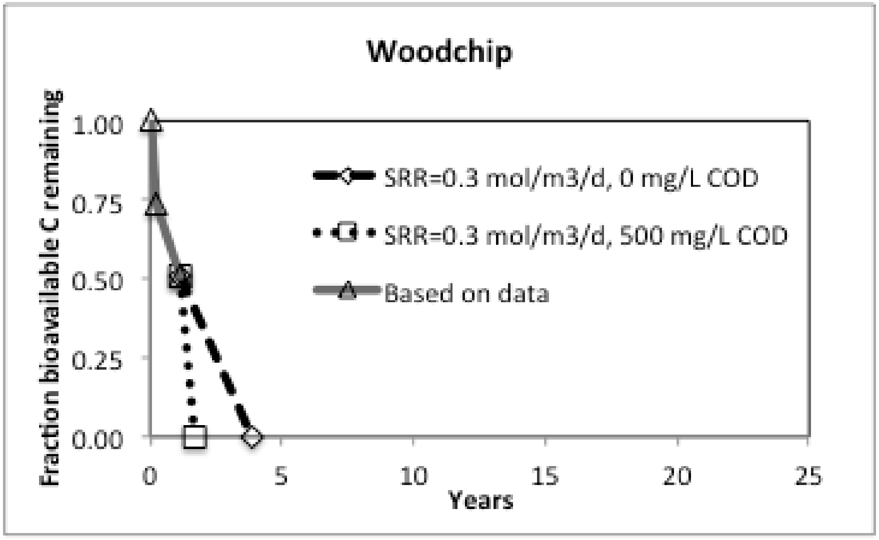

***Figure 3** Estimated bioavailable carbon utilized through 1.2 years and predicted bioavailable carbon remaining with time for woodchip under two scenarios of effluent carbon concentration and sulfate reduction rate.*

It is important to establish a method to estimate the expected longevity of sulfate reducing bioreactors to appropriately evaluate the comparative costs relative to other technologies. The expected life-time of sulfate reducing bioreactors has been projected to be up to 50 years (Gusek and Schneider 2010). However, there is no data to support long-term operation of sulfate reducing bioreactors at the projected sulfate reduction rate of 0.3 mol/m^3/d. In a recent review of sulfate reducing bioreactors, the rate of sulfate reduction was reported to range from 0.02 to 3.5 mol/m^3/d (Fitch 2015). The longevity of sulfate reducing bioreactors for metal removal will depend on amount of biodegradable organic substrate, the rate of carbon release and utilization by the microbial community. Two methods were used to estimate bioavailable organic carbon from initial total organic content of the organic substrates. Methods to predict the rate of organic carbon release and utilization are still needed. The effect of the assumed rates of carbon release and utilization resulted in a wide range of predicted longevity.

Conclusions

Our data suggests that predicted sulfate reducing bioreactor life-time of decades is overly optimistic. Half of the bioavailable carbon in both the alfalfa and woodchip columns was utilized in the first 1.2 years of operation and primarily was related to effluent carbon. The estimated longevity of the columns was influenced by the effluent carbon and the sulfate reduction rate assumptions. Our work supports a conservative estimate of sulfate reducing bioreactor substrate longevity in the 2 to 5 year range.

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Development of a pilot-scale semi-passive system for the bioremediation of ARD

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Abstract

Acid rock drainage from diffuse sources such as waste rock dumps, tailings impoundments and discard coal dumps represents a significant environmental risk to South Africa, particularly with respect to sulphate salinity. Passive or semi-passive remediation options may be more practical, sustainable and affordable in many cases. Where sulphate salinity is a concern, biological sulphate reduction (BSR) plays a key role. Widespread application of BSR has been constrained by the cost of the electron donor, process kinetics and management of the sulphide product. The system developed addresses the challenge of biomass retention by employing submerged carbon microfibers to provide a large surface area for microbial attachment. Electron donor for the sulphate reduction and sulphide oxidation is provided by the anaerobic degradation of complex organic carbon sources (eg grass, algae, manure) in a separate hydrolysis reactor. Finally, sulphide management is achieved through the partial oxidation of aqueous sulphide to elemental sulphur, which is recovered as a value-adding product. Extensive laboratory-scale tests have demonstrated proof of concept, achieving sulphate reduction efficiencies of over 90% at a feed concentration of 1 g/l. Efficient biomass retention resulted in volumetric sulphate reduction rates over 50% higher than in corresponding stirred tank reactors. In excess of 70% of the sulphur in the feed (as sulphate) was recovered as elemental sulphur in the harvested biofilm. Process optimisation, at laboratory scale, suggested a 2 day hydraulic residence time (HRT), with biofilm harvesting every 4-5 HRTs. A pilot scale system consisting of three 2000 l reactors has been installed at a colliery in South Africa, to initially treat 1000 l/day. Sulphate reducing inoculum was prepared in a series of 210 l and 1000 l containers. A number of technical and logistical challenges have been overcome, leading to successful re-inoculation and demonstration of proof of concept at pilot scale.

Key words: Semi-passive process, sulphate reduction, sulphide oxidation, minewater remediation

Introduction

The contamination of surface and groundwater by acid mine drainage (AMD) and acid rock drainage (ARD) and the consequences for the environment, agriculture and human health are serious concerns in the regions of South Africa impacted by mining activities. The longer-term impact of mining activities, particularly coal mining, is predicted to be worse in South Africa than other countries as a result of a unique combination of climate, geography, scale of deposits and population distribution (McCarthy, 2011).

Acid drainage is generated via the oxidation of sulphide minerals, typically pyrite, when exposed to oxygen and water (Johnson and Hallberg, 2005; McCarthy, 2011). In South Africa, mine water can be divided into two broad categories. The first, AMD, originates from the rebound of groundwater through abandoned mine workings, once dewatering has ceased and is characterised by large volumes of heavily impacted water. The volume and composition of the AMD precludes the application of biological treatment options in most cases. The second type, referred to as acid rock drainage (ARD) in this paper, originates from diffuse sources, such as waste rock dumps, tailings impoundments, coal discard heaps and unworked pits. These sites are more numerous, are likely to affect a greater area and can persist for decades. Acid rock drainage, from diffuse sources as well as end-of-pipe sources, is more amenable to biological treatment.

A variety of technologies have been developed for the treatment of AMD and ARD. The established methods are based on oxidation, neutralisation, precipitation and sedimentation. The most appropriate treatment is dependent upon the volume of the effluent, concentration type of contaminants and the pH of the water (Gazea *et al*., 1996). Acid drainage treatment technologies can be divided into two broad categories, active and passive treatment systems.

Active treatment typically involves the installation of agitated reactors or similar units, which require constant energy input. Furthermore, the addition of alkaline chemicals and reagents to treat the acidic effluent can become costly, given that the drainage may persist for several decades, or longer, at decommissioned mine sites (Gazea *et al*., 1996). The energy intensity and extensive use of lime mean the long-term sustainability of many active treatment technologies is questionable, both from an economic and environmental perspective.

Passive systems depend on processes that are kinetically slower than those involved in active systems and thus require longer hydraulic retention times (HRTs) and larger areas to achieve similar results. Passive treatment options include anoxic limestone drains, permeable reactive barriers, natural and constructed wetlands and engineered biological treatment systems.

Biological treatment has the potential to be more cost effective and sustainable than the physical and chemical processes mentioned above. The biological treatment of ARD is centred on the activity of sulphate-reducing bacteria (SRB), which are able to reduce sulphate to sulphide, coupled to the oxidation of an electron donor, typically an organic carbon molecule. The sulphate is reduced to sulphide, coupled to the simultaneous generation of alkalinity, predominantly as bicarbonate (HCO_3^-). From an ARD treatment perspective the alkalinity acts to neutralise the acidity while the sulphide is available for the precipitation of metals as metal sulphides (Johnson and Hallberg, 2005).

A number of active commercial processes, based on biological sulphate reduction, have been developed (Janssen *et al*, 1995; Rose, 2013), but their widespread application has been constrained by three factors. These are the cost of the electron donor, the relatively slow growth of sulphate reducers and the associated kinetic constraints and the management of the sulphide product. The disadvantages of conventional active and passive biological systems has led to the development of semi-passive or managed passive systems and South African researchers have played a leading role in this. The Integrated Managed Passive (IMPI) process was developed by Pulles Howard and de Lange with the aim of achieving high rates of sulphate reduction over a sustained period, utilising lignocellulosic material as the source of electron donor. The hydrolysis of lignocellulose was identified as the rate limiting step and long-term reactor studies allowed the characterisation of five distinct phases of sulphate reduction in passive systems (Molwantwa *et al*, 2010).

A demonstration scale IMPI system, designed to treat 200 m^3 of minewater, was constructed at the Middelburg mine in Mpumalanga. The system contained a novel sulphide oxidation reactor, the linear flow channel reactor (LFCR) which made use of a floating sulphur biofilm to achieve partial oxidation of sulphide. The system was affected by a number of construction and operational issues, as well as challenges with the LFCR and performance did not meet expectations. A detailed study into the LFCR was conducted at the University of Cape Town, leading to further optimisation in design and operating parameters (van Hille and Mooruth, 2013).

A parallel research project, investigating options for biomass retention to enhance sulphate reduction performance and low hydraulic residence times (van Hille *et al*, 2015) demonstrated that carbon microfibres provided an ideal support matrix for the attachment of SRB. The reactor was sealed with an air-tight lid, but sufficient oxygen entered the reactor to support the formation of a floating sulphur biofilm at the air-liquid interface. This suggested that the sulphate reduction and sulphide oxidation reactions could occur simultaneously within a single reactor. The detailed hydrodynamic study performed on the LFCR (Mooruth, 2013) showed no turbulent mixing within the reactor and confirmed the existence of a microaerobic zone within the floating biofilm, while the majority of the bulk liquid remained anaerobic.

Previous research at UCT investigating the anaerobic digestion of microalgal species showed that the digestate produced during fed-batch operation retained significant (2-4 g/l) soluble COD and that this was primarily composed of acetate and propionate, potential electron donors for SRB. The digestate was used as the base for an SRB feed medium and the results showed similar or improved sulphate reduction performance in CSTRs when compared to parallel reactors fed on lactate-based Postgate medium (van Hille *et al,* 2015).

The data from the various research programmes led to the conceptual design of an integrated semi-passive process for ARD treatment consisting of an LFCR, containing carbon microfibers, which could support simultaneous sulphate reduction and partial sulphide oxidation, with the recovery of a value adding elemental sulphur product. Effluent from a biogas digester or similar anaerobic reactor could be used as the electron donor and carbon source. This paper provides a summary of the proof of concept of the combined channel reactor, the study to determine optimal HRT and describes the process of scale-up to a pilot scale system at the New Vaal Colliery.

Methods

Microbial cultures

The sulphate reducing bacteria (SRB) mixed microbial community was obtained from the Department of Microbiology, Biochemistry and Biotechnology at Rhodes University, originally from the anaerobic compartment of a facultative pond at the Grahamstown sewage treatment works, and has been maintained on modified Postagate B medium at UCT since 1999 (van Hille and Mooruth, 2013). The sulphide oxidising bacteria (SOB) culture was obtained from previous studies (van Hille and Mooruth, 2013) on sulphide oxidation conducted within the Centre.

Linear flow channel reactors (LFCRs)

The channel reactor provided a flow-through system with no turbulent mixing. It was constructed from Perspex (11 mm thickness) and had internal dimensions of 250 mm (l) x 10 mm (w) x 15 mm (h). The front wall of the reactor was fitted with nine sample ports, allowing sampling in a horizontal and vertical direction. The reactor was fitted with three ports in the left wall and three at equivalent heights in the right wall. Effluent flowed from the top outlet port, maintaining a liquid height in the reactor of 85 mm, giving a working volume of 2.125 l. A plastic strip (10 mm wide) holding carbon microfibers (AMT Composites, Cape Town) was suspended between the middle ports. The strip had bundles of microfibers (90 mm long) protruding from each side. A heat exchanger (4 mm ID) was fitted between the lower ports and facilitated temperature control by pumping warm or cold water through it. Feed was pumped in continuously from the uppermost port and effluent flowed from the equivalent port on the far side.

The pilot scale channel reactors were constructed of Plexiglass (15 mm thickness) with dimensions of 3 050 mm (l) x 1 350 mm (w) x 750 mm (h). At a working liquid height of 500 mm the volume was just over 2 000 l. The front wall of the reactor was fitted with 15 sampling points. The left and right side walls contained a single port (30 mm diameter) for fresh feed and effluent outflow. The reactor contained three parallel beams, manufactured from two pieces of aluminium angle between which the carbon fibres were held. The fibres extended approximately 200 mm from each side of the beam. The sulphur harvesting screen was constructed of aluminium square tubing which created a frame that held the same plastic mesh as shown in the laboratory scale reactor. The constructed pilot scale LFCR, fitted with the carbon fibre beams and harvesting screen and loaded into the support stand at the New Vaal site is shown in Figure 1.

Analytical methods

All pH testing was done on a Cyberscan 2500 micro pH meter. The meter was calibrated daily using standard (pH of 4.0 and 7.0) buffer solutions. Aqueous sulphide was quantified using the colorimetric DMPD method (APHA, 2005).

Figure 1 *Image illustrating the pilot scale LFCR reactor on site, prior to inoculation*

For the laboratory-scale experiments anions (sulphate, chloride, phosphate and nitrate) were measured using a Dionex ICS-1600 system. The system was equipped with an AS22 anion column, a 10 µl injection loop and a conductivity detector with suppression. Mobile phase (22 mM NaOH) was pumped through at a rate of 1.5 ml/min. Anion standards (20, 40, 60, 80 and 100 mg/l) were prepared using sodium salts. Dissolved sulphate concentrations at the pilot site were measured using the barium sulphate method (APHA, 2005).

A full volatile fatty acids (VFAs) analysis was conducted to quantify the concentration of lactic, acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acids. The concentration of each VFA was determined using HPLC on a Waters Breeze 2 HPLC system equipped with a Bio-Rad Organics Acids ROA column and a UV (210 nm wavelength) detector (van Hille and Mooruth, 2013).

Proof of concept study

To test proof of concept the small LFCR was inoculated with a mixture of the SRB and SOB cultures and fed with modified Postgate B medium (1 000 mg/l SO_4^{2-}) at a rate equivalent to a 4 day HRT. The temperature was controlled at 30˚C. Samples (2 ml) were removed daily from the middle (FM) and lower (FB) sample ports in the first and third (BM and BB) rows, as well as from the effluent port. The pH and sulphide concentration were measured immediately, after which the remainder of the sample was prepared for chromatographic analysis (VFAs and anions). Biofilm formation was observed visually and once a thick, stable biofilm had been formed it was periodically harvested by physically breaking it apart so that the fragments sank onto the submerged screen. The sulphur product was recovered by removing the screen.

Hydraulic residence time study

The effect of HRT on the performance of the system was investigated by changing the feed rate to the reactor. Prior to the start of the study, stable performance was established at a 4 day HRT. The biofilm was harvested on day 0, when monitoring of the experiment began. The reactor was fed with modified Postgate B medium at a flow rate of 0.53 l/d and sampled daily, as described above. Effluent from the reactor was collected in a sealed bottle over varying time intervals and the volume quantified to confirm the HRT. A portion of the collected effluent was treated for chromatographic analysis, while the rest was used to measure pH and redox potential.

After approximately 3 HRTs the biofilm was collapsed, by physically breaking it up and allowing the fragments to sink and settle on the screen. The biofilm reformed within 24 hours and after another 3 HRTs the biofilm was collapsed again and the sulphur harvested by removing the screen and transferring the solids to a glass petri dish for drying and further analysis. Following harvesting, the feed rate was increased to achieve the next HRT and the process was repeated, terminating at an HRT of 0.5 d. The one exception to the procedure described above occurred after the first biofilm collapse in the 4 d HRT study, where the biofilm was allowed to persist for just over 7 HRTs to determine whether the biofilm would collapse, unassisted, under the mass of accumulated sulphur.

Inoculum scale-up and pilot plant inoculation

The microbial inoculum, containing the sulphate reducing and sulphide oxidising consortia, was scaled-up in order to inoculate the 2 000 l pilot scale reactors. Inoculum build-up was started at laboratory scale in a series of 10 and 15 l glass containers, maintained in batch mode on an acetate based medium with an initial sulphate concentration of 3 500 mg/l. Stock cultures from these reactors were blended into four 25 l plastic drum, transported to the mine site and used to inoculate four 210 l drums containing raw mine water. Each 210 l drum was supplemented with 500 g of sodium acetate and 100 g of yeast extract. More recently, a 1000 l tank was inoculated so that over 1 800 l of active inoculum can be maintained.

The first of the 2 000 l channel reactors was filled with raw minewater from the active pit, diluted to a sulphate concentration of 2 000 mg/l and inoculated with 380 l of SRB inoculum on 3 November 2015. During December 2015 ingress of clean water into the pit reduced the suphate concentration to below 250 mg/l, negatively affecting the reactor and inoculum cultures. Subsequently, sodium sulphate from the mine's freeze crystallisation plant was used to supplement the raw feed. The channel reactor was reinoculated at the beginning of May 2016, with 1 200 l of active SRB inoculum.

Results and discussion

The results from the proof of concept and optimisation of HRT studies have been described in greater detail elsewhere (van Hille *et al.*, under review) and will be summarised here to provide context for the scale-up to pilot scale.

The reactor was inoculated with an active SRB culture and the initial sulphide concentration was approximately 250 mg/l. This decreased rapidly during the first hours following inoculation as a result of unimpeded oxygen mass transfer across the liquid surface, resulting in the sulphide oxidation at the surface. However, within 24 hours a thin, but complete biofilm was observed over the entire surface. The biofilm provides a barrier that slows down oxygen mass transfer and creates the necessary redox microenvironment to support partial oxidation of sulphide to elemental sulphur.

Once the biofilm had formed the aqueous sulphide concentration in the bulk liquid began to increase steadily, from around 80 mg/l to over 230 mg/l by day 10. This indicated effective sulphate reduction, which was confirmed by the residual sulphate data that showed between 85% and 95% sulphate reduction efficiency. No significant sulphide was measured in the effluent from the reactor, suggesting that sulphide oxidation within the biofilm was complete. The rate of sulphide oxidation was significantly higher than that achieved in an actively aerated abiotic system (van Hille and Mooruth, 2013), confirming the activity of the sulphide oxidising microbes.

Harvesting the biofilm resulted in a rapid and significant decrease in the sulphide concentration in the bulk liquid, again a consequence of removing the barrier to oxygen mass transfer and the sulphide concentration only increased again once the biofilm had reformed. Sulphate reduction rates were not affected at all, indicating that all oxygen entering the reactor was consumed at the surface and the bulk of the reactor liquid remained anaerobic (confirmed by redox potential data).

After approximately seven days the biofilm was thick and had a characteristic white to yellow colour, indicative of elemental sulphur (Figure 2a). Physical disruption of the biofilm caused the fragments to sink and these were collected on the submerged harvesting screen (Figure 2b). The final product was a mixture of elemental sulphur and organic material (Figure 2c).

The reactor was operated for just under 100 days, through a series of biofilm development and harvest cycles and demonstrated consistently effective sulphate reduction (>80%) and removal of the sulphide product. The pH remained stable (pH 7.5-7.8) and loss of sulphide as H_2S gas was insignificant. The experiment demonstrated that effective sulphate reduction and partial sulphide oxidation was possible within a single reactor unit and that the sulphur product could be easily harvested.

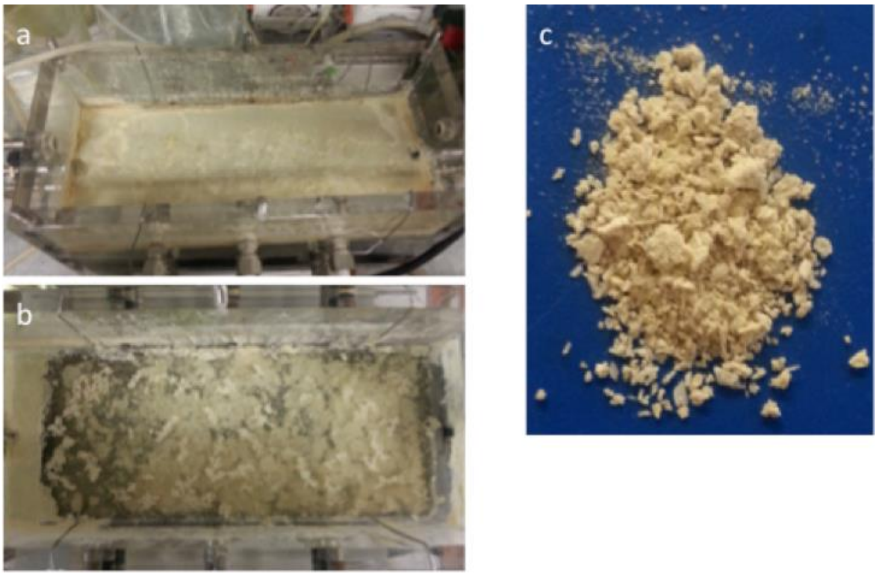

Figure 2 *Photographs showing (a) complete biofilm prior to collapse, (b) the biofilm following collapse onto the submerged screen and (c) the dried sulphur product*

The next phase of the research was aimed at determining the optimal hydraulic retention time. The sulphate reduction and sulphide oxidation reactions occur in spatially distinct regions of the reactor. The sulphate reduction occurs in the bulk volume, while the sulphide oxidation is essentially confined to the air-liquid interface, so is surface area rather than volume dependent. For the system to be effective, the rate of sulphate reduction cannot significantly exceed the rate of sulphide oxidation.

The aqueous sulphide data (Figure 3) showed a similar trend to that observed during the proof of concept study, with a steady increase in sulphide concentration followed by a raid decrease immediately after collapse or harvesting of the biofilm.

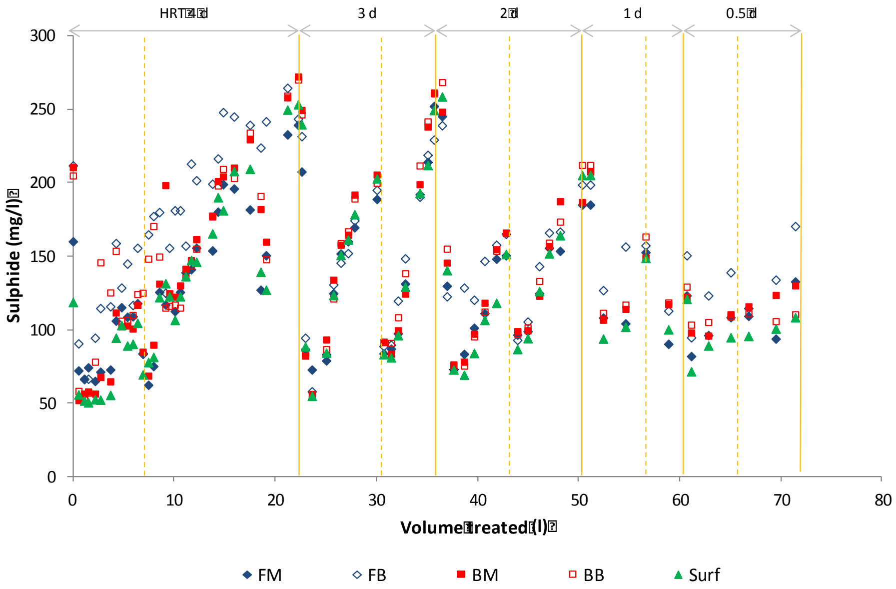

Figure 3 *Aqueous sulphide concentration at different points in the reactor as a function of HRT. Dashed vertical lines indicate biofilm collapse, while complete vertical lines indicate biofilm harvesting*

The data are presented as a function of volume treated, rather than time, to prevent compression of the data points at the low HRTs. The maximum sulphide concentration attained decreased with decreasing HRT, suggesting that sulphate reduction efficiency may decrease at low HRT. Concentrations in excess of 200 mg/l were achieved at HRTs between 4 and 2 days.

The sulphate reduction data (Figure 4) were consistent with the sulphide data. Initially, while the SRB were colonising the carbon fibres, the sulphate reduction efficiency was around 50%, but this increased significantly after about 30 days. Almost complete sulphate reduction (>95%) was achieved at a 3 and 2 day HRT. While the residual sulphate concentration did increase at the lower HRTs, it remained above 70% at an HRT of 12 hours. This equates to a volumetric sulphate reduction rate of 62.5 mg/l.h, which is significantly higher than the maximum observed in a conventional CSTR (39 mg/l.h) and similar to that achieved in a hybrid system using membrane filtration to achieve biomass retention.

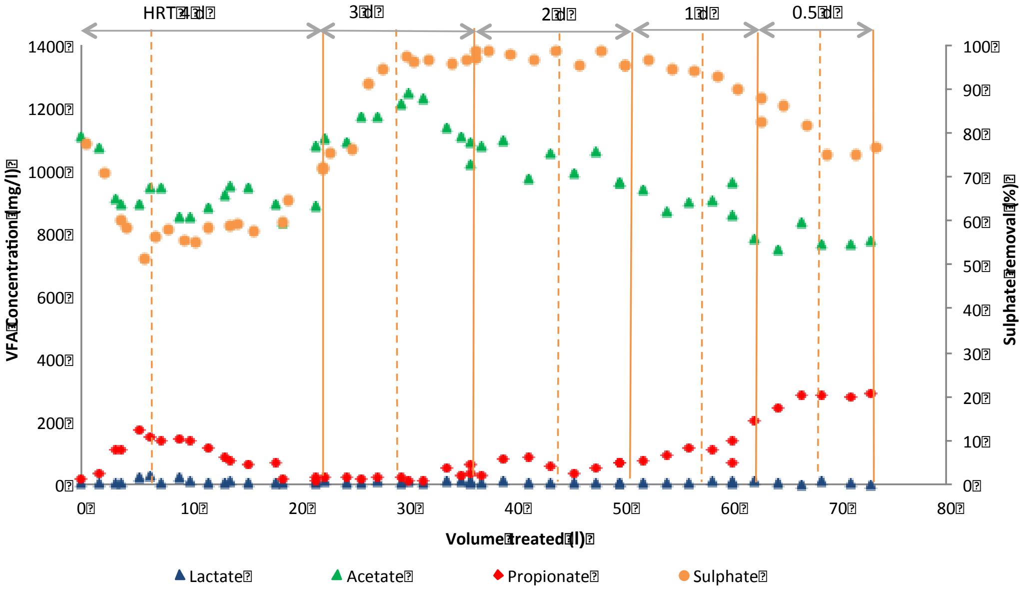

Figure 4 *Mean sulphate reduction efficiency and residual VFA concentrations measured during the HRT optimisation study*

At the 1 day HRT sulphide was detected in the reactor effluent and this concentration increased at the 12 hour HRT, indicating that sulphide oxidation became rate limiting. In addition, the volatile fatty acid data suggested a shift in microbial metabolism at HRTs below 1 day. While lactate utilisation remained complete, significant concentrations of propionate were detected in the effluent. Propionate is indicative of lactate fermentation, rather than oxidation, confirming a shift in microbial community structure. This phenomenon was observed previously in CSTRs (Oyekola *et al*., 2012) and was attributed to a combination of the decrease in sulphide concentration, to levels which no longer inhibit lactate fermenters, and increase in available lactate as sulphate reduction efficiency decreased.

The performance data suggest that a 2 day HRT is optimum for achieving a high volumetric sulphate reduction and sulphide oxidation rate. Gravimetric analysis of the harvested biofilm, used to complete the sulphur mass balance, confirmed the highest sulphur recovery efficiency was achieved at a 2 day HRT.

Inoculum scale-up and pilot plant inoculation

The three 2 000 l channel reactors have been set up on site at the New Vaal Colliery outside Vereeniging. Each reactor has been placed on a purpose built steel stand, which provides additional structural support to prevent bulging of the walls of the Perspex reactors. The height of the stands has been staggered to facilitate gravity flow between the reactors when connected in series.

The first reactor was inoculated with around 380 l of SRB inoculum on the 2nd of November 2015. The original intention was to use sufficient inoculum to achieve an initial sulphide concentration of around 150 mg/l, to provide enough sulphide to form a complete biofilm across the surface of the reactor. However, due to a limited volume of inoculum being available the initial sulphide concentration was only 67 mg/l. After 24 hours a thin sulphur film had formed on the surface on the reactor, with the aqueous sulphide concentration being reduced to below 10 mg/l at all points sampled.

These data confirmed the presence of an active sulphide oxidising community. The reactor was sampled again on the 10th of November and the aqueous sulphide concentrations remained low. The sulphate concentration had decreased from approximately 2 000 mg/l to just over 1 700 mg/l. While this showed some sulphate reduction activity, the rate (1.56 mg/l/h) was significantly lower than equivalent rates achieved in the laboratory reactors.

Following the challenges resulting from the significant improvement in pit water quality additional SRB inoculum was grown up. This allowed the channel to be reinoculated with a greater volume of active culture and resulted in a higher initial sulphide concentration (180 mg/l). Sampling after 48 hours revealed a complete biofilm over the entire reactor surface, the expected stratification in residual sulphide (70-80 mg/l near the surface and 160-180 mg/l near the bottom) and an average residual sulphate concentration of 1 400 mg/l. This represented a sulphate reduction rate of 12.5 mg/l/h.

Conclusions

The research conducted to date has demonstrated the feasibility of a novel reactor configuration that simultaneously facilitates high rates of sulphate reduction and sulphide oxidation in a low cost unit, suitable for passive or semi-passive operation. The efficient retention of the SRB on the carbon microfibres supports the high sulphate reduction rates, while the sulphur product can be easily recovered by collapsing the biofilm onto a removable screen.

The successful demonstration of the reactor at laboratory scale has prompted the evaluation of the technology at pilot scale, with three 2 000 l units installed at the New Vaal Colliery. The first reactor was inoculated in November 2015. A number of challenges, particularly relating to water quality, have been experienced on site, but these have been overcome and the system was re-inoculated at the beginning of May 2016, with very encouraging results.

Acknowledgements

The authors gratefully acknowledge the Water Research Commission for financial support of the laboratory-scale research, Anglo American for funding the capital cost of the pilot plant, Coaltech for covering the running costs and New Vaal Colliery for hosting the pilot plant and assisting with commissioning. Tynan Marais acknowledges support from the South African Research Chairs Initiative (SARChI) of the Department of Science and Technology (DST) and the National Research Foundation (NRF) of South Africa. Rob van Hille acknowledges support from the NRF through a Competitive Support for Unrated Researchers (CSUR) grant.

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On site feasibility study on biotechnical sulphate reduction

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Abstract

Reduction of sulphate load in groundwater and surface water are one of lignite mining related tasks in Germany. *On site* investigations on biotechnical sulphate reduction in surface water were realized by Vita 34 on a pilot scale. This test was financed by LMBV, who is in charge of the mining liabilities of lignite mining. Sulphate rich water demands long-lasting treatment to minimize environmental impacts.

At a former lignite mining site near Leipzig (Saxony, Germany), a pilot system for sulphate removal using a fixed bed system was constructed, operated and monitored (Schumann and Hebner 2012) . For efficient pollutant removal the following main processes were applied:

- microbial reduction of sulphate to sulfide ions
- oxidation of iron to ferrous iron
- reaction of sulfid ions with ferrous iron and precipitation of iron sulphide.

Sulphate rich surface water from a nearby channel (fig. 1) was pumped into the pilot system consisting of three treatment stages. Most important advantages of this technology are: subsurface installation of a fixed bed, no treatment residues are be generated, low demand on energy and technical equipment.

***Figure 1** Ariel view of former lignite mining site in Saxony (Source: LMBV)*

Beside the pH-value, TOC, TIC, sulphate, sulfide and iron content, calcium concentration and acid capacity were monitored during six months at several monitoring points along the treatment chain.

The sulphate content of about 1,120 mg/L was reduced to <300 mg/L (target value) in surface water. During pilot investigations a maximum sulphate reduction rate of about 6.7 mol/(m^3*d) respectively

3 mol/d was achieved. Figure 1 shows cumulated sulphate load in the inlet and outlet of the pilot system during operation.

Besides, dependency of sulphate reduction rate on temperature, carbon and sulphate availability, changes in pH-value and content of dissolved iron were verified.

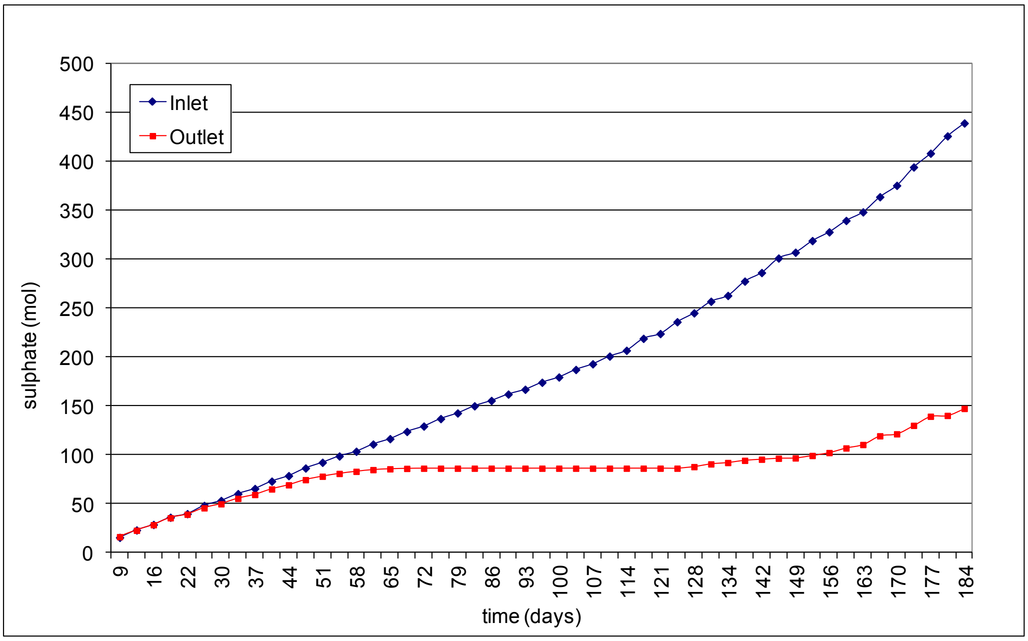

Figure 2 *cumulative sulphate amount in inlet and outlet of pilot system [1]*

Key words: sulphate, water, treatment, microbial sulphate reduction, on site, in situ, feasibility study

Introduction

At many German lignite coal mining areas sulphate containing water derives as well as sites are related to impacts on groundwater.

Lots of investigations were developed focusing management options for sulphate rich surface and groundwater.

In Saxony and Brandenburg several open mine pits were or will be recultivated. Recultivation measures are associated in many cases with procedures on water treatment.

Vita 34 together with LMBV has developed an *on site* pilot trial at a lignite coal mining area situated in southern part of Saxony (Germany).

The treatment concept is based on earlier R&D-investigations on microbial sulphate reduction which were developed on a small and a technical scale.

The concept for treatment of sulphate rich water incorporates needed processes for pollutant removal using following stages (fig. 3):

1) oxygen depletion within a retaining basin with addition of a liquid carbon and nitrogen source,
2) sulphate reduction and sulfide immobilization within a sealed system with a fixed bed made from gravel with addition of granular iron,
3) carbon degradation within a planted gravel filter.

The last stage is needed because an organic carbon source has to be added to catalyse microbial sulphate transformation. Sulphate is transformed to sulphide which reacts with ferrous iron and precipitates as iron sulphide.

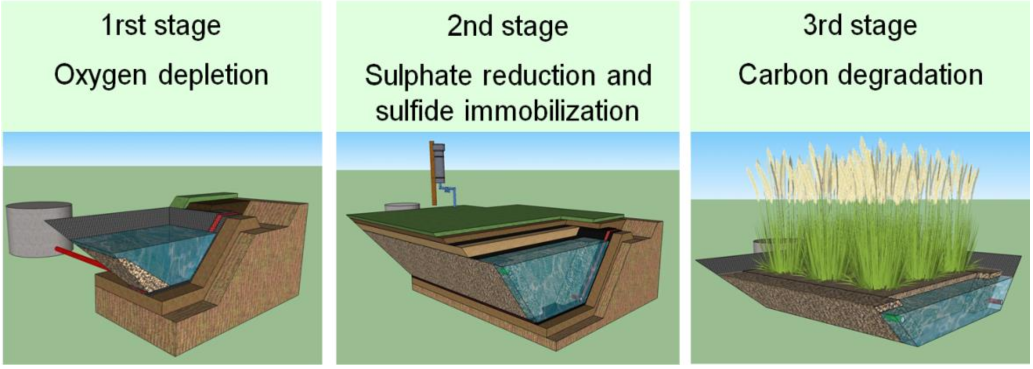

Figure3 *3D-illustration on treatment stages*

Methodology

For *on site* investigation a pilot system was installed, operated and monitored for about six months. Sulphate rich surface water was taken from a channel which dewaters a flooded open mine pit to river Pleiße (fig. 4).

Sulphate concentration in water is about 1,120 mg/L and pH-value between 4 and 7. Dimension and operation parameter of the pilot plant are listed in table 1.

During continuous operation and monitoring of the pilot plant the flow rate and added amount of carbon source was increased several times.

Figure 4 *Pilot plant at former lignite mining site*

Table 1 *main design and operation parameter*

	stage 1	stage 2	stage 3
volumetric capacity	0.5 m³	3.8 m³	1.3 m³
pore volume	0.5 m³	ca. 1 m³	0.4 m³
retention time (min.)	0.5 d	2.5 d	0.7 d
flow distance	-	18 m	2.5 m

Results and discussion

At least 20 days after the start of operation microbial sulphate reduction became effective (fig. 4) and after additional 40 days the sulphate concentration fell below target value.

As stable conditions were accomplished the flow rate was increased step by step and the amount of organic carbon source was optimized. Figure 5 illustrates monitored sulphate concentration in effluent of the overall system corresponding to air temperature.

Lab results of samples which were taken at several sampling points of second treatment stages proofed an efficient sulphate removal. Sulphate concentration was partly after 6 m of in total 18 m flow distance below target or detection limit.

Microbial sulphate reduction was partly limited by insufficient sulphate supply given by combination of chosen flow rate, retention time and sulphate content in surface water, which had to be treated previously.

Oxidation of iron followed by precipitation of iron sulfide was suitable to prevent measurable concentrations of sulfide in the effluent. At the beginning of the pilot operation high amounts of ferrous iron in the effluent had to be managed. During the pilot operation a temporary sedimentation stage was needed to prevent discharge of iron to the environment.

By the end of monitoring of the pilot plant scheduled changes in operation as well as a decrease of air temperature in autumn led to declining treatment efficiency.

Additionally oxidative release of ferrous iron seemed to decline. This was caused by inerting of surface of iron granulate.

A mass balance for iron, sulfur and calcium in the fixed bed was conducted. Based on these results, the amount of generated precipitates was estimated (Schöpke and Preuss 2012). After six months of pilot operation investigated characteristics of fixed bed material, as well as results of mass balances, indicated no significant changes of hydraulic conditions caused by precipitates.

Altogether retention time could be decreased from 7 to 4 days by more or less constant efficiency. This led to an optimization of dimension and investment costs for targeted full-scale application.

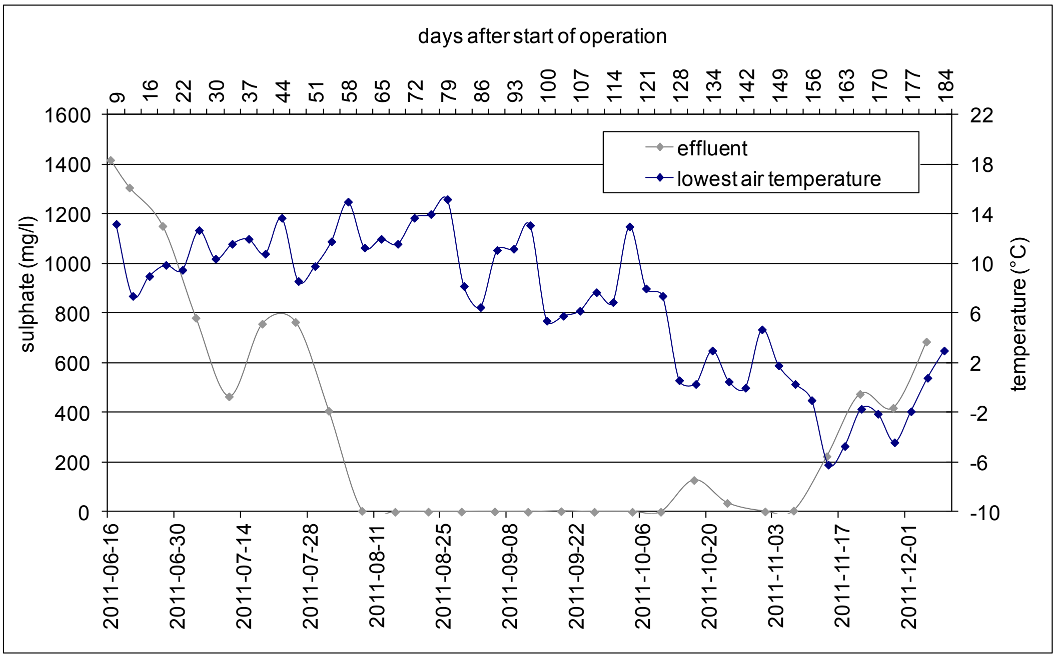

Figure 5 *Monitoring results – sulphate concentration versus time*

Conclusions

Numerous coal mine pits in Germany were flooded by re-rise of groundwater level after mine closure or controlled feeding using surface water of nearby rivers. The water quality of created lakes is influenced by interactions with sulphate containing groundwater.

Vita 34 has realized a six months *on site* water treatment pilot test on sulphate reduction and sulphide immobilisation in a biological active filter. Average sulphate concentration of about 1,120 mg/L decreased below target value of 300 mg/L. In the *on site* pilot test even a higher sulphate reduction rate could be obtained than in own previous investigations on a technical scale.

Changes in release of ferrous iron as well as influence of air temperature during winter periods need to be managed to ensure compliance with regulations.

The decrease of rate of oxidation of iron to ferrous iron can be compensated by subsequent delivery of iron granulate. The impact of low temperatures on treatment efficiency can be decreased by construction of stages below ground level. Additionally, temperature-dependent sulphate transformation kinetics has to be considered during the design of treatment plants for full-scale application.

Innovative technical approaches which allows selective replacement of parts of the fixed bed makes this technology favorable for full-scale and long term application *on site* as well as *in situ*.

During operation no residues have to be managed. Reaction products and by-products were immobilized and remain as solids in the treatment plants. In case fixed bed has to be replaced or when treatment plants are taken out of operation then sustainable and secure re-utilization of the fixed bed material is required. Special attention has to be paid to the professional utilization because it is charged with iron sulphide. One strategy is to depose material in anoxic conditions in underground.

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Characteristics and treatment of mine water from three historical coal workings in Yorkshire, UK: interrelationships between rates in geochemical, environmental and operational processes

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Abstract

Oxidation processes in three ferruginous coal mine water systems in Yorkshire, UK - studied over a period of some 20 years - are summarised. Filtered mine water samples from the Sheephouse Wood (SHW) system gave rates of iron(II) oxidation in homogeneous medium (determined in the laboratory in terms of the thermodynamic rate constant k) consistent with authoritative long-established literature reported for other aquatic systems. The calculated mean value of k was 2.35 x 10^{13} $M^{-2}atm^{-1}min^{-1}$ (pH 6.4-7.0; relative standard deviation ±12.5%). For similar measurements in heterogeneous medium – in the presence of a set large excess of pre-precipitated hydrated iron(III) oxide, ochre (360 times by mass of initial dissolved ferrous iron) – a (conditional) rate constant k_c was found to be some two orders of ten greater. This represented an example of rate enhancement by autocatalytic reaction. Field measurements in a well-defined mine water channel at SHW provided semi-quantitative evidence that practical rates of mine water oxidation are also relatively greatly affected by seasonal environmental factors.

Observations of a pilot plant at the Woolley (W) system confirmed that net alkaline mine water was rapidly oxidised via autocatalytic reaction when passed through a tank containing a thick slurry of ochre. Carry-over of fine oxidised particulates tended to occur. Work at the full scale Bullhouse (BH) system, constructed with an unusually large lagoon, directed inlet pipework under water through settling ochre to optimise autocatalytic enhancement. Despite net acidity at this site, treatment met discharge objectives on oxidation and settlement for some 12 years, based on a long residence time (initially some 17 days). Progressive ochre build-up indicated a need thereafter for desludging. The results are discussed in terms of variable autocatalytic reaction, which is evidently normal in such systems, and, together with other parameters, relevance to the perceived state-of-the-art of treatment in coal mine water systems.

Key words: Coal mine water, oxidation rate, environmental character, mine water treatment

Introduction

Mine water (typically containing 5-100 mg/L Fe) from many thousands of abandoned coal and metal mines worldwide continues to cause, except where remediated, highly visible ochre and/or acid pollution. This can affect biodiversity, sometimes for as much as 1-10 km downstream from the discharge. Such discharges have received great attention on environmental grounds; in earlier days notably by the former US Bureau of Mines and former British Coal (e.g., reviewed in Dudeney, et al. 1994; Perry, 1997). Since 1994 many reports have been published internationally, e.g., the PIRAMID Guidelines (PIRAMID consortium, 2003) primarily on account of scientific, engineering and regulatory requirements relating to treatment or remediation. Analogous discharges or springs associated with many natural systems, have received similar attention, but more often on purely scientific grounds (e.g., Barrott, et al., 2014).

As part of this attention, fundamentals of geochemical processes occurring in emergent water from underground containing ferrous iron, and rate processes connecting them, have been studied over decades, and are mostly well documented. In particular, for synthetic and environmental waters under near neutral conditions (pH 5-8), the rate of aerial oxidation under homogeneous aqueous conditions (i.e., at low concentration of iron(II) or Fe^{2+}, in the absence of significant precipitation) is well established and quantified in terms of a fundamental rate constant (k), while (generally faster) rates under heterogeneous, autocatalytic, conditions (i.e., at higher initial concentration in the presence of significant precipitated solid), are known in less precise terms of 'increased rate at increased solids content'; e.g., Stumm and Lee (1961), Davison and Seed (1983) and Stumm and Morgan (1996). However, despite the implied wealth of published information, uncertainties remain in the literature, especially in relation to mine water effluent from sedimentary coal-bearing strata. A recent paper dealing with mine water in Wales, UK (Geroni and Sapsford, 2011), reported much higher values of the constant than previously recorded. Thus, one objective of the present paper is to re-visit fundamental factors affecting rates of oxidation, especially those relevant to remediation of discharges from disused coal mines. The rate of oxidation of iron is re-determined in terms of k from previously unpublished data and also in terms of a 'conditional' constant, quantified for a representative set of autocatalytic conditions in contact with a substantive mass of ochre.

As another part, related flow processes underground and in the open environment, have been similarly studied and the general principles largely elucidated. Thus, partial oxidation of sulphide strata underground typically leads to the formation and mobilisation of iron(II), which, once out in the open, is progressively oxidised to iron(III) downstream of a source. However, conditions are usually poorly defined: effective direct access to reactive strata underground is normally impractical while emerging water often flows in an ill-defined channel or direct into a receiving stream. In particular, for ochreous mine water, many studies have tracked levels of contamination and interactions downstream from a discharge, but with limited access to details of processes spatially and temporarily. A second objective is thus to provide new data and discussion on such time-dependent processes, especially regarding environmental exposure and seasonal effects on mine water, employing flow from underground in an unusually well-defined mine water channel (leet).

As a third part, many polluting discharges have been successfully treated. In addition to fundamental and environmental data, treatment scheme design and operation has taken account of multifarious site-specific conditions and relevant regulation. Thus, unsightliness and toxicity associated with the generation of ochre and acidity have been alleviated at many operating and disused mine workings, with treated water discharged to the environment. In the UK, under the auspices of the Coal Authority (Coal Authority, 2014), a growing number of full scale mine water treatment schemes (now more than 70) treat ochreous mine water from abandoned coal mines. However, notwithstanding many years of development leading to a largely successful generalised approach (Table 1), a number of issues remain for improvement, e.g., matching plant configuration optimally to local conditions, reacting effectively to changing operational conditions as plants age, optimising the use of special geochemical effects (especially autocatalysis) and developing generally acceptable markets for recovered ochre. Once again rates of change are central, especially rates of oxidation and sedimentation in operational plant and changes occurring to system aging. Therefore, a third objective is to touch on issues around the interdependence of fundamental, environmental and treatment plant characteristics, and their different impacts on rates of change.

To introduce the provisions of Table 1, the perceived state of the art includes mine water capture, channel/cascade aeration, lagoon/wetland ochre settlement/deposition, water overflow to a local river, and gravel bed dewatering/drying of ochre for periodic recovery. Thus, the table encompasses the main technical requirements for effective removal of ochre, which are normally optimisation of rates of oxidation, settlement, dewatering and drying; typically translated into maximum effective turbulence for oxidation, quiescent water volume/surface area for adsorption/settling, and open solid standing area for water removal from ochre. Pumping is often needed to control underground levels and lift mine water to a plant level; and chemical dosing is sometimes employed (in addition to aeration) to enhance rates of oxidation and, perhaps, reduce the land area needed for treatment. Processes can also be intensified (at a cost) by selective use of mechanical equipment such as an industrial centrifuge. The table is thus an attempt to collect together technologies employed to maximise effectiveness of iron removal (particularly process rates), despite differences in local conditions, e.g., in land character, availability and accessibility for construction, linkage to mine water sources and drainage, environmental enhancement and other issues consistent with regulatory planning approval.

Table 1 *Typical sequences of oxidative mine water treatment processes and ochre isolation from abandoned coal mines in the UK*

Process	Means	Purpose	Equipment
Water capture	Forced flow (gravity)*	Provide process head and required water level underground	Pump (channel flow)
Water conditioning	Aeration (dosing/aeration)	Increase DO/reduce CO_2 causing iron oxidation (enhance rate)	Open cascade/channel (chemical plant**)
Water/ochre disengagement	Settlement/ deposition	Reduce linear flow, causing sedimentation of ochre and overflow of clarified water	Lagoon and/or constructed wetland
Ochre dewatering	Filtration	Remove occluded water	Gravel filter bed
Ochre drying	Exposure	Evaporate adsorbed water	Gravel filter bed

*Items in brackets are occasionally relevant alternatives **Adding lime, caustic soda or peroxide

The present work has been based on field study, and on associated laboratory study, carried out over a period of some 20 years with ochreous mine water from discharges and treatment products primarily involving Coal Authority treatment schemes at Sheephouse Wood (SHW), Bullhouse (BH) and Woolley (W) in Yorkshire (UK National Grid refs: SK232000, SE215028 and SE319132, respectively). The three systems have basic similarities governed by geochemistry at near neutral pH (and broadly consistent with Table 1). All three operate with pumping but no dosing (termed ‘pumped passive’). However, they have many distinctions in detail, e.g., in iron concentration, flow rate and flow path and different site-specific conditions - especially different access, surface topography, land availability and technological development. For example, mine waters at SHW and BH have shown no effective diminution in iron concentration (*Ca* 30 and 50 mg/L Fe, respectively) over many years at the point of emergence from underground (adit) while at W, a progressive decrease has continued since 1994 from >100 to <10 mg/L Fe. Flow rates are typically some 2, 1 and 5 x 10^3 m^3/day, respectively, but greater in winter. Typical initial pH ranges at BH, SHW and W are 5.5-6.5, 5.9-6.6 and 7.5-8.0, respectively, while final values on samples after equilibration in air are correspondingly 3.5-4.0, about 5.5-6.0 and 7.0-7.5 (net acid, slightly net acid and net alkaline).

Fundamental and environmental rate processes, mainly rate constants and flow characteristics of iron oxidation, were determined on samples taken at SHW (at the adit and along the mine water leet), while corresponding applied issues, here mainly considering autocatalysis, were studied at W (pilot plant) and BH (full scale plant).

Oxidation rate constants

Sampling, sample management and analysis were undertaken in general accordance with established methods (e.g., Greenberg, et al., 1992). On-site analyses were made with commercial electronic probes for pH, DO, and CO_2. For iron analysis rapid colorimetric methods based on absorbance of the red Fe(II)-o-phenanthroline complex at 510 nm were used. Specific experimental rationales, procedures and quality assessments are reported in detail in Perry (1997). For precise determination of k, mine water samples, taken at the SHW adit in 500 mL plastic bottles, were immediately purged (preserved) with carbon dioxide gas for 10 minutes (using a small gas cylinder, delivery tube and glass frit), sealed and stored in a cool box at 4ºC for transport to London. Subsequent measurements were carried out in a specially constructed reaction chamber. Results were converted to plots of log Fe(II) versus time and values of k calculated from the slope of the straight line so obtained, based on the standard equation (eqn 1), valid for pH 5-8 (Stumm and Lee, 1961), relating the rate of oxidation to the concentration of iron(II), the square of the activity of hydroxyl ion (constant at buffered pH) and the partial pressure of oxygen (constant at set inlet flow rate):

$$-\frac{d[Fe(II)]}{dt} = \mathrm{k[Fe(II)]}(a_{OH^-})^2 pO_2 \qquad (1)$$

For comparison of homogeneous and heterogeneous oxidation, 20 ml wet ochre was added to aged mine water, together with quantities of iron(II) sulphate and sodium bicarbonate sufficient to yield 5 mg/L Fe^{2+} and 250 mg/L HCO_3^-, respectively, once mixed. The precise proportion of ochre present was determined as 1.81 g/L by washing, oven drying and weighing a separate 20 ml of wet ochre. Kinetic experiments were carried out as above at pH 6.0 and 10º C.

Fig. 1 shows a plot of log[Fe(II)] versus time, identified with the integrated form of eqn (1) and approximated, for constant pH and pO_2, as a straight line having slope $(k/2.30)(a_{OH-})^2pO_2$. Similarly to Stumm and Lee (1961) and Davison and Seed (1983), a_{OH-} and pO_2 can be calculated, respectively, from pH (making use of the temperature dependent ionic product of water) and pO_2 (from direct measurement). Thus, k can be determined. In the present work, seven replicate runs carried out in the range pH 6.4-7.0, were used to calculate a mean value of k of 2.35 x 10^{13} $M^{-2}atm^{-1}min^{-1}$ (relative standard deviation ±12.5%). This value compares favourably with the range of rate constants determined up to 1983 and thus with the variable 'universal' rate constant given as (1.5-3.0) x 10^{13} $M^{-2}atm^{-1}min^{-1}$ (Davison and Seed, 1983). Lower precision quoted in the earlier work (e.g., relative standard deviation ±48.5%) may be attributed in part to difficulties of reliable measurement and control of pH during iron(II) oxidation, for which the rate of reaction increases some 100 fold for each pH unit increase and precipitating hydrated iron(III) oxide progressively interferes with measurements.

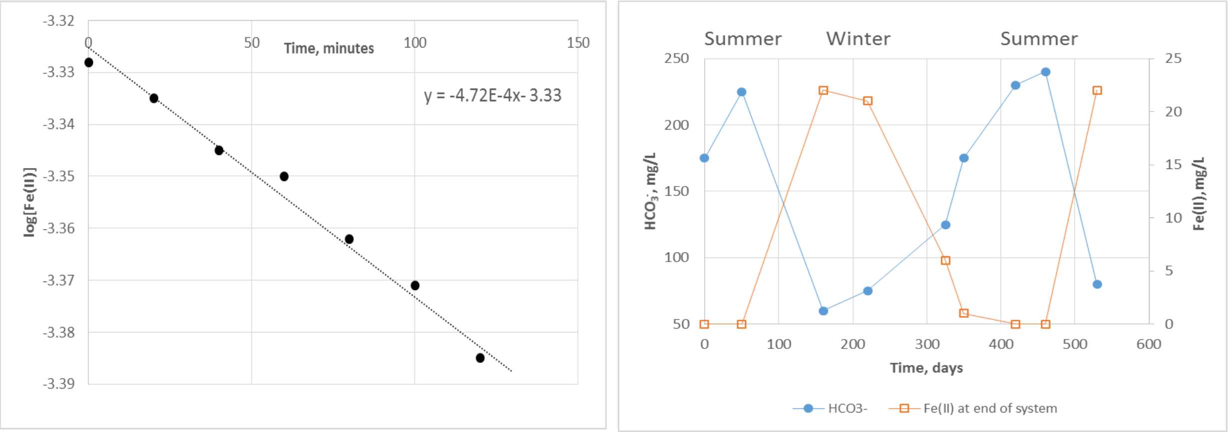

Figure 1 *Left: plot of log[Fe(II)] against time at 10ºC, pH 6.7, pO_2 0.20, initial Fe^{2+} 30 mg/L. Right: plot of seasonal variation of iron(II) concentration at far end of leet in relation to initial bicarbonate concentration. Initial iron(II) 30-45 mg/L (Summer) and 25-30 mg/L (Winter).*

An analogous plot of log[Fe(II)] versus time (not shown) for a semi-synthetic mine water at pH 6.0 and 10 ºC, initially containing 5 mg/L Fe^{2+} and 1.81 g/L ochre (dry mass, but not pre-dried), i.e., a mass large enough to overwhelm any second order effects. Once again, a good straight line was obtained having much greater slope than without added ochre. Six replicate samples, gave an average value of a conditional constant (termed $k_{1.81}$) of 2.05 x 10^{15} $M^{-2}atm^{-1}min^{-1}$ (relative standard deviation ±9.1%) This $k_{1.81}$ is some 87 times greater than k, equivalent to increasing pH by approximately one unit.

Environmental oxidation rates

At SHW mine water, once in the open, flowed along the leet approximately 3 km, with a tracer-estimated residence time of approximately 90 minutes, before discharge to the River Little Don. Notwithstanding responses to rainfall, leaf fall and routine maintenance (including sweeping-off loose accretion) the mode of flow was quite uniform, normally exhibiting laminar 'plug' flow over most of the length, but turbulent flow (reminiscent of an aeration cascade) during a final steep 200 m descent to the river. The pH increased as dissolved carbon dioxide evolved, giving final values of approximately 7-8 and 1.7-15 mg/L, respectively, at the point of discharge to the river. Turbidity also increased via iron oxidation and precipitation, acid so generated being largely consumed by reaction with contained bicarbonate. The pH was substantially higher in summer throughout the system (largely because of less dissolved carbon dioxide and more bicarbonate), but in inverse relation to iron(II) discharged to the river. As shown in Fig. 1 (right), iron was essentially fully oxidised in summer (equivalent to an average oxidation rate of roughly 0.3 mg(Fe)/L/min), but most of it (20-30 mg/L) remained un-oxidised in winter (rate effectively zero), even though the water was 100% air-saturated by the far end of the leet.

A picture emerges from one end of the leet to the other of gas exchange between carbon dioxide and air, iron oxidation ranging from near zero to essentially complete depending upon the season, and, despite substantial exposed leet surface area subject to significant progressive fouling, a low proportion of undisturbed ochre retention (as accretion). Such observations are apparently consistent with the basic characteristics and environmental behaviour of many mine water discharges, albeit most exhibiting less controlled dispersion. Additionally they provide an unusually precise indication of the (large) variations in seasonal geochemical characteristics of mine water emerging from underground and flowing in the open environment.

Applied rates

In order to re-assess (at pilot scale) catalytic oxidation as the basis of a separate intensified ‘passive’ process, coal mine water at W was first employed because of ready access to a well-defined mine water source (bleed) at the pump head and ochre from the drying beds there. In 1997, mine water feed (typically 7 L/min containing 27 mg/L Fe^{2+}) was passed for several days through a thick, slowly stirred, ochre slurry (approximately 0.75 m^3 containing approximately 15 vol% ochre) contained in a 1 m^3 tank fitted at one end with a submerged inlet manifold and at the other with an overflow pipe to two similar settling tanks in sequence. The slurry was prepared by ‘blunging’ (in this case treading) mine water with ochre from the W drying beds. Suitably blunged ochre slurry (*cf* ceramic ‘slip’) formed a dense medium, with a ‘mud line’ below supernatant mine water, which gravitated up and through towards the outlet. Routine analyses showed iron(II) to be barely detectable at the outlet. Thus, these early results confirmed that catalytic adsorption and oxidation were relatively efficient when mine water was suitably mixed with a large excess of ochre.

However, carry-over of fine-grained ochre particles contained more iron than that entering, except at very slow flow rate, and (unless occasionally replenished) the dense medium was slowly degraded. Thus, downstream bulk solid-liquid separations were expected to partially negate any benefits of more rapid oxidation and denser deposition. In fact, in more conventional processes, oxidation and ochre disengagement from the bulk of water often occur essentially together, so a greatly increased rate of oxidation after full aeration may not be helpful as a similar lagoon or wetland volume would still be needed to retain the finer sized solid.

The BH mine water treatment scheme provided an opportunity, at full scale, to examine a modified form of autocatalytic oxidation. This scheme, associated with workings on the same coal seam as SHW, but separated from it by an underground fault, was one of the earliest Coal Authority treatment schemes, operational since 1998 (Laine and Dudeney, 2000). It relies in part on pumps delivering raw mine water to the lagoon, in this case via a 0.8 km pipeline (in some respects mirroring the leet system at SHW), which transports the water up some 26 m in elevation, along a flat stretch, down some 8 m and through an aeration cascade to the main settling lagoon. Treated mine water is pumped back along the same route before discharge. The system relies on an exceptionally large void for ochre settlement (the main settling lagoon of capacity some 50 000 m^3), made available in nearby older, near-surface, coal workings after (timely) completion of pipe-clay quarrying there by Hepworth Building Products. This provided a relatively long working retention time initially (17-25 days) and overall lifetime to full with sludge (16-20 years), but left no space (or apparent need at the time) for a substantial ‘polishing’ wetland and drying bed. To make full use of the retention time (and mitigate the effects of relatively large ‘net acidity’ in this mine water), inlet pipes to the lagoon were directed under the water surface, thereby aiding distribution and preventing channelling to the outlets (Dudeney, et al., 2000). As the system aged, inlet water came into contact with increasing quantities of ochre suspension and sediment and was thus increasingly subject to catalytic iron oxidation – perhaps offsetting effects of reduced free volume as ochre accumulated. In any event, the system operated efficiently for more than 12 years, with little iron discharged (Fe typically <5 mg/L), net acidity in the effluent being fortuitously absorbed by natural alkalinity in the river. However, more recent large winter flows (>2000 m^3/day), greater iron content (>60 mg/L) and longer operation (some 16 years in 2014) have led to excessive particulate overflow and renewed contamination in the receiving river as the lagoon became increasingly filled with ochre. There is a need to de-sludge the lagoon and suitably dispose the ochre: major undertakings at this site.

An alternative enhancement of rates, predating considerations of autocatalytic reaction highlighted, was studied in an earlier pilot plant (Dudeney, et al., 1994, Perry, 1997) operating on SHW mine water. It employed chemical (alkali) dosing and (polyacrylamide) flocculation, which respectively increased rates of oxidation and disengagement (settling), to facilitate treatment at a space-restricted site. The pilot plant was sited near the far end of the leet but was designed to model a full scale treatment system near the SHW adit. The design was one of the first to be examined on modern environmental grounds for full scale treatment following the (then) recent closure of many UK coal mines; and was based on a gravity fed operation occupying a restricted area of land between the leet (and the adjacent A616 trunk road) and the receiving river. However, although the scheme proved technically satisfactory, the land envisaged turned out to have disadvantages, e.g., periodic water saturation and difficulty of access. Being close to the adit, the design would also have required some form of forced aeration to expel dissolved carbon dioxide ahead of dosing. More recent studies, e.g., Jarvis (2006), were spurred by a catastrophic mine water breakout at the site (which closed the A616 road for several days). A new plant, finally commissioned in 2014, instead elevates the mine water 25-30 m to a larger relatively flat area above the former mine (on the other side from the river), which has been made available for un-dosed treatment. For this purpose a hydrostatic dam, borehole and pump system are employed to shut off the original leet system and raise the water to the treatment system. The surface layout conforms to the treatment state-of-the-art (Table 1), and no doubt benefitting from a measure of autocatalytic reaction. Observation in April 2016 indicated satisfactory operation based on pumped mine water, although some seepage occurred direct from the hillside. Ochre management is based on a built-in dewatering and drying system, designed to be routine, thus avoiding the situation developed at BH.

Conclusion

Eqn (1) indicates the main variables affecting the rate of iron oxidation as iron(II) and oxygen concentration, and (especially) pH. Based on this equation, the present work confirmed that the homogeneous rate of oxidation of iron in coal mine water (determined as the fundamental rate constant) is consistent with measurements on other (synthetic and environmental) waters. However, under environmental and practical mine water treatment conditions, the present work also highlights additional factors, notably autocatalysis of iron(II) oxidation and seasonal change (particularly of ambient temperature and bicarbonate concentration) have large effects on practical rates of oxidation. Evidently such rates can be increased, in principle at least, by effective control of variables, e.g., by minimising carbon dioxide and optimising autocatalysis. Nonetheless, as significant variation in all variables should be considered as normal in particular schemes, between schemes and with the age of schemes, practical oxidation rates are not usefully generalised (or quantified). Additionally, because discharge consents may be based on total iron content in effluent, effective retention (settlement) of oxidised iron is as important as iron(II) oxidation: increase in oxidation rate may not be helpful if particulates are ineffectively retained. Of course, siting and configuration of treatment schemes also have different impacts; as emphasised here between chemical dosing on a site of limited size and access, and passive treatment on an elevated site subject to seepage via porous strata. Differences in design and outcomes mentioned exemplify the types of changes that can be consequent on prioritisation of a secure and practical procedure, consistent with regulatory approval, including constraints in matching plant configuration optimally to local conditions.

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Characterisation of fly ashes for minimisation of acid mine drainage from coal mining waste rocks

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Abstract

Acid mine drainage (AMD) due to the oxidation of sulphide bearing waste rock (WR) is a common environmental problem associated with coal extraction. Therefore, WRs from a lignite producing coal field in Pakistan and Lignite (PK), bituminous (FI) and biomass (SE) fly ashes (FAs) were mineralogically and chemically characterised to i) estimate the potential of WRs for generating AMD ii) estimate their deteriorating effects on natural waters, and iii) evaluate the FAs for their potential to minimise the impacts of WRs by preventing and/or neutralising AMD.

The WRs were composed of quartz, pyrite, arsenopyrite, kaolinite, hematite and gypsum with traces of calcite, malladerite, spangolite, franklinite and birnessite. The major elements Si, Al, Ca and Fe were in the range (wt. %) of 8 – 12, 6 – 9, 0.3 – 3 and 1 – 10, respectively, with high S concentrations (1.94 – 11.33 wt. %).

All FAs contained quartz, with iron oxide, anhydrite and magnesioferrite in PK, mullite and lime in FI and calcite and anorthite in SE. The Ca content in SE was 6 and 8 times higher compared to PK and FI, respectively.

The WRs had considerable potential for generating AMD with net neutralisation potential corresponding to -70 to -492 kg $CaCO_3$ $tonne^{-1}$. FAs showed to have sufficient acid neutralisation potential corresponding to 20 – 275 kg $CaCO_3$ $tonne^{-1}$, SE being the most alkaline probably due to the higher Ca content.

The element leaching varied between the WRs due to their chemical and mineralogical composition and pH conditions during the weathering cell test for 28 weeks. However, in general, the leachates from the more acidic WRs were enriched about 3 to 4 orders of magnitude for certain elements compared to the less acidic WRs.

The concentrations of Ca, SO_4^{2-}, Na and Cl in the leachates were much higher compared to other elements from all FA samples. Iron, Cu and Hg were not detected in any of the FA leachates because of pH ranging from 9 to 13.

Overall, the WRs had considerable potential for AMD generation and element leaching, therefore, deteriorate natural waters within the mining area. FAs, on the other hand, possess potential to minimise the impacts of WRs on the environment, due to their buffering capacity. However, the FAs vary in chemical composition and buffering capacity depending on their source, which makes it a possible challenge for utilisation.

Key words: Coal, Mining waste, Acid mine drainage, Neutralization, Fly ash.

Introduction

Despite the latest developments for cleaner alternative fuels, coal still shares about 28% of the total world's primary energy supply (IEA 2015). It is a very large scale activity by which ca. 7.8 billion tonnes of coal were estimated to be extracted worldwide in 2013 (WCA 2014). Global increase in electricity demand is causing coal industry to expand further (IEA-CIAB 2010). However, coal mining raises particularly strong concerns e.g. it produces waste rock (WR) that often contains sulphides, principally high contents of iron sulphides such as pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$) with trace elements such as As, Cu, Hg, Zn, Ni, Co, Mo, Se and Cr.

The sulphide rich WRs are considered environmentally sensitive because the sulphide minerals are unstable when exposed to the surface atmospheric conditions. The sulphide minerals, in presence of water and oxygen, produce acidic leachates with elevated concentration of major and trace elements that one way or the other end up in natural water resources. Such a process is commonly referred to as acid mine drainage (AMD).

Utilisation of coal releases noxious gases (such as CO_2, SO_2 and NO_X; that are implicated in global climate change) and Hg (US EIA 2015). Burning coal generates fly ash (FA) containing ecologically harmful substances (including As, B, Cd, Cr, Cu, Pb, Se and Zn (ACCA 2014)). Additional to that, FAs also contain approx. 10 – 15 % of particle size less than 10 µm (PM_{10}) that is breathable by humans and, therefore, is seriously harmful, causing damage to the human respiratory system (Medina et al. 2010). FA has been utilised in different ways such as concrete/concrete products, blended cement, road base/sub-base and soil modification/stabilization etc. (ACAA 2015) because of its physical (self-hardening) properties.

However, in recent years, several studies have shown that FA and its composites are effective in the neutralisation of AMD (Jia et al. 2014, Prasad and Mortimer 2011, Backstrom and Sartz 2011, Pérez-López et al. 2009, Pérez-López et al. 2007, Gitari et al. 2006).

The reviewed literature here indicates that the FAs are potential prevention and/or neutralisation agents for AMD. The FAs can be used as a dry cover material over WR dumps to isolate them from the surface atmospheric conditions and prevent AMD generation or the FAs can be mixed with WRs to backfill the underground coal mines and prevent or neutralise any AMD that might generate from the WRs.

Therefore, WRs from one of the large lignite producing coal field in Pakistan with an estimated reserves of 1.3 Bt and spread over 1309 km^2 (GoS 2012) and FA (PK) from a coal fired power station (utilising coal from the same field) were studied in this research. For comparative purposes, a bituminous coal FA from Finland (FI) and a biomass FA from Sweden (SE) were also included.

The main objectives of the study were to characterise WRs for determination of acid generating potential and FAs for acid neutralising potential. For this purpose, the mineralogical and chemical characterisation of WRs and FAs was performed. The acid generating and acid neutralising potentials of WRs and FAs were determined by acid-base accounting (ABA) and buffering capacity tests, respectively. The leaching of elements from WRs and FAs was also studied to estimate their deteriorating effects on natural waters.

Materials

Fly Ashes

Fly ashes were sampled from a lignite fired power plant in Pakistan (PK), bituminous coal fired power plant in Finland (FI) and a biomass FA from a pulp and paper industry in Sweden (SE). The selection of materials was based on their fuel source for a comparative study. PK (generated from fluidised bed combustor and captured using filter bags) was collected from a dumping pile and is, therefore, assumed to be cured to some extent, while FI (generated from boilers) was collected from an electrostatic precipitator and SE (generated from fluidised bed combustor) from multi-cyclone dry collectors.

Coal mine waste rocks

Samples were collected from four WR deposits near three underground coal mines (designated M1, M2 and M3) in a coal field, located 45 km NW of Hyderabad, Sindh province, Pakistan. The WR samples were designated WR1 and WR2 (collected from M1), WR3 (collected from M2) and WR4 (collected from M3). Each WR sample was composed of nine different sub-samples. WR1 was piled for about 2–3 months (therefore, weathering is assumed to have started), while the others were fresh, a few days to a few weeks old.

Methods

Mineralogical examination was achieved by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (with CuKα radiation at 45 kV and 40 mA, and scanning range in Bragg–Brentano geometry from 5° to 90°).

The *Scanning Electron Microscope* (SEM) analyses were also carried out using a FEI Magellan 400 XHR SEM on the thin sections that were prepared by Vancouver Petrographics Ltd., Vancouver, BC Canada. The SEM was equipped with an INCA Energy 450 system with an X-MAX80 EDS detector. The detectors used were through-lens detector (TLD) and Everhart–Thornley detector (ETD), the operating voltages were set to 10 kV.

Chemical characterization was performed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; (Martin et al. 1991)) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; (Long and Martin 1991)) at a SWEDAC-accredited laboratory (ALS Scandinavia, Luleå, Sweden). The ICP-AES analyses were performed using a Perkin Elmer Optima DV 5300 instrument following US EPA Method 200.7 (modified). The ICP-MS analyses were performed using a Thermo Scientific Element instrument following US EPA Method 200.8 (modified). LOI was determined at 1000 °C.

The determination of *chemical composition* was also realised by X-ray fluorescence (XRF) method using Olympus DELTA Premium Handheld XRF analyser to assess variation in composition within each WR deposit. ICP-AES and -MS analyses were performed on three subsamples of each WR, whereas, XRF was performed on all WR samples.

FAs were classified according to guidelines of ASTM C618 standard (ASTM 2012), which classifies FAs in two classifications, Class-F and Class-C. FAs having the sum of SiO_2, Al_2O_3 and Fe_2O_3 concentrations ≥70 wt. % and maximum LOI of 12 wt. % are classified as Class-F, which means that the FAs should have pozzolanic properties. Whereas, Class-C FAs have sum of SiO_2, Al_2O_3 and Fe_2O_3 <70 wt. % with maximum LOI of 6 wt. % are supposed to have cementitious properties in addition to pozzolanic.

Particle size distribution of FAs was determined by laser diffraction analysis using a CILAS 1064 laser granulometer (CILAS, Orléans, France). Prior to analysis, the sample was suspended in distilled water and the particles dispersed in the water by sonication. The particle size distribution was calculated using the CILAS software (de Boer et al. 1987).

A *batch leaching* test of the FA samples was performed with a liquid–to–solid (L/S) ratio of 10 (mL/g) following the procedure (modified) outlined in the Swedish standard SS-EN 12457-4 (SIS 2003).

The *Acid neutralisation potential* (ANP) of FAs was determined by the buffering capacity of FAs following a modified version of the batch titration method described by Wyatt (1984). The ANP was calculated as the $CaCO_3$ equivalent in kilograms per tonne (Eq. 1) required to neutralise the AMD and maintain a near-neutral pH of the solution.

$$CaCO_3 + 2\,H^+ \rightleftarrows Ca^{2+} + H_2CO_3 \qquad (1)$$

A modified procedure of the Swedish standard SS-EN 15875 (SIS 2011) for *acid base accounting* (ABA) analysis was applied to evaluate the acidifying and neutralisation potentials of WR samples.

To evaluate the sulphide reactivity, oxidation kinetics, metal solubility and overall leaching behaviour of the sampled materials, WRs were subjected to kinetic testing using *weathering cells* and procedures similar to those described by Cruz et al. (2001). The samples were subjected to 28, 7-day, cycles (192 days) consisting of exposure to ambient air for 2 days, leaching on the third day, followed by a further 3 days of exposure to air and a further leaching on the seventh day.

Results and Discussion

Mineralogical, chemical and physical composition of the materials

The mineralogical composition determined by XRD is shown in Table 1. The minerals detected by XRD were also confirmed by SEM.

***Table 1** Mineralogy of FAs and WRs determined by XRD.*

Sample	Minerals
PK[a]	Quartz (SiO_2), iron (III) oxide (Fe_2O_3), anhydrite ($CaSO_4$) and magnesioferrite ($Mg(Fe^{3+})_2O_4$)

FI[a]	Quartz, iron (III) oxide, mullite ($Al_6Si_2O_{13}$) and quicklime (CaO)
SE[a]	Quartz, calcite ($CaCO_3$) and anorthite ($CaSi_2Al_2O_8$).
WR1[b]	Dominated by arsenopyrite (FeAsS), quartz (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$), with variable amounts of pyrite (Fe_2S), calcite ($CaCO_3$) and gypsum ($CaSO_4{\cdot}2H_2O$)
WR2[b]	Dominated by kaolinite ($Al_2Si_2O_5(OH)_4$), Hematite (Fe_2O_3) and gypsum ($CaSO_4{\cdot}2H_2O$), with variable amounts of quartz (SiO_2)
WR3[b]	Dominated by pyrite (FeS_2), quartz (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$), with variable amounts of malladerite (Na_2SiF_6), spangolite ($Cu_6Al(SO_4)(OH)_{12}Cl{\cdot}3(H_2O)$), franklinite ($ZnFe_2O_4$)
WR4[b]	Dominated by pyrite (FeS_2), kaolinite ($Al_2Si_2O_5(OH)_4$), quartz (SiO_2) and TiO_2, with variable amounts of birnessite ($(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5\ H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$)

[a]*after Qureshi (2014),* [b]*after Qureshi et al. (2016)*

The XRD analyses revealed that, besides the organic material, only quartz was common in all three FAs. The SEM, however, helped to determine two more minerals (mullite and albite) in PK. FA particles usually consist of three distinct regions, namely a core composed of amorphous aluminosilicate glass, an inner layer composed of a network of mullite crystals and an outer layer of deposits (Kukier and Summer 2004). The particular conditions created during the melting, evaporation and condensation of a coal mineral admixture determine the specific structure of the formed FA. For instance, thermal transformation of phyllosilicates present in coal particles commonly leads to the formation of glass and mullite (Kukier and Summer 2004).

The WRs examined here were rich in pyrite (the main acid generator), hematite, quartz, calcite, lime, gypsum and kaolinite, in accordance with findings for coal mining wastes in South Africa (Bell et al. 2001, Equeenuddin et al. 2010). In addition, in WR1, As is bound in arsenopyrite, as previously observed by Hower et al. (2008) in Kentucky. Some of these minerals (hematite and kaolinite) additional to pyrite may also contribute in weathering reactions, depending on the pH. Notably, sulphate minerals may contribute to acid generation (Nordstrom 1982), especially Fe^{II} or Fe^{III} sulphates, which hydrolyse Fe upon dissolution to form $Fe(OH)_3$ (Jennings et al. 2000). While the others (such as calcite and gypsum) may make important contributions to the self-neutralisation potential of WRs.

The mineralogy and chemistry of FAs is mainly governed by the fuel type, burning processes, storage and handling processes (Baker 1987) along with adsorption, condensation and chemical transformation (Jones 1995, Ratafia-Brown 1994), whereas, the mineralogy of WRs varies on the type of mineral or metal being extracted.

The chemical characterisation (Table 2) showed that the FAs were completely dry when sampled, while WRs contained some moisture content varying from 10 to 30 wt.%. Obvious differences in major and trace element composition of FAs and WRs were observed. The principle reason for such differences is their source of production. The FAs were produced from three different fuels and processes and WRs were sampled from different mines. Overall, the FAs were enriched in Si, Al, Ca and Fe mainly. The WRs were enriched in Si, Al and Fe mainly, additionally Ca in WR1. The WRs contained significantly high S content varying from 1 to 11 wt.%, which may indicate high enrichment of sulphide minerals.

Table 2 *Chemical composition of FAs and WRs (Mean ± standard deviation, n=9).*

		PK[a]	FI[a]	SE[a]	WR1[b]	WR2[b]	WR3[b]	WR4[b]
TS	%	98.7 ± 0.1	100 ± 0	100 ± 0	90.53 ± 5.38	77.33 ± 0.12	83.93 ± 0.23	80.73 ± 2.39
Si	Wt %	26.6 ± 0.9	42.2 ± 1.4	28.35 ± 0.4	8.33 ± 5.79	11.14 ± 2.04	9.54 ± 3.97	12.47 ± 1.94
Al	Wt %	17.9 ± 0.7	20.1 ± 1.3	6.65 ± 0.5	6.84 ± 4.7	9.24 ± 1.72	6.26 ± 2.35	9.35 ± 1.13
Ca	Wt %	5.49 ± 0.2	3.5 ± 0.3	33.35 ± 0.1	3.69 ± 5.64	0.44 ± 0.1	0.36 ± 0.06	0.33 ± 0.03
Fe	Wt %	31.2 ± 2	5.51 ± 0.08	2.53 ± 1	3.9 ± 4.26	1.57 ± 0.42	10.07 ± 3.88	5.63 ± 2.91
K	Wt %	0.51 ± 0.01	1.94 ± 0.02	5.56 ± 0.01	0.4 ± 0.25	0.41 ± 0.11	0.33 ± 0.16	0.35 ± 0.03
Mg	Wt %	2.02 ± 1	1.52 ± 0.01	3.63 ± 0.4	0.51 ± 0.09	0.54 ± 0.01	0.28 ± 0.04	0.26 ± 0.01
Mn	Wt %	0.07 ± 0	0.04 ± 0	1.72 ± 0	0.05 ± 0.07	0 ± 0	0.01 ± 0	0.02 ± 0.01

Na	Wt %	1.6 ± 0.04	1.13 ± 0.08	1.62 ± 0.03	0.16 ± 0.09	0.21 ± 0.04	0.21 ± 0.02	0.14 ± 0.01
P	Wt %	0.06 ± 0.01	0.57 ± 0.02	3.25 ± 0.01	0.02 ± 0.01	0.02 ± 0	0.02 ± 0.01	0.03 ± 0
Ti	Wt %	1.85 ± 0.1	0.71 ± 0.06	0.2 ± 0.02	0.41 ± 0.31	0.57 ± 0.13	0.69 ± 0.34	0.87 ± 0.19
LOI	Wt %	7.93 ± 0.1	4.45 ± 0.07	9.9 ± 0.03	n.d	n.d	n.d	n.d
S	Wt %	2.38 ± 0.2	0.12 ± 0.0014	1.40 ± 0.15	10.79 ± 12.05	1.94 ± 0.15	11.33 ± 4.73	7.43 ± 0.68
SiO_2+ Al_2O_3 +Fe_2O_3	Wt %	75.7 (Class-F)[c]	67.8 (Class-C)[c]	37.53 (n.c)[c]	n.d	n.d	n.d	n.d
As	mg/kg TS	7.49 ± 0.6	17.3 ± 0.1	28.7 ± 0.3	8.15 ± 8.13	0.3 ± 0.08	3.88 ± 0.73	2.06 ± 0.41
Ba	mg/kg TS	211 ± 8	1330 ± 0	2550 ± 5	98.53 ± 61.46	123 ± 22	83.33 ± 36.15	101 ± 18
Be	mg/kg TS	7.25 ± 0.4	3.91 ± 0.05	0.72 ± 0.3	2.3 ± 1.48	3.48 ± 0.42	1.84 ± 0.32	2.01 ± 0.78
Cd	mg/kg TS	0.97 ± 0.1	0.35 ± 0.02	13.05 ± 0.04	0.3 ± 0.04	0.22 ± 0.07	0.25 ± 0.12	0.45 ± 0.37
Co	mg/kg TS	88.6 ± 8	22.6 ± 0.28	9.88 ± 6	40.23 ± 26.07	15.43 ± 4.55	43.5 ± 21.88	75.37 ± 35.54
Cr	mg/kg TS	168 ± 7	70.1 ± 7.9	143 ± 1	67.63 ± 52.6	111 ± 20	101 ± 37	102 ± 38
Cu	mg/kg TS	119 ± 12	55.7 ± 0.99	100.05 ± 8	73.43 ± 53.26	101 ± 30	24.97 ± 2.04	68.13 ± 24.55
Hg	mg/kg TS	0.49 ± 0.1	0.19 ± 0	0.44 ± 0.04	0.22 ± 0.07	0.14 ± 0.02	0.1 ± 0.02	0.12 ± 0.05
Ni	mg/kg TS	155 ± 15	57.4 ± 0.99	61.95 ± 10	87.83 ± 38.94	50.27 ± 14.26	61.1 ± 30.57	107 ± 28
Pb	mg/kg TS	18.9 ± 2	27.7 ± 0.21	84.75 ± 1	14.54 ± 9.14	20.27 ± 5.02	8.88 ± 3.57	13.01 ± 3.69
Sr	mg/kg TS	1510 ± 61	1235 ± 21	875 ± 28	302 ± 103	241 ± 10	126 ± 18	167 ± 34
V	mg/kg TS	339 ± 7	102 ± 9	33.3 ± 1	178 ± 139	256 ± 38	139 ± 47	153 ± 38
Zn	mg/kg TS	218 ± 24	94.4 ± 1.56	2585 ± 16	70.6 ± 7.6	50.1 ± 3.9	49.67 ± 15.15	105 ± 109
Zr	mg/kg TS	277 ± 5	252 ± 5	95.55 ± 0.01	75.03 ± 56.56	119.7 ± 22	135 ± 50	135 ± 33

[a]after Qureshi (2014); [b]after Qureshi et al. (2016); [c]Classification of FAs (ASTM 2012); n.c, not classified; n.d, not determined

The classification of FAs revealed that the PK was a Class-F and FI was a Class-C FA, whereas, SE could not be classified according to the ASTM C618 guidelines. Therefore, PK and FI can be potentially used as cover or mixture material for WR dumps or mine backfilling, respectively.

FA particle surfaces are often enriched in highly environmentally reactive elements (such as As, Se, Mo, Zn and Cd (Hansen and Fisher 1980, Jones 1995)). As a result, these elements readily react when the FA particle is exposed to water and release into the environment. However, the release of the elements from FAs is controlled by precipitation or dissolution mainly, and possibly by desorption.

The classification of fine (≤63 µm) and coarse (>63 µm) particles in FAs (Table 3) was carried out in accordance with current guidelines in ISO 14688-1 (ISO 14688-1 2002); however, results for the < 1 µm size fraction are associated with some uncertainty because of the instrumental limitations. The high proportions of fine particles suggest that all three FAs have large surface areas (Pathan et al. 2003) that provide more chance for enrichment of many elements. This can play an important role in the context of AMD remediation but may also elevate the concentration of elements in leachates if proper pH conditions are not controlled and maintained.

***Table 3** Proportion of coarse and fine particles in FAs.*

Fly Ash	Fine (%)	Coarse (%)
PK*	75	25
FI*	87	13
SE*	99	1

**after Qureshi (2014)*

AMD situation

Materials with neutralisation potential ratio (NPR) values <−20 kg $CaCO_3$ tonne^{-1} and >20 kg $CaCO_3$ are usually regarded as acid producing and not-acid producing, respectively, and uncertain otherwise

(Miller et al. 1991, SRK 1989). Alternatively, AMD potential of WRs can also be determined using neutralisation potential ratio (NPR). A material is typically considered not-acid producing if NPR > 2.5, uncertain if 2.5 > NPR > 1, and acid-producing if NPR < 1 (Adam et al. 1997).

The ABA test (Table 4) showed that the WRs possess significant potential for producing AMD. Kinetic leaching tests indicate deteriorating effect of WRs on water quality by leaching elements (Table 5) in excess quantity compared to WHO standards (WHO 2011).

Table 4 *AMD generation potential of the WRs (mean ± standard deviation, n=3).*

Measured as kg $CaCO_3$ tonne^{-1} (except NPR)	WR1*	WR2*	WR3*	WR4*
Acid potential (AP)	123 ± 93	61 ± 5	354 ± 148	245 ± 4
Neutralisation potential (NP)	-21 ± 19	-9 ± 3	-138 ± 30	-107 ± 1
Neutralisation potential ratio (NPR)	-0.15 ± 0.03	-0.15 ± 0.05	-0.42 ± 0.11	-0.43 ± 0.01
Net neutralisation potential (NNP)	-144 ± 112	-70 ± 6	-492 ± 178	-352 ± 5

**after Qureshi et al. (2016)*

The physicochemical characterisation of leachates from weathering cell test of WRs showed that the WRs were consistently producing acidic leachates throughout the test duration (i.e. 192 days). WRs 3 and 4 were identified as the most acid producing WRs, confirming ABA test results. However, WR1 (which produced near neutral leachates) probably contains some acid neutralising agents (such as calcite indicated by XRD) that were depleting with time as shown by decreasing pH trend in Figure 1. WR2 possesses the moderate AMD potential as indicated by the ABA results and its behaviour in kinetic leaching tests but may contribute to acidity with time.

Table 5 *Concentrations of selected elements in leachates from WRs 1 – 4 in the kinetic leaching tests compared to WHO (2011) drinking water standards.*

	WR1*	WR2*	WR3*	WR4*	WHO
	Min – Max	Min – Max	Min – Max	Min – Max	
Al (µg/L)	2 – 1,145	58.7 – 2,715	5,600 – 1,525,000	7,285 – 1,310,000	900
As (µg/L)	0.5 – 1	0.5 – 1	2.9 – 1,009.5	1.08 – 708	10
B (µg/L)	422 – 12,250	244 – 23,000	280 – 15,750	186 – 10,450	2400
Cd (µg/L)	0.05 – 6.9	0.07 – 3.36	0.6 – 233	3.25 – 327.5	3
Co (µg/L)	6.7 – 3,050	37.35 – 1,050	157 – 32,350	105 – 57,700	Not specified
Cr (µg/L)	0.5 – 1.3	2.36 – 42	92.5 – 6,590	247.5 – 4,425	50
Cu (µg/L)	1 – 17.3	1 – 34.4	89.3 – 2,640	137 – 26,750	2000
Mn (µg/L)	1,980 – 59,550	305 – 8,125	355 – 54,350	319 – 75,700	400[P]
Ni (µg/L)	6.36 – 3,040	36.2 – 951.5	133 – 33,050	182 – 57,150	70
Pb (µg/L)	0.2 – 3.16	0.2 – 7.5	4 – 130	1.41 – 20	10
Zn (µg/L)	6.87 – 2,500	44.3 – 1,030	139 – 45,150	148 – 74,350	10 – 50
Ca (mg/L)	346 – 513	31.85 – 372	2.68 – 469.5	4.11 – 404	Not specified
Fe (mg/L)	0.004 – 140	0.3 – 4.8	391.5 – 36,450	221 – 17,900	0.5 – 50
K (mg/L)	6.7 – 32.4	8.83 – 26.8	1.25 – 20	0.7 – 13.7	Not specified
Mg (mg/L)	9.14 – 1,370	15.9 – 1,380	0.6 – 1,255	0.5 – 695.5	Not specified
Na (mg/L)	2.27 – 556	0.6 – 801	0.6 – 928	0.7 – 336	<20
Cl (mg/L)	3.88 – 1,030	3.1 – 1,130	2.3 – 524.5	1.5 – 136.5	5
SO_4^{2-} (mg/L)	777 – 8,625	189 – 7,240	985 – 101,940	548 – 91,510	500[P]
pH	5.6 – 7.3	2.7 – 4.9	0.945 – 2.3	1.2 – 2.5	Not specified
EC (mS/cm)	1.2 – 10	0.4 – 11.18	3.5 – 58.2	1.8 – 34.85	Not specified

**after Qureshi et al. (2016), [P] Preliminary*

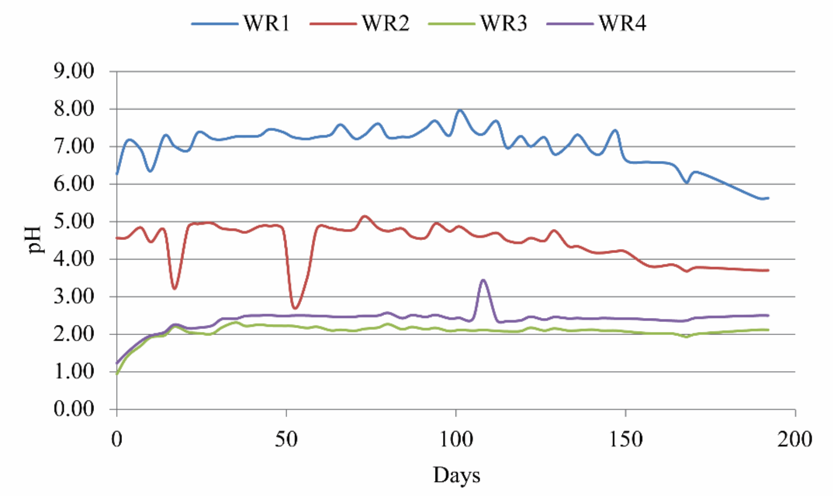

***Figure 1** pH trends over the complete duration of weathering cell test.*

AMD neutralising potential of FAs

The ANP of FAs is mainly determined by its total calcite content (Gitari et al. 2006), although it is also affected by the particle size of the FA. Finer FAs perform better than coarser FAs, because the larger total surface area of finer FAs increases the area of interaction with the surrounding water (Vadapalli et al. 2007).

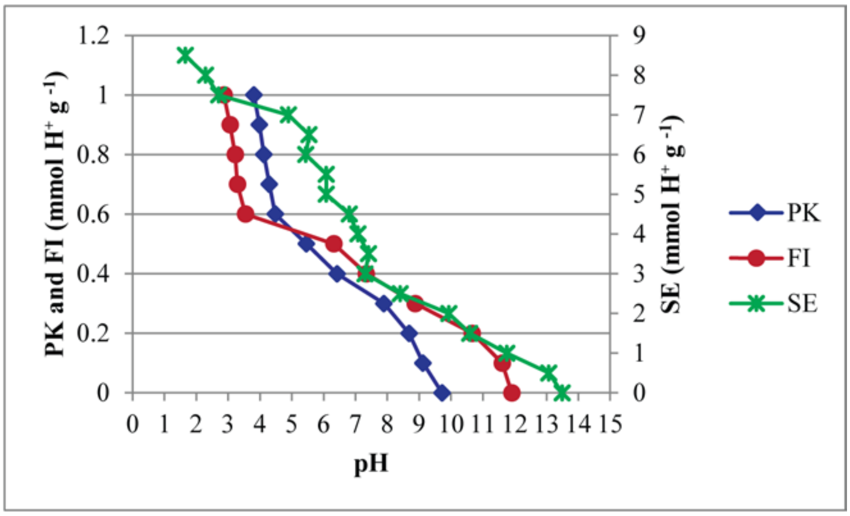

***Figure 2** Acid titration curves of FAs against 1M HCl.*

In the present study, significant differences in the ANP of the FAs were observed. The ANP calculations, based on Figure 2 and Eq. 1, showed that the SE FA had the highest ANP of 275 kg $CaCO_3$ tonne^{-1}, because of its higher calcite content and larger proportion of fine particles. The PK and FI possess an ANP of 20 and 25 $CaCO_3$ tonne^{-1}, respectively. Therefore, all FAs possess potential to neutralise AMD but larger quantities of less reactive FAs would be required than SE to do the same amount of work. However, due to the fact that the SE comes from a biomass source and that sometimes the coal producing and utilising countries produce significantly large quantities of coal FAs (requiring environmentally safe disposal) than biomass FAs, the less reactive coal FAs might be the only available option for mining companies. Furthermore, the coal fired power stations are usually situated near the coal mines, therefore, ease of availability of coal FAs makes them an economically promising solution as well.

The physicochemical composition of FAs contributed to leaching of some major and trace elements during batch leaching tests (Table 6). The most abundantly leached elements in FAs were Ca, K (in SE), Na, Al, Ba, Cr and Mo. Due to the strongly alkaline nature of FAs, mobility of some elements (such as Fe, Mg, As, Co, Cu and Hg) was restricted to minimum levels. However, probably the smaller grain size of the SE FA contributed to a small increase in the leaching of some major elements, compared to the other two FAs.

Table 6 *Physicochemical characterisation of FA leachates (mean ± standard deviation, n = 3).*

		PK*	FI*	SE*
pH		9.55	12.25	13.48
Eh	mV	-145	-296	-155
EC	µS/cm	3.07	2.25	23.09
Ca	mg/L	497 ± 20	222 ± 4.27	644 ± 38
Fe	mg/L	<0.004	<0.004	<0.004
K	mg/L	8.86 ± 0.28	5.16 ± 0.09	1835 ± 106
Mg	mg/L	57.87 ± 6.24	<0.09	<0.09
Na	mg/L	364 ± 7	21.43 ± 0.54	319 ± 26.16
DOC	mg/L	1.18 ± 0.29	1.03 ± 0.05	2.50 ± 0.57
Cl	mg/L	53.67 ± 11.96	2.65 ± 2.56	401 ± 16
F	mg/L	4.10 ± 0.36	1.375 ± 0.13	0.90 ± 0.14
SO_4	mg/L	2123 ± 141	132 ± 7	1630 ± 212
Al	µg/L	131 ± 26	118 ± 21.75	2.53 ± 0.38
As	µg/L	1.83 ± 0.37	<0.5	<0.5
Ba	µg/L	78.23 ± 5.13	288 ± 10.61	257 ± 2.12
Cd	µg/L	0.36 ± 0.03	0.39 ± 0.02	0.21 ± 0.013
Cr	µg/L	1.13 ± 0.26	139 ± 1.71	600 ± 38.89
Mo	µg/L	330 ± 8	360 ± 4	265 ± 2.83
Pb	µg/L	<0.2	<0.2	19.7 ± 0
Zn	µg/L	2.11 ± 0.21	20.01 ± 23.74	135 ± 3.54

*after Qureshi (2014)

Conclusions

The mineralogical and chemical characterisation of the FAs and WRs showed large variations in composition and elemental concentrations. The principle reason for that is the source of sampled materials and their storage and handling processes.

The results from ABA tests along with weathering cell tests performed over WRs showed that the studied WRs possess considerable potential for producing AMD and leaching elements in excess concentrations that may end-up in natural water resources and deteriorate their quality.

The physicochemical composition of FA leachates indicates their potential for deteriorating ecosystem quality. However, their ANP is advantageous, making them a possible and potential solution for AMD.

Therefore, utilisation of FAs and WRs together (as cover or mixture material for WR dumps or mine backfilling, respectively) may potentially result in better environmental conditions. However, methods for utilisation must be investigated by scaled-up laboratory experiments due to the fact that the chemical composition of both materials contains elements of concern. Mixed utilisation may or may not contribute towards reduction in mobility of those elements, which also, to some extent, depend on pH conditions of the final mix.

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The Use of Limestone as a Strategy to Remove Sulphate from Mine Waters with Suphate Concentrations Below the Limit Defined by Gypsum Solubility

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Abstract

The precipitation of sulphate, iron and aluminium is the main factor accounting for armouring during limestone treatment of acid mine drainages, which renders the acidity neutralization processes ineffective. Based on this observation, limestone is proposed herein as a sorbent for sulphate removal, from neutral mine drainages. Therefore the present work investigated sulphate removal from a pH 6.5 mine water through sorption on limestone. Batch equilibrium tests showed that sulphate loading on limestone can be described by the Langmuir isotherm with a maximum loading of 0.248mmol/g. Fixed-bed experiments were utilized to produce breakthrough curves at different bed depths (15cm-25cm) and flow rates (2mL/min-10mL/min). The Thomas model was selected to describe the breakthrough data and revelead sulphate loadings of up to 0.21molSO_4^{-2}/L-bed as the flow rate increased. Sulphate sorption on limestone might be a cost-effective alternative to treat mine waters with sulphate concentrations below the values set by gypsum solubility (1500-2000mg/L) and for which only more expensive processes are available.

Key words: Sulphate, mine water, limestone, bed length, sorption models.

Introduction

Sulphate is a major anion in effluents of the industries which utilize sulphuric acid in their processes (Mulinari and da Silva 2008; Roonasi and Holmgren 2009) and is also produced during acid mine drainages (AMD) (Cao *et al.* 2009). In drinking water, sulphate can affect taste and have laxative effects at concentrations in excess of 600mg/L (Haghsheno *et al.* 2009). In mine waters, sulphate is of less concern than both acidity and metal content notwithstanding environmental agencies in mine countries establish regulations to control sulphate, usually by setting a limit between 250mg/L and 500mg/L in different type of effluents. Even when there is not a specific guideline for sulphate, total dissolved solids are usually specified, which include sulphate concentrations (INAP 2003).

Sulphate-bearing wastewaters or mining drainages are usually treated by different techniques such as ettringite precipitation, ion exchange and membrane techniques. The selection of the process aiming at treating such effluents is defined by several factors such as chemical availability, local regulations, commercialization of the produced water and process economics (INAP 2003), but gypsum precipitation is usually applied as the first step, particularly when acidity needs to be controlled. One good example is the production of drinking water from AMD originated from different sites by the eMalahleni Project in South Africa. AMD is first treated by oxidation and precipitation prior to being subject to ultrafiltration and reverse osmosis to produce a <200mg/L total dissolved solids water

(Hutton *et al.* 2009). Sulphate removal by shrimp peelings (Moret and Rubio 2003), modified zeolites (Oliveira 2006) and coconut pith (Namasivayam and Sangeetha 2008) has also been investigated.

Limestone is an inexpensive material widely available in many parts of the world, which has been the primary option for treating mine-affected waters containing high acidity and dissolved metals, particularly iron and manganese (Sun *et al.* 2000). Limestone consumes acidity according to equation 1, increasing the drainage pH and then inducing metal removal (Rose and Elliott 2000) through precipitation and/or adsorption (Komnitsas *et al.* 2004). However, its efficiency as acidity neutralizer is reduced if the mine water is only mildly acidic. Also contributes to this lower reactivity the precipitation of either iron and aluminium oxy-hydroxides or calcium sulphate on the limestone surface, which create a layer of inert material strongly reducing its reactivity (the so-called armouring effect).

$$CaCO_3 + 2H^+ \leftrightarrows Ca^{2+} + H_2O + CO_2 \tag{1}$$

The formation of calcium sulphate on the limestone surface can be utilized to devise a new process for sulphate removal from neutral mine waters (in which acidity is low) based on sorption principles. This process does not have the drawback of the high residual sulphate concentrations observed when gypsum precipitation is used for sulphate precipitation from mine waters, usually in the 1500-2000mg/L range. Therefore, a new approach is proposed in the current work whereby limestone is applied for sulphate sorption, particularly in those mine waters with moderate anion concentrations (below 1500mg/L), which are above the discharge limit set by environmental agencies.

Experimental

A calcite limestone sample assaying 53.7% calcium and 0.28% magnesium had its particle size between 0.42mm and 0.59mm (0.774 m^2/g specific surface area) selected for a series of fixed-bed experiments performed with neutral mine water (pH 6.5) samples assaying 588.0mg/L sulphate, 45mg/L Mn and 2.4mg/L Fe.

The fixed-bed experiments were performed with limestone particles with an average diameter of 505µm. The solid particles were transferred to a glass column (20mm diameter) to produce bed depths ranging from 15cm to 25cm. The column diameter/particle size ratio enabled the wall effect to be neglected during experiments. Subsequently the particle bed was washed with distilled water to remove fine particles. During the experiments, the column was fed upwards by peristaltic pumps and the flow rate (Q) was varied between 1 and 10mL/min, regulated by a constant-speed pump (Milan). From the column effluent, samples were collected regularly for analysis as total sulphur in an ICP-OES (Varian, 725). Such concentration was assumed to represent sulphate in the both the mine- and treated water. Sulphate loading on limestone was determined by mass balance and the experiments were carried out at 23±1°C.

For modelling purposes, a pseudo adsorption isotherm was produced using synthetic sulphate solutions. The procedure comprised shaking (at 300min^{-1}) limestone particles (0.42mm-0.59mm) added to 250mL Erlenmeyer flasks containing 120mL of sulphate solutions. The anion concentration varied from 50.0mg/L to 3000.0mg/L at (pH 9.6-9.8), the pulp contained 25.0g/L solids and the experiments run for 9 hours. Sulphate (as S_{tot}) was analysed in an ICP-OES (Varian, 725) and the loading on limestone was determined by mass balance.

Results and discussion

The precipitation of calcium sulphate on the limestone surface has been demonstrated during the characterization of armoured limestone beds treating typical AMD (pH 2.9, 2200mg/L sulphate) (Hammarstrom *et al.* 2003). Therefore sulphate sorption by limestone would be an option for lowering the anion concentration, particularly from neutral mine water in which there is negligible limestone dissolution and the solid beads would behave like a solid substrate for sulphate sorption (either sorption or precipitation). This approach is not constrained by gypsum solubility and thus mine waters with moderate sulphate content (below ±1500mg/L) could be treated. Such value is not high enough to enable gypsum precipitation, but remains above the discharge limit (usually 250mg/L) set by environmental agencies

To prove such a concept a pseudo-sorption isotherm was produced using synthetic solutions containing different sulphate concentrations at pH 6.5 as depicted in figure 1. Figure 1 indicates that sulphate sorption on limestone can be described by the Langmuir isotherm ($r^2 = 0.99$) with a maximum sulphate loading of 0.25mmolSO_4^{2-}/g-limestone. Several adsorbents have been applied to remove sulphate from industrial effluents and it may be cited as example chitin flakes in which sulphate sorption was also described by the Langmuir isotherm with 1.6 mmolSO_4^{2-}/g as maximum capacity (Moret and Rubio 2003). Another example is sulphate uptake by the strong base ion exchange resin Purolite A500, which also followed the Langmuir isotherm and the maximum uptake was 0.61mmol/L-resin (Guimarães and Leão 2014). Likewise, sulphate sorption in the Lewait K6362 resin produced good fittings to both the Langmuir and Freundlich and the maximum loading was 1.73mmolSO_4^{2-}/g (Haghsheno *et al.* 2009).

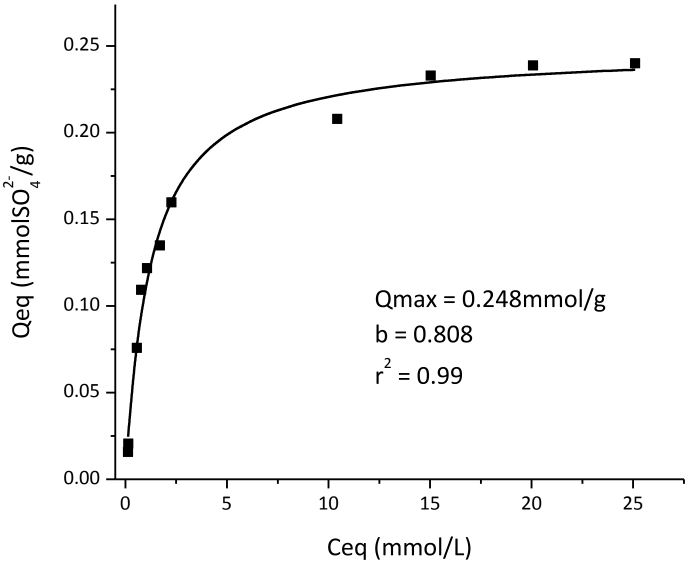

Figure 1. *Sulphate sorption isotherm (a) and effect of bed depth on sulphate sorption. Experimental conditions: 23±1°C, initial pH 6.5; particle size 0.42-0.59mm; 10mL/min;* $C_0 = 6.12$ *mmol*SO_4^{2-}*/L.*

A good fitting to the Langmuir isotherm as observed herein implies in a chemisorption process, characterized by the presence of a monolayer on the sorbent surface. Bonding between sulphate and calcium ions present on the limestone surface would account for the formation of such monolayer (Hammarstrom *et al.* 2003).

Fixed bed sorption was selected for further sulphate sorption studies. It is very often applied in mine water treatment because of both (i) its high selectivity and efficiency and (ii) the removal of harmful species even at very low concentrations (Reynolds and Richards 1995). Again a neutral mine water (containing 6.12mmol/L SO_4^{2-} at pH 6.5) was used in the fixed-bed tests with limestone as the sorbent. In this particular series of experiments the effects of flowrate and bed depth on the sulphate breakthrough curves were assessed. Subsequently, fixed-bed sulphate sorption was modelled according the Thomas model, which provided the solid loading and the rate constant of the sulphate sorption process.

The Thomas model for fixed-bed columns assumes that sulphate sorption on limestone can be described by the Langmuir kinetic equation (eq. 2) (Chu 2010). At equilibrium equation 2 is converted to the familiar Langmuir expression.

$$\frac{\partial q}{\partial t} = K_{T1}\, C(q_m - q) - K_{T2} q \tag{2}$$

In equation 2, q_m represents the sulphate loading in limestone (mg/g); K_{T1} and K_{T2} are rate constant and q is the limestone loading (mg/g) at time t.

Being ν the axial velocity (cm/s) and ε is the bed porosity, a mass balance for a fixed-bed column in the absence of axial dispersion is:

$$v\frac{\partial C_t}{\partial Z} + \frac{\partial C_t}{\partial t} + \frac{1-\varepsilon}{\varepsilon}\frac{\partial q_t}{\partial t} = 0 \tag{3}$$

An analytical solution for equation 3 was proposed by Thomas (1944) as follows:

$$\frac{C_t}{C_0} = \frac{J(\frac{n}{r},nT)}{J\left(\frac{n}{r},nT\right)+\{1-J(n,\frac{nT}{r})\}\exp\{\left(1-\frac{1}{r}\right)(n-nT)\}} \tag{4}$$

Where $$r = 1 + bC_0 \tag{5}$$

$$n = \frac{\rho_p\, q_m k_T Z(1-\varepsilon)}{\varepsilon v} \tag{6}$$

$$T = \frac{\varepsilon\left(\frac{1}{b}+C_0\right)}{\rho_p q(1-\varepsilon)}\left(\frac{vt}{Z} - 1\right) \tag{7}$$

And $$J(x,y) = \frac{1}{2}\{1 - \mathrm{erf}(\sqrt{x} - \sqrt{y}) + \frac{\exp(-(\sqrt{x}-\sqrt{y}\,)^2}{\sqrt{\pi}\,(\sqrt{y}+ (xy)^{0{,}25})}\} \tag{8}$$

Equations 4-8 were solved using Mathematica 9.0 to produce the q_m and k_T values which resulted in the best fit between experimental and model data. As it can be seen in figures 2 - 4, Thomas equation reproduces fairly accurately the breakthrough curves for sulphate sorption on limestone under the experimental conditions investigated.

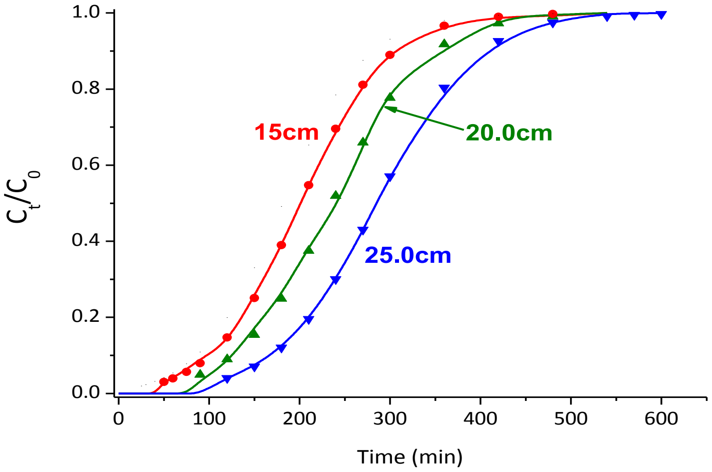

Figure 2. *Breakthrough curves for sulphate sorption on limestone at different bed depths. Experimental conditions: Q = 2mL/min 23±1°C, initial pH 6.5; particle size 0.42mm-0.59mm;* $C_0 = 6.12$ *mmol*SO_4^{2-}*/L.*

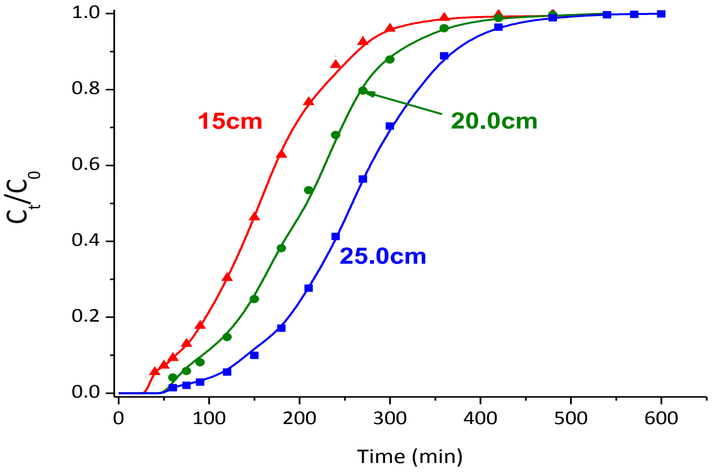

Figure 3. *Breakthrough curves for sulphate sorption on limestone at different bed depth. Experimental conditions: Q=3mL/min 23±1°C, initial pH 6.5; particle size: 0.42mm-0.59mm;* $C_0 = 6.12$*mmol*SO_4^{2-}*/L.*

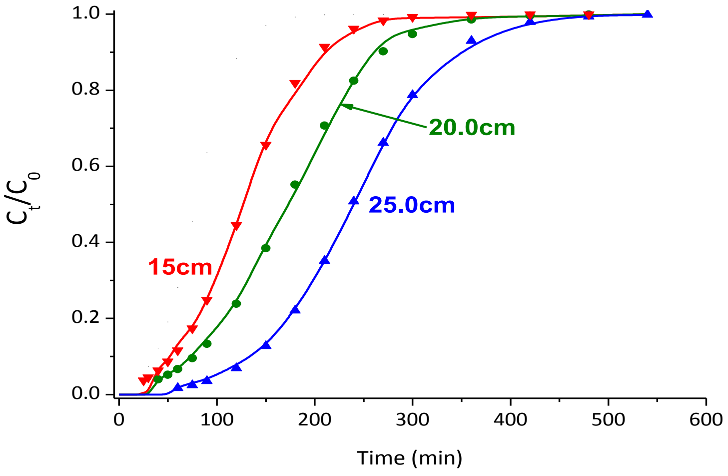

Figure 4. *Breakthrough curves for sulphate sorption on limestone at different bed depths. Experimental conditions: Q = 10mL/min 23±1°C, initial pH 6.5; particle size: 0.42mm-0.59mm;* $C_0 = 6.12$*mmol*SO_4^{2-}*/L.*

The Thomas model revealed solid phase (q_m) and bed loading (N) values which were roughly independent of the bed depth at the same flow rate (table 1). Table 1 also shows that the bed capacity is increased when the influent flowrate (Q) was also increased at the same bed depth, Z (e.g. 20 cm). Likewise, the rate constant (k_T) decreased with increasing bed depth, at the same flow rate, implying in a larger resistance to mass transfer in the liquid phase. This reflected a change on the form of the breakthrough curves with bed-depth as also observed elsewhere (Srivastava *et al.* 2008; Chauhan and Sankararamakrishnan 2011; Patel and Vashi 2012). In addition there was also a small increase in the rate constant with flowrate (at the same bed length), which implies that chemical control may play a significant role on the sulphate sorption process. This is reinforced by the second-order kinetics observed in batch kinetics experiments carried out by Silva et al. (2012) with the same mine water and limestone. Furthermore, the presence of gypsum on the calcium sulphate surface was showed by Hammarstrom et al. (2003) and also Booth et al. (1997). The latter used sulphate containing neutral solution at pH 5-6 to demonstrate partial limestone dissolution prior to gypsum formation over the attacked rock surface.

Table 1. *Parameters produced during fitting of the Thomas model to sulphate sorption on limestone.*

Z (cm)	Q (cm^3/min)	k_T (mL.mmol^{-1}min^{-1})	q_m (mmol/g-limestone)	N (mol/L-bed)	SSE
15	10	4.916E-04	1.065E-04	2.00E-01	5.20E-03
20	10	3.840E-04	1.067E-04	2.00E-01	2.98E-03
25	10	3.711E-04	1.186E-04	2.22E-01	3.67E-04
15	3	3.779E-04	3.861E-05	7.24E-02	1.23E-03
20	3	3.528E-04	3.728E-05	6.99E-02	2.73E-03
25	3	3.508E-04	3.756E-05	7.05E-02	8.29E-04
15	2	3.639E-04	3.261E-05	6.12E-02	6.34E-04
20	2	3.359E-04	2.851E-05	5.35E-02	3.67E-03
25	2	3.257E-04	2.740E-05	5.14E-02	1.50E-04

Gypsum precipitation with lime still appears to be the best technical and economical alternative to reduce high sulphate loadings from mine waters because of its high efficiency in reducing the anion concentrations regardless of the pH of the process. Nevertheless, when the wastewater is undersaturated with respect to gypsum (sulphate concentrations below ~1500mg/L), sulphate sorption on limestone would be a cost-effective alternative to treat such waters in order to comply with environmental regulations. Such technology would be particularly suitable for those countries where water is widely available and where mine water treatment costs must remain as low as possible because there is no possibility to commercialize the treated water.

Conclusions

Limestone is a promising low-cost adsorbent for sulphate removal from neutral mine waters containing low concentrations of metals such as iron and manganese. Sulphate removal, likely as gypsum sorbed onto limestone particles, suggests a chemisorption process described by the Langmuir isotherm with a maximum uptake of 0.248mmol/g. Such hypothesis was reinforced by the application of the Thomas model to breakthrough curves produced in fixed bed experiments, which revealed only a small effect of the flowrate on the rate constant.

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Reduction of salinity and hardness of water using copolymerized biopolymers

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Abstract

In this study two adsorbents were systematically synthesized through grafting using different biomaterials to target specific pollutants. Ethyl acrylate was grafted to guar gum using potassium persulfate as initiator to form the guar gum-graft-poly(ethylacrylate) (GG-g-PEA) for the reduction of the hardness of solutions; while the polyacrylamide (PAM) was grafted on the backbone of chitosan to form chitosan-g-polyacrylamide (C-g-PAM) for the reduction of salinity of solutions. The adsorbents were characterized to confirm their properties using scanning electron microscope (SEM) and they were tested for the removal of calcium and magnesium, and sulfate respectively from solutions. The results show that the grafting process was successful for both GG-g-PEA and C-g-PAM formation. Both adsorbents showed good removal potential of the respective pollutant, and their adsorption behaviour was predicted by kinetic and isotherm models. It was observed that GG-g-PEA did not exhibit exactly the same behaviour for the removal of calcium and magnesium; as the adsorption capacity predicted by the pseudo second order kinetic model for the adsorption of Ca (q_e = 32.87 mg/g) was relatively high compared to Mg (q_e = 30.45 mg/g). The removal of sulfate by C-g-PAM fitted the Langmuir model (q_m = 277.78 mg/g) and the pseudo-second order kinetic model (q_e = 128.21 mg/g).

The study has shown that improvement of the properties of biopolymers through grafting could allow their application in the reduction of hardness and salinity of water.

Key words: Grafting, copolymer, adsorption, water hardness and salinity

Introduction

Effluents from acid mine drainage or activities such as coal preparation as well as other anthropogenic activities often contain high concentration of sulphate, calcium, sodium, magnesium and chlorides. Mines, smelters, kraft pulp, paper mills, textile mills and tanneries are some of the major sources of sulphates discharged into environmental water; metallurgical roasting processes and combustion of fossil fuels produce atmospheric sulphur dioxide which is converted to dilute sulphuric acid and falls as acid rain contributing to the sulphate content of surface water. Calcium and magnesium are naturally abundant in soils or rocks and become available in water through the weathering/dissolution of exposed ore, waste rock and tailings (Banks et al. 1997; Schmiermund et al. 1997; Mendez-Ortiz et al. 2007). It has been found that these dissolved ions in combination have a negative effect on the aquatic life and balance of its ecosystem. Sulphate may cause health problem to human only if it occurs at high concentrations in drinking water; vulnerable people such as children, transients and elderly are considered as the subpopulation more sensitive to the cathartic effects of exposure to high concentrations of sulphate, because of the potential high risk of dehydration from diarrhoea that may be caused by high levels of sulphate in drinking water (US EPA 1999a, b). Magnesium is reported to have a more toxic effect on the aquatic life than calcium (van Dam et al. 2009). However, these contaminants have been neglected because of the lower effect on human being. Common practices for the removal of sulphate and calcium, mainly consist of the use of coagulation/flocculation processes or reverse osmosis which are either ineffective, costly or result in toxic byproducts. Adsorption is a better alternative to remove such pollutants from water, giving the opportunity to recover and control the pollutant while regenerating the adsorbent. Biopolymers are suitable adsorbent for the fact that they are widely available and are biodegradable. Among these, agricultural wastes, organic polymeric resins, polysaccharide such as chitin and starch, and their derivatives (cyclodextrin and chitosan) (Robinson et al. 2002; Synowiecki and Al-Khateeb 2003; Bailey et al. 1999; Yuryev et al. 2002; Babel and Kurniawan 2003; Varma et al. 2004; Crini and Morcellet 2002). Intrinsic properties of biopolymers such as high reactivity due to the presence of chemical reactive groups, physico-chemical characteristics, chemical stability, renewability and biodegradability make them very attractive adsorbents (Ciesielski et al. 2003; Polaczek et al. 2000; Fosso-Kankeu et al. 2011, 2015, 2016). Cross-linking agents can be used to improve the performance of biopolymers as adsorbents through enhancement of their mechanical properties and their stability in acid solutions (Chiou et al. 2004); example of cross-linking reagents include ethylene glycon diglycidyl ether, epichlorohydrin, formaldehyde, glutaraldehyde, glyoxal and isocyanates (Crini and Badot 2008).

In this study two adsorbents were systematically synthesized through grafting using different biomaterials to target specific pollutants, namely calcium and magnesium (hardness) as well as sulphate (salinity).

Methods

Reagents

Guar gum (GG), de-acetylated chitosan (high molecular weight) and sodium sulfate were purchased from Sigma-Alrdrich (SA). Ethyl acrylate, acrylamide and potassium peroxodisulfate were purchased from Merck Chemical Co. Ltd., and calcium nitrate, acetone, magnesium chloride and ammonium ceric nitrate were purchased from ACE Pty. Ltd.

Synthesis of copolymers

Synthesis of guar gum-graft-poly(ethylacrylate) (GG-g-PEA)

Guar gum was dissolved in 15 mL of distilled water using a magnetic stirrer. The solution was stirred for 10 minutes in a 600 mL beaker. To this 3 mL of ethyl acrylate (0.17 M) was added to the GG solution and was stirred for 10 minutes. Potassium persulfate (0.0035 M) was added to the reaction mixture and solution was stirred for another 5 minutes. The reaction mixture was irradiated in a domestic microwave (Hisense microwave grill, 900 MW, microwave frequency 2450MHz) at a known microwave power (60%, 80%, and 100%) for a definite time (1 min, 2 min and 3 min) period. After exposure the reaction mixture was allowed to cool down to room temperature and was precipitated with an excess amount of acetone. The copolymer was then washed with acetone. The grafted copolymer samples were then placed in a Soxhlet apparatus for 3 hours to dissolve the homopolymer. The GG-g-PEA samples were then dried in an oven for 24 hours at 40°C to a constant weight. The samples were then crushed using a pestle and mortar and the polymer was weighed. The copolymer at optimum microwave power and time was used in adsorption experiments. The microwave power was varied from 60% to 100% in increments of 20%. The exposure time was varied from 1 min to 3 min in increments of 1 min.

Synthesis of chitosan-g-polyacrylamide (C-g-PAM)

The grafting of the PAM onto the chitosan backbone was done using the ceric ammonium initiation method (Yuan et al. 2010). 100 mL of a 1% acetic acid solution was prepared in a 250 mL Erlenmeyer flask, into which, 0.4 g of chitosan was added and shaken at 100 rpm for 30 minutes. The same weight of ceric ammonium nitrate was added with a pre-determined amount of PAM and the mixture was allowed to react for 3 hours. After the 3 hours, the mixture was precipitated in acetone and the white, jelly like copolymer was washed with more acetone two more times, to remove any homopolymer. All the copolymer was added into a single beaker and this was dried in a vacuum oven at 50ºC for 24 hours.

Characterization of synthesized copolymers

SEM analysis was done to identify the compound morphology. The model used was a FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive x-ray spectrometer.

Adsorption experiments

Removal of calcium and magnesium

The synthesized guar gum-graft-poly(ethylacrylate) (GG-g-PEA) copolymer was evaluated for the removal of Mg^{2+} and Ca^{2+} from aqueous solutions and conditions of adsorptions parameters were optimized. Different adsorption parameters were changed while keeping the others constant. The adsorption experiments were carried out in a temperature controlled incubator shaker set at a speed of 200 rpm, keeping temperature constant at 30 °C for 2 h and 30 min. The adsorption of Mg^{2+} and Ca^{2+} was investigated at various time intervals (5, 20, 40 and 60 mins) while keeping constant the other parameters: the concentration was fixed at 50 mg/L, total volume of solution was 25 mL and an adsorbent dosage of 25 mg was used. The effect of initial metal ion concentration was also investigated. The concentration of the metal ions in solution ranged from 25-100 mg/L. The suspensions were centrifuged at a speed of 4000 rpm for 10 min. The supernatant was then transferred into glass vials for analysis. Control experiments revealed that no sorption occurred on glassware.

Removal of sulphate

The adsorption experiment was carried out in a batch system. Sodium sulphate was added to 100 mL of de-ionized water and shaken lightly until the sulphates were dissolved. Chitosan-g-polyacrylamide (C-g-PAM) copolymer was then added and allowed to adsorb the sulphates before a small sample of the solution was removed and centrifuged. 1 mL of the centrifuged liquid was mixed with 10 mL of a 1% nitric acid solution and sent for ICP-OES analysis to find the concentration of sulphur still present in the water. For the tests, four different parameters were tested, one at a time with the others kept constant.

The parameters tested included the copolymer concentration (0.1 g/100 mL, 0.2 g/100 mL, 0.3 g/100 mL, 0.4 g/100 mL), sulphates concentration (500 mg/L, 1000 mg/L, 2000 mg/L, 3000 mg/L) and adsorption time (15 min, 30 min, 60 min, 90 min). One parameter was varied while the others were kept constants.

Isotherms and kinetics models

The adsorption affinity of the copolymer adsorbent for the removal of the adsorbate was evaluated using the Langmuir and Freundlich isotherms. The Langmuir isotherm model assumes monolayer adsorption in single solute systems with its linear form given by (Fosso-Kankeu et al. 2011; Mittal et al. 2013; Fosso-Kankeu et al. 2015):

$$\frac{C_e}{q_e} = \frac{1}{k \cdot q_m} + \frac{C_e}{q_m} \quad (1)$$

The Freundlich model is not restricted to monolayer adsorption and it can be applied in heterogeneous systems where its linear form can be expressed by:

$$\log q_e = \log k_f + \frac{1}{n} \cdot \log C_e \quad (2)$$

In the isotherm models C_e is the concentration of adsorbate at equilibrium in (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in (mg/g), q_m is the adsorption capacity in (mg/g), k is a Langmuir constant related to energy released during adsorption in (L/mg), k_f is the Freundlich adsorption capacity parameter in (mg/g) and n is the intensity of adsorption.

To aid in identifying the adsorption rate the pseudo first- and second order models are used (Patil and Nayak 2011; Fosso-Kankeu et al. 2011; Mittal et al. 2013; Fosso-Kankeu et al. 2015). The pseudo first- and second-order kinetic models are given by:

$$\log(q_e - q_t) = \log q_e - k_1 \cdot \frac{t}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \quad (4)$$

where: q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in (mg/g), q_t is the amount of adsorbate adsorbed at time t in (mg/g), k_1 is the first order rate constant in (min^{-1}), k_2 is the second order rate constant in (g/mg.min^{-1}) and t is the time in (min).

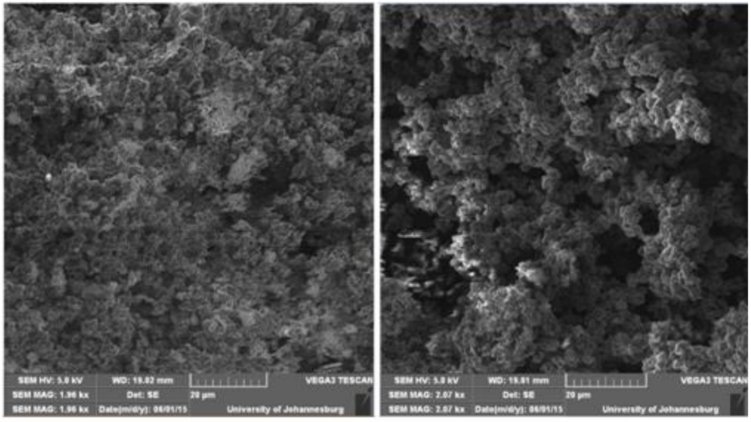
Results and discussion

Physicochemical characteristics of copolymers

Morphology of copolymers

Guar gum (GG) and GG-g-PEA

The surface morphology of guar gum (GG) and GG-g-PEA was studied by using a scanning electron microscope to investigate the grafting of PEA onto GG. It can be seen from Figure 1a that the fibrous nature of the guar gum particles and it suggests that the biopolymer is amorphous by nature. The grafted copolymers particle size is significantly higher than GG, which is evidence that Ethyl acrylate was grafted successfully onto GG and the particles also differ in shape.

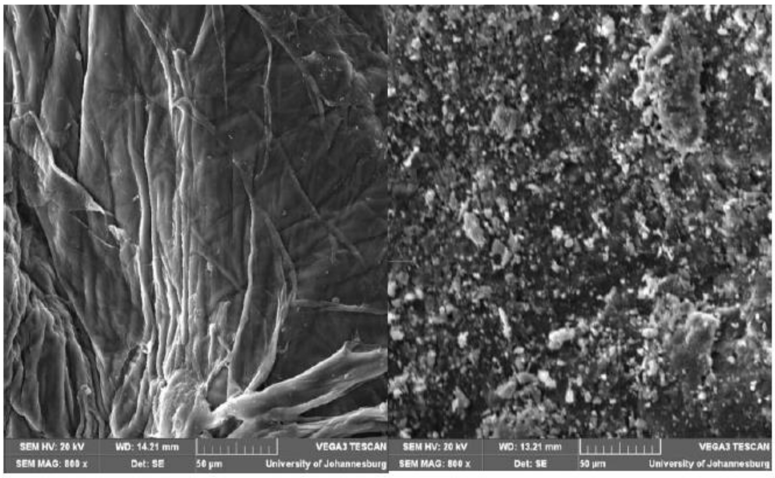


(a) (b)

***Figure 1** SEM micrograph of guar gum (a) and GG-g-PEA (b)*

Chitosan and C-g-PAM

The SEM images in Figures 2a and b show the pure chitosan and C-g-PAM at 800x magnification, respectively. The main difference that indicates successful grafting is the tiny dots and particles on the surface of the copolymer which is where the PAM was grafted to the chitosan backbone. These images compare very well with other SEM images from literature (Shanmugapriya et al. 2011; Patil and Nayak 2011).



(a) (b)

***Figure 2** SEM micrograph of pure chitosan (a) and C-g-PAM (b)*

Adsorption isotherm study

Langmuir model

The Langmuir graph was made by plotting C_e/q_e vs. C_e where the slope = $1/q_m$ and the intercept = $1/K_Lq_m$.

Removal of Ca(II) and Mg(II)

The Langmuir isotherm is valid when monolayer adsorption is assumed due to a finite number of sites available on the surface of the adsorbent. The linear relation of the Langmuir model is used to calculate the maximum adsorption capacity (q_m mg/g) and the Langmuir constant (k) using the slope and the y-intercept. According to the results, summarised in Table 1, this model does not fit the data for the adsorption of Ca(II) and Mg(II) as shown by the values of the coefficient of determination (R^2) which are relatively low (0.7276 and 0.8158 for the adsorption of Ca(II) and Mg(II) respectively). It implies that the Langmuir model is not suitable for the prediction of the adsorption behaviour, therefore homogeneous binding does not take place.

Removal of SO_4^{2-}

From the Langmuir plot of the adsorption of sulphate the adsorption parameters were obtained; the value of q_m was 277.78 (mg/g) and K_L was 0.00349. The R^2 value was relatively close to unity, implying that the adsorption occurs mainly on the monolayer surface.

Freundlich model

Removal of Ca(II) and Mg(II)

In this model it is considered that heterogeneous adsorption takes place and that the adsorption capacity depends on the concentration of the copolymer. This type of model is usually used for solutions of low concentration of adsorbate (Mittal et al. 2013). The constants such as K_f, 1/n and R^2 are listed in Table 1. The Freundlich constants were calculated from the slope and y-intercept from a linear plot of $\log q_e$ vs. $\log C_e$. It is observed that the values of the coefficient of determination are close to unity (for the adsorption of Ca(II), R^2 = 0.914 and for the adsorption of Mg(II), R^2 = 0.955), implying that the Freundlich model is suitable for the prediction of the adsorption behaviour. The value of K_f is a rough indicator of the adsorption capacity and 1/n is an indicator of the adsorption intensity. As the value of K_f increases the adsorption capacity of adsorbent for a given adsorbate also increases. The value of the exponent, 1/n gives us an indication of the favourability of adsorption. It is observed that GG-g-PEA has a greater adsorption capacity for Ca(II). If the values of 1/n are less than 1.0, this indicates that the adsorption process is favourable over the whole range of concentrations studied and if the values of 1/n are bigger than 1.0 then this indicates that the adsorption process is favourable at higher concentrations but not favourable for lower concentration (Fosso-Kankeu et al. 2015, 2016).

Removal of SO_4^{2-}

The Freundlich isotherm graph, plotted as $\log q_e$ vs. $\log C_e$, had a much worse fit with the very low R^2 value indicating the poor fit. Thus the values that could be calculated from this method will be disregarded.

***Table 1** Calculated parameters for the adsorption isotherm models*

Isotherms	Parameters	Ca(II)	Mg(II)	SO4
Langmuir	q_e	No fit	No fit	277.8
	b			0.0035
	R 2			0.9
Freundlich	1/n	4.288	3.26	No fit
	K_f	0.0029	0.00019	
	R 2	0.914	0.9553	

Adsorption kinetics study

Pseudo-First order

Removal of Ca(II) and Mg(II)

The pseudo first order model was applied for the kinetic study of the adsorption of Ca(II) and Mg(II) onto GG-g-PEA. The plot of log(q_e-q_t) vs t allowed to determine the kinetics parameters (Table 2) of the pseudo first order for both Mg(II) and Ca(II) adsorption. The adsorption data for Ca(II) does fit with the pseudo first order model and is indicated by the value of R^2 (0.9860), the adsorption data of Mg(II) does not fit the pseudo first order model and is indicated by the value of R^2 (0.879). Thus the pseudo first order kinetics can be used to describe the adsorption of Ca(II) but cannot be used to describe the adsorption of Mg(II).

Removal of SO_4^{2-}

The value (6.803) of the coefficient of determination from the plot of log(q_e-q_t) vs t for the pseudo first order, was relatively low and therefore not suitable to predict the adsorption behaviour for the removal of sulphate.

Pseudo-Second order

The pseudo second order model was also applied for the kinetic study of the adsorption of Ca(II) and Mg(II) onto GG-g-PEA. The model fits well with the adsorption data of Ca(II) and Mg(II) and is indicated by the values of R^2 (Table 3). The kinetic parameters of this model are tabulated in Table 3. The R^2 values for the adsorption of Ca(II) and Mg(II) are 1 for both Ca(II) and Mg(II) which suggests that the pseudo-second order rate model is an appropriate assumption, demonstrating that the adsorption occurs via a chemisorption process (Mittal et al. 2013; Fosso-Kankeu et al., 2014). The adsorption capacity of GG-g-PEA is relatively high for both metals and it is q_e = 32.87 and q_e=30.45 for Ca(II) and Mg(II) respectively. Metal ions with higher atomic weight can generate higher momentum energy, which may promote the adsorption of the metal ion by increasing the probability of effective cohesion between the metal ion and the sorbent surface; it therefore ensues that a higher atomic weight leads to higher adsorption preference by the sorbent. This explains the preferential binding of Ca(II) on the copolymer (Fosso-Kankeu et al. 2011; Fosso-Kankeu and Waanders 2014).

Removal of SO_4^{2-}

The values from the time tests were used to plot the pseudo-second order graph, by plotting t/q_t vs. t. The graph has a R^2 value closer to unity which indicates the suitability of the model to predict the adsorption behaviour of the copolymer and thus the K_2 value of -0.00092 (g/mg min) and q_e value of 128.21 (mg/g) were calculated.

Table 2 *Calculated parameters of the adsorption kinetics*

Kinetic Model	Parameters	Ca(II)	Mg(II)	SO_4^{2-}
Pseudo first order	K_1	0.05	0.047	No fit
	q_e	17.53	19.88	
	R 2	0.986	0.879	
Pseudo second order	K_2	0.268	0.3835	-0.009
	q_e	32.87	30.45	128.21
	R 2	1	1	0.98

Conclusions

The GG-g-PEA and C-g-PAM were successfully synthesized in this study as shown by the SEM results. The application of the synthesized adsorbents for the reduction of the hardness and salinity of water, showed that their capacity could be easily predicted using the pseuso-second order kinetic model. It was therefore deduced that the GG-g-PEA had higher affinity for Ca(II) than Mg(II) while

C-g-PAM exhibited a relatively high adsorption capacity for SO_4^{2-}. The developed adsorbents can therefore be considered to remediate surface water pollution.

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Removal of iron and suspended solids in mine water treated by vertical flow reactor

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Extended Abstract

Mine drainages with dissolved iron and suspended solids (SS) contaminate streams in mining areas. A vertical flow reactor (VFR) with iron ocher could be used to remove iron in mine drainages due to filtration of iron hydroxides particles, surface-catalysed oxidation of ferrous iron and subsequent accretion of iron hydroxide [1]. This study was carried out to evaluate contaminant removal capacity of VFR treating mine water of circum-neutral pH on site.

The VFR 1 and 2 were 1.5m wide, 1m long and 1.4 m deep. Mine water flowed down through a 1.5 m^2 bed of gravel which sat on porous stainless steel plate 10cm afloat from bottom of the reactor. Another horizontal flow reactor with baffles, control, was prepared to compare between vertical and horizontal system. Water flow of the control was horizontal such as oxic wetlands in passive treatment systems. The control had no function of filtration through the iron hydroxide and just flowed horizontally by baffles.

The influent flow rates of VFR 1 and 2 were around 1500 mL/min and the control 1000 mL/min. Maximum retention time of VFRs was less than 5 hours and the control was about 25 hours. Difference of retention time arose from level of outlets even though dimensions of reactors were almost same. Water samples of influent and effluent were collected periodically and analyzed using standard methods. Water parameters like pH and EC were measured on site

Concentration of Fe and SS in influent showed changes over monitoring period. Concentration of non-filtered Fe in effluent at VFR 1 was around 1mg/L and VFR 2 was below 1 mg/L **(Figure 1)**. The iron content in effluent of control showed changeable reflecting fluctuation of iron in influent and ranged from 1 to 4 mg/L except for some periods. Concentration of SS in effluent at VFR 1 and 2 were measured about 5 mg/L. Contents of SS in effluent of control was around 10 mg/L. Removal pattern of VFR were more stable than the control regardless of iron and SS content. It is concluded that VFR with layer of iron hydroxide could be applied for removing iron and SS in mine drainage as an passive treatment system. The decrease in permeability in VFR might be related to longevity of the system.

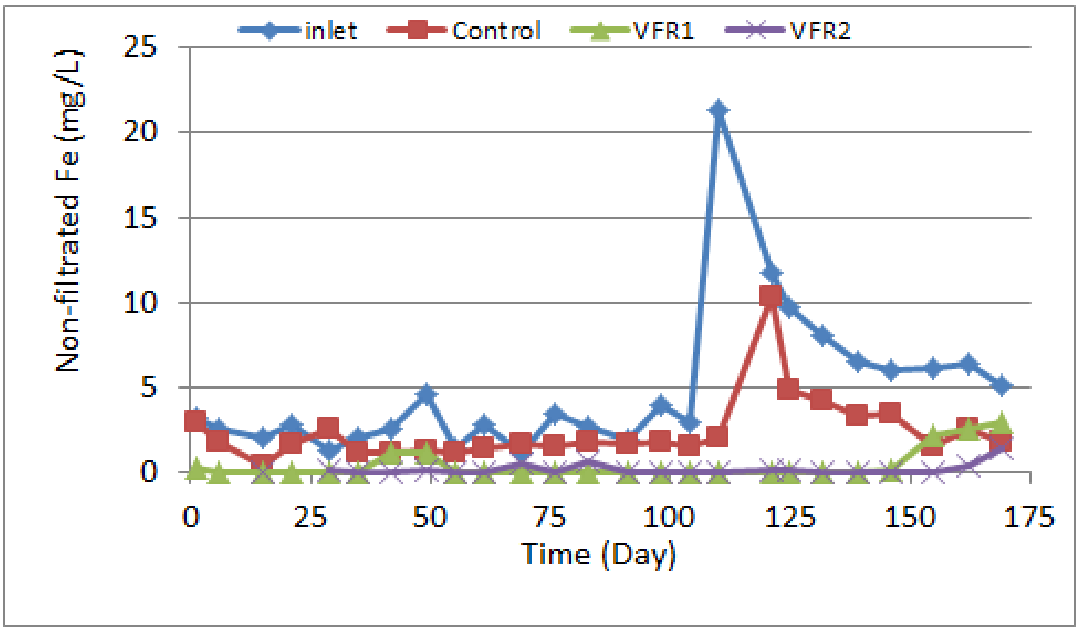

Figure 1 *Comparison of non-filtered iron concentration in inlet and effluents*

Key words: mine drainage, vertical flow reactor, iron, suspended solids

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Removal of Oxoanions From Water: Comparison of a Novel Schwertmannite Adsorbent and an Iron Hydroxide Adsorbent

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Abstract

An agglomerated, filter stable adsorbent was developed based on biotechnologically synthesized schwertmannite (SHM) from lignite mine water containing iron and sulfate. The adsorbent 'SHM-sorpP' was obtained by compacting SHM in a briquette press. As investigated by Fukushi et al. (2003) and Peiffer et al. (2012), SHM and SHM-based adsorbents offer excellent adsorption properties towards arsenic.

SHM-sorpP was tested in comparison to the commercially available iron hydroxide adsorbent Ferrosorp®Plus (HeGoBiotec GmbH) with regard to its suitability for the removal of the oxoanions antimonate, molybdate, vanadate, chromate or phosphate from synthetic water. For this purpose, laboratory batch tests with c(oxoanion) = 20 mg/L and c(phosphate) = 100 mg/L respectively and c(adsorbent) = 0.5 g/L were performed for 21 days to estimate adsorption kinetics and capacities for the adsorbents mentioned above. The oxoanions where added as salts to tap water, the starting pH was adjusted to pH 7.5 with 1 M NaOH. During the test time, no pH-buffering was done.

Phosphate was adsorbed more efficiently by Ferrosorp®Plus than by the schwertmannite adsorbent (36.6 mg/g Ferrosorp®Plus vs. 24.7 mg/g SHM-sorpP within 24 hours). In contrast, antimonate, molybdate and vanadate were adsorbed significantly more efficiently to the schwertmannite adsorbent: within 24 hours, between 11.2 and 17.9 mg oxoanion/g adsorbent could be removed from the solutions in the batch tests with SHM-adsorbent, whereas only between 1.1 and 10.7 mg oxoanion/g Ferrosorp®Plus were analysed. The removal of chromate was markedly lower, about 5 mg chromate/g schwertmannite adsorbent and no chromate adsorption to Ferrosorp®Plus were determined.

Key words: schwertmannite, oxoanions, water treatment

Introduction

Within the recently finished BMBF funded research projects SURFTRAP and SURFTRAP II two different methods were investigated to develop filter stable adsorbents based on biotechnologically synthesized schwertmannite (Janneck et al. (2015)). This schwertmannite is generated in a worldwide unique pilot plant (Janneck et al. (2010)) which is located as a bypass at the water treatment plant of the open pit lignite mine Nochten (Lusatia/ Germany) and is operated by Vattenfall Europe Mining AG and G.E.O.S. company. These adsorbents showed maximum adsorption capacities to arsenite and arsenate in former laboratory tests (Janneck et al. (2015)). With this study we investigated the adsorption behaviour of further oxoanions as antimonate, molybdate, vanadate, chromate, and phosphate to the schwertmannite based adsorbent SHM-sorpP versus Ferrosorp®Plus to demonstrate further applications in industrial waste water purifying.

Materials and Methods

Adsorbents

SHM-sorpP (fig. 1) was fabricated by high pressure compaction of the schwertmannite from the pilot plant. Details of the high pressure compaction are given in EU patent application EP2664376A1. The adsorption properties relating to the different oxoanions of the new SHM-based adsorbent should be compared to a commercially available iron hydroxide adsorbent like Ferrosorp®Pus (HeGo Biotec GmbH).

Figure 1 *SHM sorpP*

Test solution

All laboratory tests were done with tap water which was stocked with 20mg/L of the oxoanion, respectively with the exception of phosphate where a concentration of 100mg/L was used. Table 1 summarizes the used chemicals.

Table 1 *Chemicals for stocking the test solution*

oxoanion	chemical
chromate	K_2CrO_4
molybdate	$Na_2MoO_4*2H_2O$
antimonate	$NaSbO_3*3H_2O$
vanadate	NaO_3V
phosphate	$NaH_2PO_4*H_2O$ and KH_2PO_4

Methods

Several batch tests were performed to investigate the adsorption kinetic of the oxoanions. A water volume of 250 mL and an adsorbent concentration of 0.5 g/L were used. Within the 21 d test period 12 samples were taken, filtrated (0.2µm) and analyzed by ICP-OES (Optimal 3200XL, Perkin Elmer) for Sb, Mo, V and Cr and UV-vis (UV-vis spectrometer Lambda 10, Perkin Elmer, wave length 80 nm) for PO_4. The start pH value was adjusted to 7.5 with 1M NaOH but no pH buffering was done during the test.

Results

In the following graphs (figures 2 a-d) the adsorption behaviour of the determined oxoanions is shown. Chromate, molybdate, antimonate and vanadate were removed significantly more efficiently by the new schwertmannite based adsorbent SHM-sorpP.

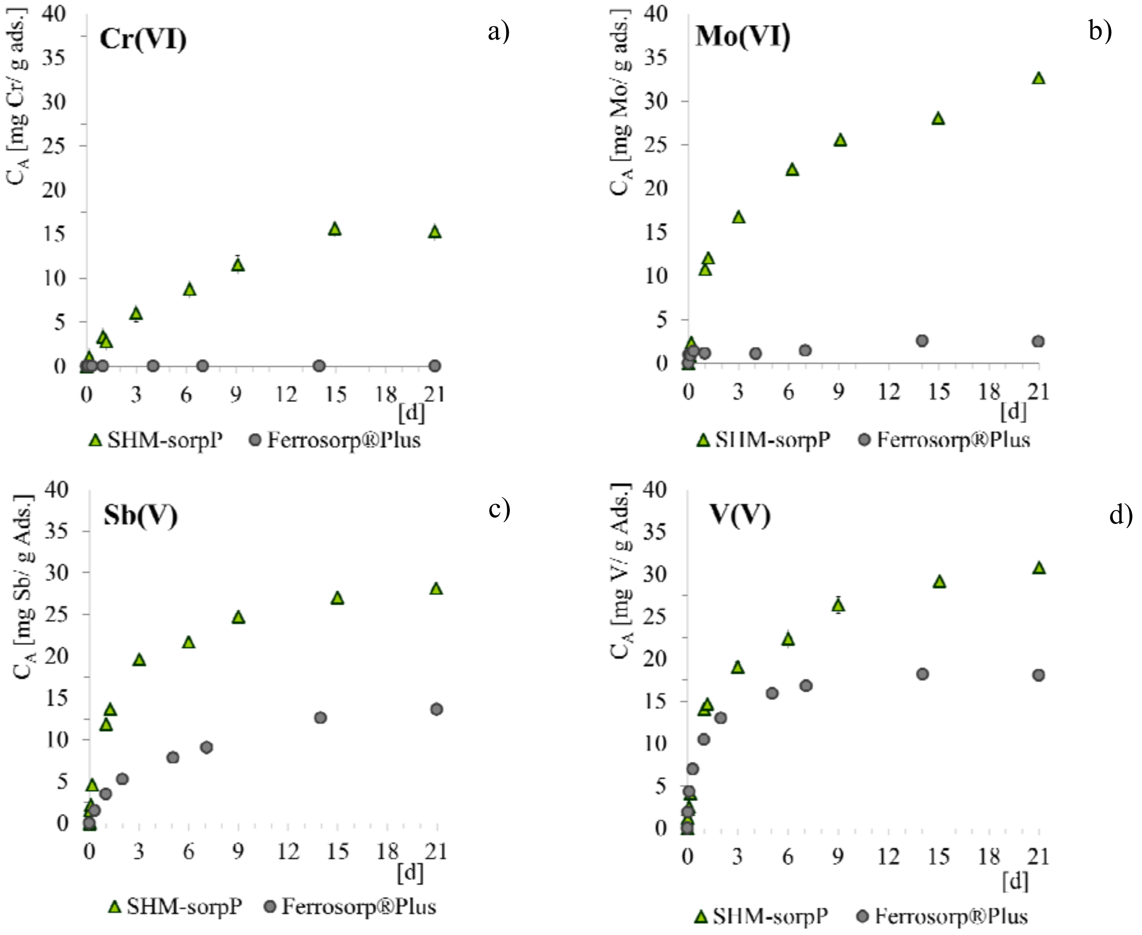

Figure 2 *a-d Adsorption behaviour of the oxoanions chromate, molybdate, antimonite and vanadate*

In contrast, phosphate was removed slightly more efficiently by Ferrosorp®Plus within the first days of the batch experiment. At the end of the test period no significant difference between the load of SHM-sorpP and Ferrosorp®Plus was measured (figure 3).

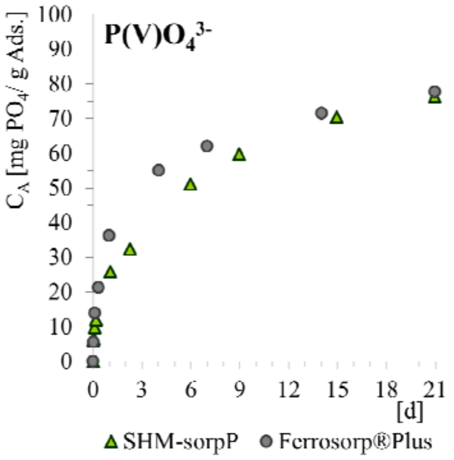

Figure 3 *Adsorption behaviour of phosphate*

Table 2 compares the adsorbent loadings of SHM sorpP and Ferrosorp®Plus related to the oxoanions chromate, molybdate, antimonate, vanadate, and phosphate.

Table 2 *Adsorbent loadings of SHM-sorpP and Ferrosorp®Plus after 21 days*

adsorbent	chromate	molybdate	antimonate	vanadate	phosphate
		(mg oxoanion/g adsorbent)			
SHM-sorpP	15.80	32.66	28.15	30.77	76.41
Ferrosorp®Plus	0.00	2.47	13.61	18.08	77.59

Conclusions

The new schwertmannite based adsorbent 'SHM sorpP' for the use in passive water treatment systems showed a very effective removal of the oxoanions chromate, molybdate, antimonate, vanadate, and phosphate from synthetic water. In comparison to the commercially available Ferrosorp®Plus SHM-sorpP significantly better loadings were reached for chromate, molybdate, antimonate, and vanadate respectively and nearly similar loadings for phosphate. These results are very promising for further application of SHM-sorpP in passive water treatment plants to purify different industrial waste waters.

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Application of Biomass Ashes for Treatment of Acid Mine Drainage

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Abstract

Acid mine drainage (AMD) is the largest environmental problem facing the world mining and processing industry because it has low pH and can contain high concentrations of potential pollutants (e.g., Zn, Pb, Cd, Cu, As, Sb, Hg). Biomass ash (BA), which is a by-product of burning biomass in conventional power station, can be considered as a potential material for AMD treatment. The main goal of this work was to investigate potential use of BAs for AMD remediation. Four UK biomass ashes from different fuels (i.e., straw, meat and bone meal, mixed biomass) were characterised. All biomass ashes contain high concentrations of P, Ca, and K. The bulk crystalline phases in the biomass ashes include portlandite, calcite, arcanite, quartz, apatite, and other phosphates. We used a synthetic AMD which is comparable in composition to AMD from the Almasu Mare region in Romania. Batch experiments showed that a biomass ash from straw combustion (L/S = 250) can effectively neutralise the synthetic acid mine drainage (pH=2.7; Fe=310 mg/L; Zn=95 mg/L; Mn=54 mg/L), with removal of potential pollutants (pH=7.4; Fe=0.01 mg/L; Zn=0.58 mg/L; Mn=17 mg/L) in less than 1 hour. Other series of experiments were carried out on real AMDs from the Ursk Tailings of the Gold concentration plant and from the Belovo sludge pond from the Belovo zinc processing plant which have low pH (2.73-3.83) and high concentration of heavy metals. The biomass ashes from straw and mixed biomass combustion can effectively remove pollutants from the Ursk AMD at L/S = 100 and adjust pH=5.7-7.8. For the Belovo AMD, an appropriate L/S ratio is 10-30 and pH can be adjusted to 6.0-10. The metal concentrations of these treated AMDs met water quality standards. Pollutants mainly present as phosphate which usually have very low solubility product constant.

Key words: Acid mine drainage, biomass ash, AMD remediation

Introduction

Acid mine drainage is the largest environmental problem facing the world mining and processing industry (Bogush et al. 2015; GARD/INAP; Hudson-Edwards et al. 2011; Jambor et al. 2003; Lottermoser 2007; Nordstrom 2011; Nordstrom and Alpers 1999; Wolkersdorfer 2008; Younger 2002). AMDs has low pH and can contain high concentrations of potential pollutants.

Biomass ash, which is a by-product of burning biomass in conventional power station, can be considered as a potential material for AMD treatment. BA are complex alkaline inorganic-organic mixtures with polycomponent, heterogeneous and variable composition (Vassilev 2013). Biomass combustion is an important part of the global renewable energy which is growing fast worldwide (Demirbas 2005). However, approximately 480 million tons of biomass ashes could be generated worldwide annually, which is comparable to coal ash annually production (780 million tons) (Vassilev 2013). In the UK, biomass ashes are currently landfilled or used in relatively low-value applications.

The aim of the present study was to investigate, at laboratory scale, the effectiveness of biomass ashes for removing heavy metals from AMD.

Material and Methods

Four UK biomass ashes from different fuels (i.e., EBFA from straw, EPR-Gba from meat and bone meal, TBA and EBA from mixed biomass) were characterised. Figure 1 shows the appearance of the biomass ashes.

EBFA EPR-Gba TBA EBA

Figure 1 *Visual observation of UK biomass ashes.*

The Spectro XLAB2000 X-ray fluorescence (XRF) spectrometer was used for element analysis in biomass ashes. A pH value of a water leachate (L/S=10) was analysed. XRD was used to characterise the crystalline phases present in biomass ashes. The morphologies of the particles from the biomass ashes and the residue after AMD treatment were investigated by scanning electron microscopy (SEM: JEOL JSM-6480LV) with secondary electron imaging (SEI) and backscattered electron imaging (BEI) detectors.

The synthetic acid mine drainage (SAMD) was prepared with pH and element composition comparable to AMD from the Almasu Mare mining region in Romania: SAMD - pH=2.7; Fe=310 mg/L; Zn=95 mg/L; Mn=54 mg/L. The SAMD was used in the batch experiments for SAMD remediation by the biomass ash from straw combustion (EBFA). A known amount of the EBFA (0.01, 0.035, 0.05, 0.075, 0.10 and 0.25 g) was added to the SAMD (25 mL) with agitation. The pH of the solution was measured before and after EBFA addition. After 1 h, the SAMD-EBFA mixtures were filtered through the 0.45 µm membrane filters and acidified with pure HNO_3. Element concentrations (Ca, Mg, Fe, Zn and Mn) were measured by ICP-OES (Varian 730). Then, the removal efficiency was calculated.

Other series of batch experiments were carried out on the AMDs from the Ursk tailings of the Gold concentration plant and from the Belovo sludge pond from the Belovo zinc processing plant which have low pH and high concentration of heavy metals. The biomass ashes (EBFA, EPR-Gba, TBA, and EBA) were added to AMD (Ursk AMD and Belovo AMD) with agitation at different liquid to solid ratio (L/S: 10, 50, 100, 200, 500). The pH value of the solution was measured before and after BA addition. After 1 h, the AMD-BA mixtures were filtered through the 0.45 µm membrane filters and acidified. Element concentrations (Fe, Al, Zn, Cu, Cd, Ni, Cd, and Mn) were measured by AAS. Then, the removal efficiency was calculated.

Results and Discussion

Characterisation of the Biomass Ashes

The BAs contain high concentrations of P (2.2-10%) and Ca (13-37%). The bulk of the crystalline phases present in the EPR-Gba, TBA and EBA biomass ashes include calcite, portlandite, arcanite (excluding EPR-Gba), quartz, apatite and other phosphates. The biomass ash from straw combustion (EBFA) contains portlandite, arcanite, calcium sulphate hydrate, sylvite and apatite.

The biomass ashes (EPR-Gba, TBA, and EBA) mainly contain unshaped particle (up to 1 mm), aggregates and fine materials. The spherical particles were also identified in these biomass ashes. The biomass ash EBFA mainly contains fine phases (<1 µm) and unburnt straw residues (200-300 µm) with a few glassy particles.

The pH of the water-based leachates was high due to the presence of excess $Ca(OH)_2$ in BAs and varied from 12.22 to 12.78. It should be noted that a saturated solution of $Ca(OH)_2$ has a pH of about 12.4. The pH values generally correspond to the contents of $Ca(OH)_2$ and CaO (which will be hydrated in the leaching test) determined by XRD.

Synthetic Acid Mine Drainage Remediation with Biomass Ash (EBFA)

It was shown that the biomass ash EBFA efficiently treated the SAMD at L/S = 250 in 1 hour. At this L/S ratio, the concentrations of potential pollutants in treated water were below maximum permissible concentrations (MPCs) for drinking water (SanPiN 2.1.4.1074-01, 2002) and general standards for discharge of environmental pollutants (GSDEP 1993).

The solid residues after the SAMD remediation with the EBFA are mainly amorphous materials. This residue mainly contains aggregates which consist of Ca, P, Si, K, Cl, Al, S, Fe, Mn and Zn.

Acid Mine Drainage Remediation with the Biomass Ashes (EBFA, EPR-Gba, TBA and EBA)

It was shown that the biomass ash from straw and mixed biomass combustion (L/S=100) can effectively adjust pH in the Ursk AMD with removal of potential pollutants: 1) EBFA ─ pH=7.68, Fe=0.14 mg/L, Al, Zn, Cu, Ni, and Co - below the detection limit; 2) TBA ─ pH=5.69, Fe=0.27 mg/L, Zn=0.5 mg/L, Cu=0.47 mg/L, Al, Ni, and Co - below the detection limit; 3) EBA ─ pH=7.17, Fe=0.56 mg/L, Zn=1.7 mg/L, Cu=0.62 mg/L, Al, Ni, and Co - below the detection limit.

The biomass ash from straw (EBFA) and mixed biomass combustion (TBA) at L/S=10-30 can effectively adjust pH to 6.0-10 in the Belovo AMD with removal of potential pollutants. At these L/S ratios, the concentrations of potential pollutants in treated water were below the GSDEP concentrations.

Conclusions

All BAs are alkaline material and contain high concentrations of P and Ca. Mineralogical composition of investigated BAs are complex and mainly depends on biomass composition used for combustion. The bulk crystalline phases in the BAs include portlandite, arcanite, calcite, quartz, apatite, and other phosphates.

Batch experiments showed that the BA from straw combustion (L/S = 250) can effectively treat synthetic acid mine drainage (pH=2.7; Fe=310 mg/L; Zn=95 mg/L; Mn=54 mg/L), with removal of potential pollutants (pH=7.4; Fe=0.01 mg/L; Zn=0.58 mg/L; Mn=17 mg/L) in 1 hour.

It was shown that the BA from straw (EBFA) and mixed biomass (EBA and TBA) combustion can effectively remove pollutants from the Ursk AMD at L/S=100 and adjust pH=5.7-7.8. The biomass ashes EBFA and TBA at L/S ratio=10-30 are effective for Belovo AMD treatment. Pollutants mainly present as phosphate which usually have very low solubility product constant.

Therefore, biomass ashes from straw and mixed biomass (mainly contained animal residues and wood) combustion can be considered as a potential material for AMD treatment.

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Treatment of chromate(VI) and vanadate(V) polluted wastewaters using schwertmannite adsorbents

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Extended Abstract

The toxic oxyanions chromate and vanadate found in industrial wastewaters often require expensive and high-maintenance treatment. Passive filterbed systems are a distinctly cheaper alternative. In this contribution we have tested the potential of the ferric oxyhydroxy-sulfate mineral schwertmannite ($Fe_8O_8(OH)_x(SO_4)_y$; $x = 8 - 2y$, $1 < y < 1.75$) as an adsorbent to be used in such systems for treatment of chromate (Cr(VI)) and vanadate (V(V)). Schwertmannite adsorbents can be sustainably produced from a waste product of mining and show good adsorption performance towards arsenic (DE 102 21 756 A1 2003, Janneck *et al.* 2010, Peiffer *et al.* 2012A, Peiffer *et al.* 2012B).

Adsorption kinetics of the two metal oxoanions and their adsorption isotherms were determined in batch experiments at pH 7±1 (Dou *et al.* 2013, Kolbe *et al.* 2011). Samples were taken after different time intervals, were filtered (0.20 µm) and analysed for chromium and vanadium via ICP-OES.

The concentration of both, dissolved chromium and vanadium strongly decreased within the first 24 h and approximately 40 % of the metals were bound to the schwertmannite adsorbent after this time (Figure 1a). Between 24 h and 8 days chromium adsorbed rather slowly, whereas the removal of vanadium continuously increased. Consequently, after 8 days 51 % and 87 % of the initial chromium and vanadium concentration were adsorbed on schwertmannite, respectively.

The adsorption isotherm of chromium possibly converged to a maximum chromium loading on schwertmannite of approximately 35 mmol per mole iron (Figure 1b). In contrast, even at high initial vanadium concentrations the isotherm of vanadium exhibited a linear trend implying a much higher adsorption capacity compared to chromate.

The different adsorption behaviour is probably caused by different adsorption mechanisms of chromate and vanadate on schwertmannite which will be investigated in the future.
Overall, the results of this study provide first insights into the interactions between chromate and vanadate polluted industrial wastewaters and schwertmannite adsorbents.

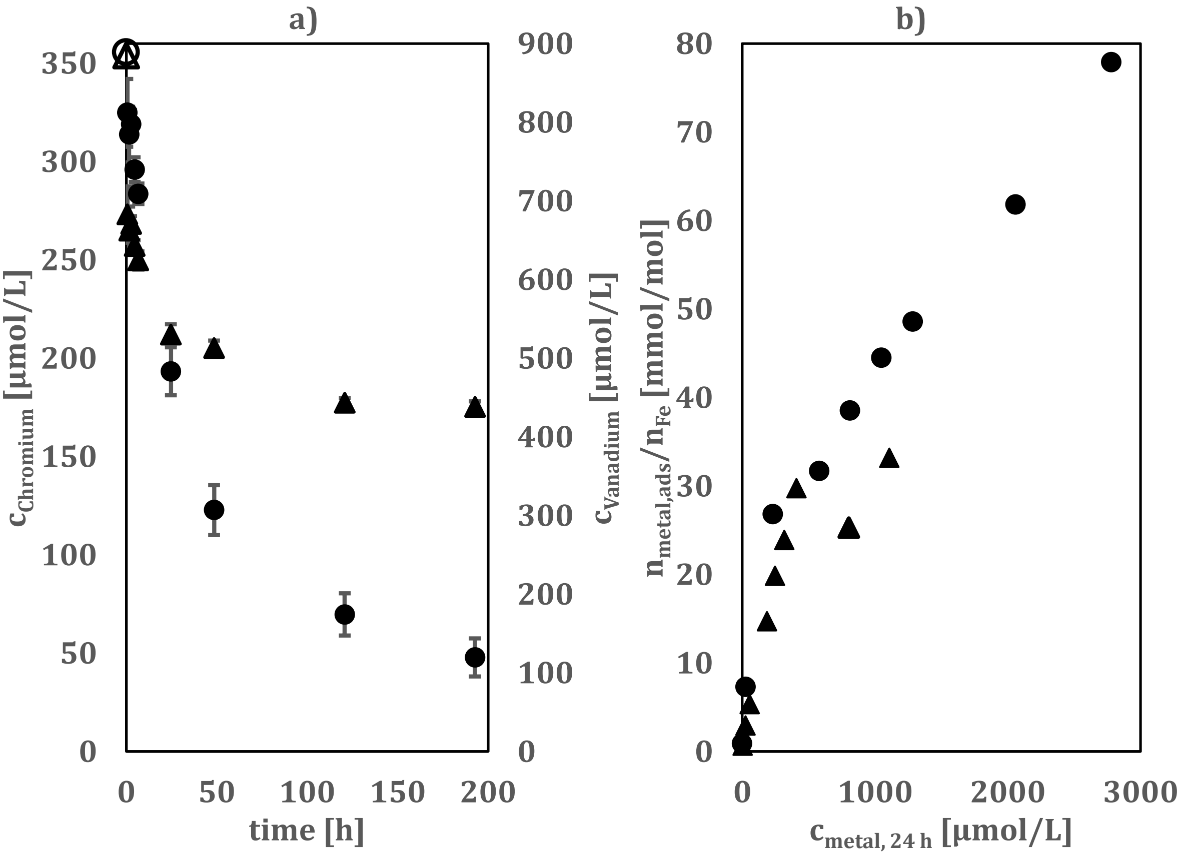

Figure 1 a) *Adsorption kinetics of chromium(VI) (filled triangles) and vanadium(V) (filled circles).* $c_{Chromium}$ *and* $c_{Vanadium}$ *are the concentrations of dissolved chromium and vanadium, respectively, after different time intervals. The unfilled triangle and circle is the calculated initial concentration of chromium and vanadium, respectively.* ***b)*** *Adsorption isotherms of chromium(VI) (filled triangles) and vanadium(V) (filled circles).* $c_{metal,\ 24\ h}$ *is the dissolved chromium or dissolved vanadium equilibrium concentration after 24 h reaction time.* n_{metal}/n_{Fe} *is the amount of chromium and vanadium adsorbed per mole of schwertmannite iron (Fe), respectively.* n_{metal} *was calculated by subtracting* $c_{metal,\ 24\ h}$ *from the initial metal concentration.*

Key words: Adsorption, vanadate, chromate, iron hydroxide, schwertmannite

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CHAPTER 9

Mine Water Microbiology and Bioleaching

Microbial Community Dynamics during the Biochemical Treatment of Acid Mine Drainage under three different Hydraulic Retention Times

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Abstract

In the Zipaquirá Mining District of Colombia, there are about 600 coal mines that generate 70,400 m^3/month of acid mine drainage. A sustainable approach to remediate AMD is to use biochemical passive reactors. However, limited data is available on the dynamics (temporal and spatial) of microbial community and their activity under different hydraulic retention times, in the long-term operation of BPR. Seven 5L biochemical passive reactors (73 × 10 cm) were operated during 36 weeks, under three different hydraulic retention time (1, 2, and 4 days). The reactors were sacrificed on 8, 17 and 36 weeks, and the reactive mixture was sampled at the bottom, middle, and top layers. The microbial community of the post-treatment reactive mixtures was monitored by sequencing (Illumina MiSeq) and correlated with physicochemical parameters. The result showed that operation time, location and hydraulic retention time had significant effects on physicochemical changes of the reactive mixture and it is rather the combination of factors affect diversity during the AMD treatment. In addition, the microbial community analysis resulted in the identification of specialized groups related to cellulose degraders and fermentative bacteria that work in synergy for degrading substrate make the organic material available to sulfate-reducing bacteria. This microbial community analysis provides a base line for future studies in the BPR

Key words: acid mine drainage; microbial diversity; Illumina; biochemical passive reactors

Introduction

Biochemical passive reactors (BPR) is a successful acid mine drainage (AMD) treatment technology with potential advantages such as low costs, few site visits required, ability to work in remote areas, opportunities to use recycled or waste materials, and natural appearance (Doshi 2006). In the Zipaquirá Mining District of Colombia, there are about 600 coal mines that generate ~70,400 m^3/month of drainages and in this region a sustainable approach to remediate AMD is to use BPR. The most efficient reactive mixture for increasing pH and alkalinity, as well as promoting sulfate reduction and metal removal during AMD treatment in Zipaquirá Mining District was selected (Vasquez et al 2016a). In addition, the effect (temporal and spatial) of hydraulic retention time (HRT) (1, 2 and 4 days) on the efficiency of BPRs and microbial activity was also evaluated (Vasquez et al 2016b). However, the microbial community dynamics of this system has not been characterized despite its importance for BPR.

The HRT is a crucial design parameter, which influences the overall performance of BPR during AMD treatment (Neculita et al 2008a). Nevertheless, little is known about how the HRT affects microbial communities during operation time in BPR. In this context, the objective of the present study was to assess the impacts of HRT, location in the reactor and operation time on the microbial community involved in the synthetic AMD remediation under a column study.

Materials and methods

BPR design and AMD characteristics

Seven up-flows BPR were constructed using acrylic columns (73 × 10 cm) and operated for 36 weeks treating synthetic AMD, characterized by high sulfate concentrations, and low metal loading (mg L^{-1} 201 ± 44 Fe^{2+}; 30 ± 2 Mn^{2+}; 19 ± 2 Zn^{2+}; 215 ± 11 Ca^{2+}; 128 ± 13 Mg^{2+} and 2,500 ± 105 SO_4^{2-}, at pH 3.0 – 3.7). The AMD was prepared according the information collected at five active mine sites in the Zipaquirá Mining District, Colombia. The columns were filled with the same reactive mixture (15% cow manure, 10% mushroom compost, 25% sajo sawdust, 15% gravel, 20% limestone, and 15% wetland sediment as inoculum). Initially three BPR were operated with 2-days of HRT and four BPR with 4-days of HRT. After 17 weeks, a strong increase of soluble sulfide in treated effluents from the columns with 4-day HRT justified the decision to change one of the reactors of 4-day HRT to 1-day HRT (Vasquez et al 2016 a, b).

Column sampling

Columns were sacrificed throughout the study to monitor the changes in the post-treatment reactive mixture and microbial activity. Four columns, two of 2-day HRT and two of 4-day HRT, were sacrificed at week 8 and 17. The other three columns (1, 2, and 4-day HRT) were analyzed at the end of the study (36 weeks). The reactive mixture from the sacrificed columns was removed from different locations at the reactor. Three layers (20 × 10 cm), one from the bottom (at 0–20 cm), one from the middle (at 20–40 cm), and one from the top (at 40–60 cm) were taken. The samples were homogenized and refrigerated at 4 °C for physicochemical analyses and stored at − 80°C until DNA extraction.

Physicochemical analysis of reactive mixture post treatment

The pH was measured (Lab 870, Schott; Mainz, Germany) using method 4972–01 (ASTM 1995a) and a ratio of solid to de-ionized water of 1:1. The organic nitrogen (TKN) was measured by Method 4500–Norg (APHA 2005), and cellulose content was determined, according to Harper and Lynch (1981). The organic carbon (TOC) was analyzed by the Walkley–Black method (Schumacher 2002). Total metal concentrations immobilized in the reactive mixtures were determined by the digestion method described by Neculita et al (2008b) and dissolved metals (Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} and Zn^{2+}) were quantified by atomic absorption spectrometry (Varian 240 FS; Agilent Technologies; Santa Clara, CA), using method 7000B (USEPA 2007). Acid volatile sulfide (AVS) were separated by Brouwer & Murphy (1994) and soluble sulfate were extracted by Sobek et al (1978) and quantified by UV-VIS spectrophotometry (Genesys 10, Thermo Scientific; Waltham, MA) using method 4500–SO_4 (APHA 2005).

Nucleic acid extraction and sequence analysis

Genomic DNA was extracted from 22 samples of post-treatment reactive mixture and 1 sample of initial reactive mixture using the MoBio® PowerSoil DNA extraction kit (MoBio Laboratories, Solana Beach, CA). PCR amplification, purification, and sequencing for illumina MiSeq of a region V4 of the 16S rRNA gene were performed following the procedure described by Caporaso et al (2011). All extractions and amplifications were realized by triplicated. Sequencing was conducted using MiSeq Illumina (2×250 pb) technology at DNA Facilities (Iowa University). Total length of the Paired-end reads (250 bp) were assembled with the Fast Length Adjustment of Short Reads tool (Magoc and Salzberg 2011). QIIME v1.7 was used for all analysis and the sequences were aligned to the Greengenes reference alignment using PyNAST at the 97% confidence level. After the sequences were quality filtered and randomly in subsampled the 10000 sequences (this number was chosen by the minimum number on reads in a control sample) that were subsequently clustered into operational taxonomic units (OTUs). The relationships between dynamic of genera (relative abundance > 0.5%), physicochemical characteristics of BPR and samples were assessed by canonical correspondence analysis (CCA) using Conoco v4.5 for Windows package with Monte Carlo permutation test and Spearman correlation coefficients. The statistic difference of the relative abundance of the genera through the layers of the BPR was evaluated by *t* -test Welch's, adjusted for Benjamini Hochberg (p = 0.05), using STAMP 2.01 (Parcks et al 2010).

Results and discussion

The CCA (Fig. 1) reveled that samples were clustered in three subgroups corresponding to the operation time (8, 17 and 36 weeks) and that these subgroups were significantly different with respect to their physicochemical characteristics and microbial community. Besides, the Spearman correlation coefficients showed that operation time had negative correlation with pH, TKN and COT (–0.884, –0.845 and –0.812; $p = 0.00$, respectively) and positive correlation with Zn, AVS, sulfate, Fe and Ca (0.817, 0.771, 0.742, 0.455, and 0.406; $p < 0.05$, respectively), indicating that organic components and pH decrease while the metal sulfides increase in reactive mixture over time. Operation time is one driver for shifting the physicochemical characteristics and microbial community composition. Previous studies have identified that lowering of the pH, re-oxidation of sulfide back to sulfate and a reduction in dissolved organic compounds contributed to change in the microbial community and decline in performance of the BPR (Baldwin et al 2015; Mirjafari et al 2011).

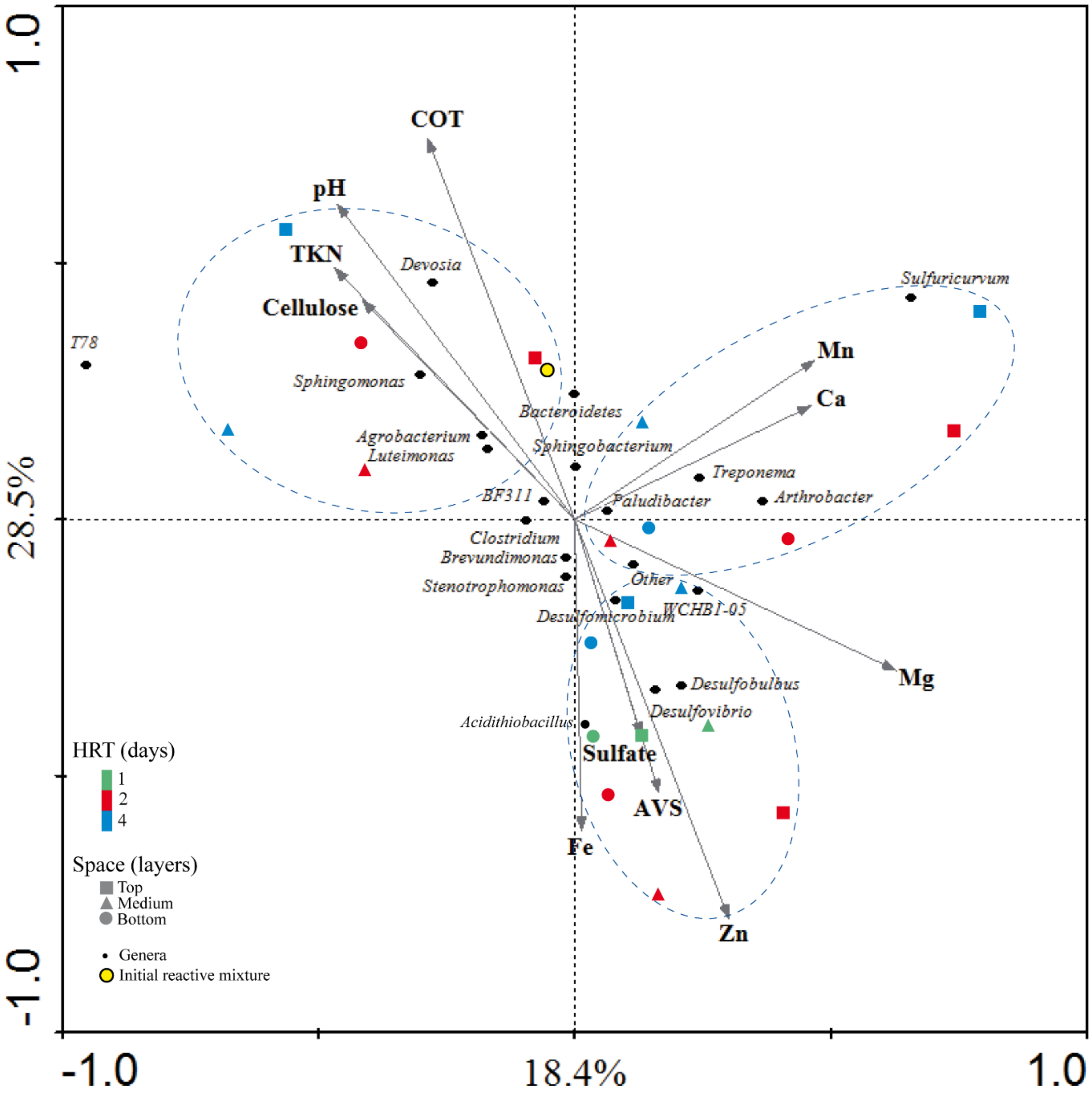

Figure 1 *Relation between the relative abundance of genera (>0.5%), physicochemical parameters and samples. CCA-triplot where the x-axis explains 18.4% and the y-axis explain 28.5% of the variation. The colors indicate samples with different HRT (1, 2 and 4 days) and its form (square, triangle and circle) show the location in BPR.*

The first group that emerge from the CCA correspond to the initial reactive mixture and 8 week samples. These samples were positively correlated (Spearman, $p < 0.05$) with pH (> 8.0) and as TKN, COT and cellulose (> 6.0, > 33.0 and > 50.7 % w/w, respectively) without difference significate between layers in the BPR. This group included the genera *Devosia* (4.6%), *Sphingobacterium* (4.2%), *Sphingomonas* (4.1%), *Agrobacterium* (3.8%), *Luteimonas* (2.0%) and *Bacteroides* (1.3 %). Members of these genera have been studied for their ability to degrade plant cell wall material and they utilize a wide variety of compounds as carbon and energy sources, including cellulose, hemicellulose, starch, and pectin. These genera have been reported in previous studies and its presence in the reactive mixture is considered an advantage during AMD treatment (Drennan et al 2015; Hiibel et al 2011). Other genera with low relative abundance (< 1.0%) were *Treponema*, *clostridium*, *Desulfovibrio*, *Desulfomicrobium* and *Desulfobacter*. The presence of SRB in the initial reactive mixture shortened the initial lag phase of the AMD treatment and contributes with low cost and improve the performance of BPR (Mirjafari et al, 2014).

Other group clustered in CCA correspond to samples extracted during the second sacrifice (17 week). In this group the genus more abundant was *Treponema* (10.8%) with significant abundance in medium layer for 4-day of HRT (t -test Welch's < 0.01). This genus has been observed to perform acetogenesis, carbon fixation and it is often associated with cellulose degradation (Do et al 2014; Sanchez-Andrea et al 2014). The second genus with the high abundance was *Sulfuricurvum* (6.4%, on average) with significant abundance in the top layer of columns with 2-day of HRT. These sulfur-oxidizing bacteria produces adverse effects in BPR because can oxidize the sulfide to sulfate (Zheng et al, 2014). Its presence possibility was due to change of pipeline in sampling ports located at the top cap of biorreactor allowing the formation of microaerobic regions. Other genera which also increased their abundance were *Desulfovibrio* (1.5%) and *Desulfomicrobium* (1.1%) with significant difference in BPR for 4-day of HRT. This increased of BSR favored that the concentration of sulfides (2,826 ± 185 mg H_2S L^1) was higher in this BPR because longer residence time allowed greater oxidation of available organic carbon and reduction of sulfate. In the week 17, the concentration of Ca (46 mg kg^{-1}) and Mn (< 1.0 mg kg^{-1}) in reactive mixture post treatment were the physicochemical parameter with higher effect on microbial community (0.406 and 0.502; $p < 0.05$, respectively). The effect of Ca could be related with the loss of nutrients in solution for formation of colloidal suspensions which precipitate making difficult the access for microorganism (Lindsay et al 2011). On the other hand, during 17 week the Mn presented low concentration in the reactive mixture post treatment and high concentration in the effluents (77 ± 4 mg L^{-1} for 4-day HRT and 60 ± 2 mg L^{-1} for 2-day HRT) which exceeded levels in the synthetic AMD (31 mg L^{-1}). This metal only was removed of the AMD at the beginning of the treatment when it was probably adsorbed on the reactive mixture but after it released causing toxicity on microbial community.

In the week 36, three bioreactors with different HRT (1, 2 and 4 d), were sacrificed. The genera most abundance in the columns with 2 and 4-day of HRT were *Treponema* (8.2% on average), and *Paludibacter* (3.2% on average). Previous studies demonstrated that *Paludibacter*, as fermentative bacteria, had appeared in enrichments of sulfate reduction systems in acidic condition (Zheng et al, 2014; Sánchez-Andrea et al, 2014). The *Paludibacter* was often accompanied by the SRB in sulfate reduction systems (Lindsay et al 2011). The presence of acid lactic producing bacteria genera as *Treponema* and *Paludibacter* suggests a potential for suitable SRB electron donor production in the system (Dennan et al 20165). In the column with 1-day of HRT, *Acidithiobacillus* (10.5% on average) was the genus with the most abundance and its presence was related with decline in pH (5.2), in the bottom layer of the reactive mixture. Members of these genera are frequently found in metal-rich acidic environments associated with metal sulfide leaching (Garcia-Moyano et al 2008). Acidophilic chemolithotrophic microorganisms play a key role maintaining a high concentration of ferric iron in AMD (Sánchez-Andrea et al 2014). In the week 36, the genera of SRB increased in the three bioreactors with significate difference in 4-day of HRT, with *Desulfovibrio* (1.5%) as most abundance follow by *Desulfomicrobium* (0.7%), *Desulfobulbus* (0.6%), and *Syntrophobacter* (0.5%). The CCA analysis showed correlation (Monte Carlo, $p < 0.05$) between sulfide, Fe, AVS and the genera *Desulfococcus*, *Desulfobulbus, Desulfomona*, *Desulfobacter* and *Desulfovibrio.* This genera of BSR were most abundance in bottom layer of BPR and its presence has been reported in rich environments with metal sulfides (Hao *et al*., 2014). Besides, this BSR have been found in BPR with low pH (< 5.0) and sediments from acid sites (Sánchez-Andrea et al 2014).

Conclusions

The findings in the present study provides critical information regarding dynamic of the microbial community present in BPR during the treatment of AMD. The operation time (8, 17 and 36 weeks), the space (top, medium and bottom) and the HRT (1, 2 and 4-day) had significant effects on physicochemical changes of the reactive mixture of BPR and these changes affected the diversity and the abundance relative (> 0.5%) of microbial community during AMD remediation. In addition, the microbial community analysis resulted in the identification of specialized groups related to cellulose degraders and fermentative bacteria that work in synergy for degrading substrate make the organic material available to sulfate-reducing bacteria. Finally, the microorganisms associated with metal-rich waters were identified with roles in the iron and sulfur cycles of AMD communities. This analysis provides a base line for future studies in field BPR.

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Comparative Genomic Analysis of Acidophilic Iron Oxidizing Bacteria from a Pilot Plant for the Microbial Remediation of AMD Water: Insights into Strategies for Speciation and Metabolic Adaptation to Life at Low pH and under Low Nutrient Concentration

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Abstract

Bacterial community analyses of samples from a pilot plant for the treatment of acid mine drainage (AMD) water from the lignite mining district in Lusatia (Germany) demonstrated the dominance of two groups of acidophilic iron oxidizers: a novel candidate genus "*Ferrovum*" and a group comprising *Gallionella*-like strains. Isolation of "*Ferrovum*" acidophilic strains as pure culture has proven difficult, though co-cultures consisting of "*Ferrovum*" and a strain of the heterotrophic acidophile *Acidiphilium* have been obtained. Similarly, *Gallionella*-like strains also proved recalcitrant to culture and isolation attempts resulted only in an enrichment culture comprising strains from several distinct taxa. Therefore, we employed a (meta)genomics approach to elucidate the metabolic potential of these microorganisms with the aim to deepen our knowledge of AMD bioremediation from lignite mines.

Introduction

Formation of acid mine drainage (AMD) is an environmental problem in many parts of the earth. The main cause of AMD formation is linked to anthropogenic mining activities during which sulfidic minerals become exposed to oxygen and water. This, in turn, leads to the oxidation of pyrite and, thus, the accumulation of sulfuric acid and the release of ferrous iron. This alteration to the environment creates an ecological niche for acidophilic bacteria that gain energy for their metabolic activity from the oxidation of ferrous iron to ferric iron. By doing this these acidophilic iron oxidising microorganisms enhance AMD formation because ferric iron represents a strong oxidant leading to further pyrite oxidation. However, these acidophilic iron oxidisers can also contribute to the remediation of AMD. For example, microbial iron oxidation is utilised in the 10-qm^3 treatment plant Tzschelln that is located within the lignite open-pit lignite mine Nochten in Lusatia, Germany (Fig. 1). This process uses aeration of AMD water followed by ferrous iron oxidation by acidophilic iron oxidising microorganisms. The average hydraulic retention time of 8 h results in a constant production of acidity that maintains the pH within the treatment plant at approximately 3 (pH 2.85 – 3.1). As a consequence, the resulting ferric iron precipitates as the amorphous iron hydroxy sulfate mineral schwertmannite ($Fe_{16}[O_{16}|(OH)_{10}|(SO_4)_3] \cdot 10\,H_2O$; Bigham et al. 1990) which has various applications as a pigment or as a sorbent for the removal of arsenic from aqueous solutions (Janneck et al. 2010).

The bacterial diversity of the treatment plant has been investigated in a series of studies covering almost ten years because it is likely to play a fundamental role in the performance of the biotechnological process. This paper summarises findings from these studies and from recent genome analyses of representative strains of the abundant bacterial taxa within the treatment plant.

Figure 1 *Treatment plant Tzschelln for the bioremediation of AMD water. The pilot plant is located at the lignite mine Nochten from which the AMD originates. Left: AMD within the oxidation basin of the pilot plant. Right: schwertmannite precipitated on carrier material within the treatment plant. (Photos: M. Mühling)*

Methods

Isolation and culture of "*Ferrovum*" strains was attempted using the APPW medium (Tischler et al. 2013). Details on the isolation and maintenance of the mixed cultures of "*Ferrovum*" and *Acidiphilium* are provided elsewhere (Tischler et al. 2013; Ullrich et al. 2015, 2016a,b). Ferrous iron concentrations were quantified using the ferrozine method (Viollier et al., 2000). Enrichment of microaerophilic *Gallionella*-like acidophiles was based on that described by Kucera and Wolfe (1957), but conducted at acidic pH (3.5). Ferrous iron sulfide was prepared according to the method suggested by Emerson and Floyd (2005).

Details on the methods used to analyse the bacterial diversity within the pilot plant Tzschelln have been provided elsewhere (Heinzel et al. 2009a,b). These include, in essence, the preparation and sequence analysis of a clone library of PCR-amplified 16S rRNA gene fragments (Heinzel et al. 2009a) and the quantification of the abundant taxa *via* terminal restriction fragment length polymorphism (TRFLP) analysis and real-time quantitative PCR (Heinzel et al. 2009b).

TRFLP analysis of the mixed cultures was also used according to the description provided by Heinzel et al. (2009b) to quantify the distribution of "*Ferrovum*" and *Acidiphilium* in enrichment cultures.

Genomic DNA was isolated from "*Ferrovum*" and microaerophilic enrichment cultures using the MasterPure Gram Positive DNA Purification Kit (Epicentre) and the PowerSoil DNA Isolation kit (MoBio), respectively. Genome sequencing was carried out at the Göttingen Genomics Laboratory (G2L) using – in the cases of "*Ferrovum*" strains JA12 and PN-J185 – a hybrid approach using both the 454 GS-FLX Titanium XL system (Titanium GS70 chemistry, Roche Life Science) and the Genome Analyzer II (Illumina, 112-bp paired-end Illumina reads). "*Ferrovum*" strain Z-31 and the microaerophilic enrichment culture were sequenced employing only the Genome Analyzer II (Illumina, 112-bp paired-end Illumina reads).

Details on the sequencing output and the assembly and automated annotation of the sequence reads are provided elsewhere (Ullrich et al. 2016a,b). Methods employed for the comparative genome analysis of the "*Ferrovum*" strains are outlined in Ullrich et al. (2016b).

Digital DNA-DNA hybridisation (DDH) values were calculated for each pair of genomes using the Genome-to-Genome Distance Calculator (GGDC 2.0: http://ggdc.dsmz.de/distcalc2.php; Meier-Kolthoff et al. 2013).

Results

Analysis of the bacterial diversity of the AMD within the treatment plant revealed the dominance of strains whose 16S rRNA gene sequence showed highest similarity to that of two bacterial groups: the proposed species "*Ferrovum myxofaciens*" (Johnson et al. 2014) and the neutrophilic iron oxidiser *Gallionella ferruginea* (Heinzel et al. 2009a,b). Using a culture medium that simulates the chemical composition of the AMD within the pilot plant, it was possible to bring several "*Ferrovum*" strains into culture (Tischler et al. 2013). However, a detailed characterisation of these novel "*Ferrovum*" strains proved impossible because these cultures were consistently contaminated with a heterotrophic strain of the genus *Acidiphilium* sp. Therefore, we employed a two-tiered genomic approach in order to obtain insights into the metabolic potential of "*Ferrovum*" within the mixed cultures. This approach consisted, in essence, of the genome analysis of the contaminating *Acidiphilium* strain isolated from a mixed culture (Ullrich et al. 2015) and the subsequent (meta)genomic analysis of the same culture. Based on both datasets it was possible to reconstruct almost the complete genome sequence of a novel strain of "*Ferrovum*" that we termed strain JA12 (Ullrich et al. 2016a). Sequence analysis of two further distinct strains (PN-J185, Z-31) of "*Ferrovum*" from the pilot plant together with the available draft genome of the proposed type strain "*Ferrovum myxofaciens*" P3G (Moya-Beltrán et al. 2013) provided the basis for a first comparative genome analysis of the genus "*Ferrovum*". Using a number of methods to calculate genomic distance between the four strains (e.g. genome-genome distance) strongly suggest that they belong to three distinct species: "*Ferrovum myxofaciens*" with the proposed type strain P3G and strain Z-31 and at least one further "*Ferrovum*" species represented by strains JA12 and PN-J185 (Ullrich et al. 2016b).

Furthermore, metabolic reconstruction of the annotated genomes of these strains revealed important insights into their metabolic potential and provided clues regarding their adaptation to low pH. For example, the presence of a urease encoding gene cluster in strains JA12 and PN-J185 indicates that urea hydrolysis is used to buffer against a potential inflow of protons (Mosler et al. 2013, Ullrich et al. 2016a). The role of urease in pH homeostasis has originally been shown for the gastric pathogen *Helicobacter pylori* (Eaton et al. 1991). Moreover, the absence of urease in type strain P3G and in strain Z-31 also provide an example for the species-specific metabolic traits within the genus "*Ferrovum*" (Ullrich et al. 2016b).

Attempts to isolate *Gallionella*-like acidophiles resulted in microaerophilic enrichment cultures (Fig. 2). 16S rRNA gene sequence based analysis of the bacterial diversity within one of these cultures indicated that it comprised at least three distinct *Gallionellaceae* strains that appear to be closely related to the neutrophilic iron oxidizer *Sideroxydans lithotrophicus* ES-1. The metagenomic data therefore proved to be particularly relevant in defining adaptive strategies to pH homeostasis since isolates belonging to the family *Gallionellaceae* are still restricted to the microaerophilic and neutrophilic iron oxidizers *Gallionella* and *Sideroxydans*. That is, the availability of the complete genome of strain ES-1 now permits the detailed comparison of the metabolic capacity of neutrophilic and acidophilic members of the genus *Sideroxydans* and, thus, the detection of biochemical features that are present in the acidophilic strains to support life under acidic conditions. For a start, the genome data of the acidophilic iron oxidizing strains indicate, similar to "*Ferrovum*" strains JA12 and PN-J185, the presence of a urease encoding gene cluster which is absent in the genome of *S. lithotrophicus* ES-1.

Moreover, metabolic reconstruction based on metagenomic data also indicates that nutrient requirements vary among taxa. This knowledge is of relevance for targeted improvements to the performance of the pilot plant. For example, the presence of genes possibly encoding proteins involved in phosphonate utilisation indicates that phosphonates may provide an alternative source of phosphorus to inorganic phosphate. However, experimental support is required to confirm this finding because not all proteins involved in phosphonate utilisation were detected within the metagenomic dataset.

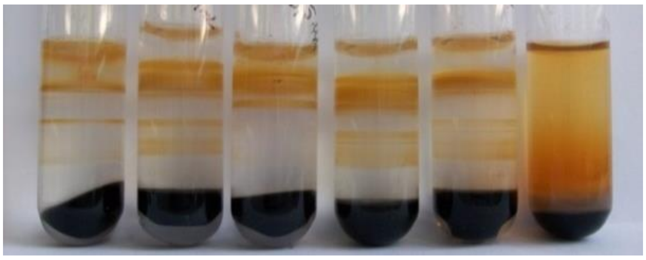

***Figure 2** Microaerophilic enrichment cultures from samples of the inflow water into the pilot plant Tzschelln. The enrichment cultures were produced using the gradient tube technique of Wolfe and Kucera (1957) in combination with a novel medium found to favour the growth of acidophilic relatives of* Gallionella ferruginea *(Tischler et al. 2013). The last tube to the right is the abiotic control (no inoculum). The photograph was taken after 28 days of incubation under microaerobic conditions at room temperature. (Photo: A. Drechsel)*

Conclusions

Based on the genome data obtained so far of these unique groups of acidophilic *Betaproteobacteria* it was possible to infer biochemical and phenotypic features which are difficult to determine *via* experimental approaches due to the lack of pure cultures. The comparative genome analyses of four "*Ferrovum*" strains were therefore the only means to reveal phenotypic features that seem to be common to acidophilic bacteria or unique to specific clades which, based on *in silico* determined genome distances, may be judged to represent at least two individual species within "*Ferrovum*". Similarly, by assigning contigs to individual taxa using phylogenetic methods, it also proved possible to reveal phenotypic traits that seem to be responsible for the adaptation of strains of the genus *Sideroxydans* to life at acidic pH. Moreover, metabolic reconstruction from *Sideroxydans*-derived contigs indicates that acidophilic strains are able to utilise phosphonates similar to their neutrophilic relatives. Fertilisation of the AMD water with phosphonate-containing substances such as waste from paper and pulp or the textile industry may, therefore, result in an improvement to the performance of the treatment plant. Addition of phosphate to a simplified laboratory experimental simulation of the treatment plant already demonstrated a positive impact on ferrous iron oxidation rate (Tischler et al. 2014).

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Mineralogical Changes within Polish Weissliegend Sandstones During Bioleaching

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Abstract

The Kupferschiefer is one of the most important sources of copper and silver in Europe, with resources located mainly in Poland and Germany. Mineralization is stratabound and hosted by sedimentary rocks comprising of sandstone, black shale, and carbonate rocks. Because Kupferschiefer-type ores are typically complex and very fine-grained, alternative approaches for metal recovery, such as bioleaching, are becoming an attractive alternative to flotation.

The focus of this study was a detailed monitoring of mineralogical changes through time during bioleaching of sandstone-hosted Cu-mineralization from two Polish Cu-mines. The change of modal mineralogy, mineral associations, microbial activity and copper recovery of a copper bearing sandstone during bioleaching with *Acidithiobacillus ferrooxidans* DSM 14882 was investigated. A series of 18 batch cultures and 18 abiotic controls in shaking flasks with a solid content of 6 wt.% was prepared and sampled every 3 to 4 days over a period of 18 days. Mineralogical analysis of leaching residues was done by mineral liberation analysis (MLA) and X-Ray powder diffraction (XRD), while chemical analysis of dissolved copper and ferric/ferrous iron was carried out with ion chromatography (IC).

The investigated sandstone ore contained 2.5 wt.% copper, mainly bound to the copper minerals chalcocite (Cu_2S, 1.3 wt.%), covellite (CuS, 1.0 wt.%) and bornite (Cu_5FeS_4, 0.9 wt.%). After 18 days the copper extraction was 84% for biotic samples and therefore significantly higher compared to abiotic controls (52%). MLA data showed that biotic dissolution was faster for all three copper ore minerals. The results of detailed mineralogical analysis indicate a passivation by jarosite during the leaching process, especially caused by ammoniojarosite. It was possible to trace progressive changes of each copper sulphide over the entire bioleaching process and calculate dissolution/formation rates by means of MLA data.

Key words: Bioleaching, *Acidithiobacillus ferrooxidans*, Weissliegend sandstone, automated mineral liberation analysis, XRD

Introduction

The Central European Copperbelt (Borg et al. 2012) is one of the most important sources for copper and silver in Europe, with several large-scale mining operations currently active in the southwest of Poland. In Poland Kupferschiefer-type resources still contain 29.79 Mt of copper in 1.47 Bt of currently known ore reserves (Borg et al. 2012).

Kupferschiefer-type mineralization is restricted to the Lower Permian (Rotliegendes) terrestrial deposits and Upper Permian (Zechstein) marine sedimentary rocks. The ore series is composed of (bottom to top): Weissliegend Sandstones, Basal Limestone, Kupferschiefer and Zechstein Limestone (Oszczepalski 1999). Stratabound sulphide mineralization occurs in all of these sedimentary rock types, with 60% of currently known reserves hosted by Weissliegend sandstone, 30% in Zechstein carbonate rocks and 10% in the Kupferschiefer black shale (Borg et al. 2012). In the Polish mining district mineralized sandstones of Weissliegend have an average copper content of 1.8% and an average thickness of 18 m. However, the grade and thickness of sandstone ore can locally vary from 0.7% to 30% copper and from few meters up to 35 m (Borg et al. 2012). Main ore minerals are bornite, galena, sphalerite, chalcopyrite and chalcocite-type sulphide minerals (Oszczepalski 1999).

The complex mineralogy and fine-grained structure of Kupferschiefer-type ores limit copper recovery with traditional processing methods, especially flotation. In the last 15 years the copper content in flotation concentrates and copper recovery decreased (Gibas et al. 2015); therefore alternative approaches for metal recovery, such as bioleaching, may become important.

Bioleaching describes the process of metal extraction by microorganisms. A common leaching bacterium is the acidophilic ferrous iron- and sulphide-oxidizing bacterium *Acidithiobacillus ferrooxidans*, formerly *Thiobacillus ferrooxidans* (Kelly and Wood 2000), that has been studied in detail. Under acidic conditions *At. ferrooxidans* catalyses the release of metal ions from metal sulphides by the production of sulphuric acid (hydrolytic attack), and by oxidation of ferrous to ferric iron (oxidative attack). For acid-soluble metal sulphides the mechanism can be generally described as follows (Schippers and Sand 1999):

$\mathrm{MS} + \mathrm{Fe}^{3+} + \mathrm{H}^{+} \rightarrow \mathrm{M}^{2+} + 0.5\ \mathrm{H_2S_n} + \mathrm{Fe}^{2+}\ (n \geq 2)$

$0.5\ \mathrm{H_2S_n} + \mathrm{Fe}^{3+} \rightarrow 0.125\ \mathrm{S_8} + \mathrm{Fe}^{2+} + \mathrm{H}^{+}$

$0.125\ \mathrm{S_8} + 1.5\ \mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{SO_4}^{2-} + 2\ \mathrm{H}^{+}$

This so called “polysulfide mechanism” applies to chalcocite (Cu_2S) and covellite (CuS) (Schippers and Sand 1999), which have been investigated in this study.

The ore mineralogy is, among chemistry and microbiology, an important parameter in bioleaching processes; because mineral composition, liberation, and solubility influence the leaching efficiency. In general, it is known that chalcocite is more easily dissolved in heap- and dump-leaching than bornite and covellite (Watling 2006). In the present study the behaviour of the copper sulphides in presence of *Acidithiobacillus ferrooxidans* DSM 14882 was of main concern. To understand and possibly improve the bioleaching process, mineralogical changes within sandstone ore were investigated every 3 to 4 days by collecting detailed data of the mineralogy with a mineral liberation analyser (MLA) and X-Ray powder diffraction (XRD). Moreover chemical analysis of leaching solutions with ion chromatography and determination of pH and redox potential were performed to get new insights into bioleaching reactions.

Methods

Bioleaching

Weissliegend sandstone-hosted ore of the Polkowice and Rudna mines (Poland) was crushed, milled and sieved. The ore fraction <125 µm was divided into homogenous portions of 12 g with a sample splitter and then used for leaching experiments. A series of 18 batch cultures with *At. ferrooxidans* DSM 14882 and 18 abiotic controls was prepared. Leaching was performed in 500 mL shaking flasks with 200 mL modified 9K Medium (Silverman and Lundgren 1958), pH 2.1, containing 50 g/L Fe(II)SO_4 x 7 H_2O. The shaking flasks for bioleaching were inoculated with 20 mL of the same pre-culture of *At. ferrooxidans* DSM 14882 (1.1 x 10^6 cells/mL). All 36 flasks were incubated at 30°C and 120 rpm.

At day 2, 4, 7, 10, 14 and 18 samples of leached ore material were taken. The number of parallels decreased each time by 6, due to stopping of 3 batch cultures and 3 abiotic controls (fig. 1). For mineralogical analysis sandstone ore was separated from the leaching solution via filtration and then air dried for further preparation. Redox potential and pH of the leaching solution were measured daily (pH Inlab Semi-Micro, Mettler Toledo and SenTix ORP, WTW). Samples for detecting copper, ferrous and ferric iron in solution were taken every 3-4 days, filtrated (0.22 µm syringe filter) and frozen for later measurement. The evaporation loss during (bio)leaching was compensated with sterile *Aqua dest.*.

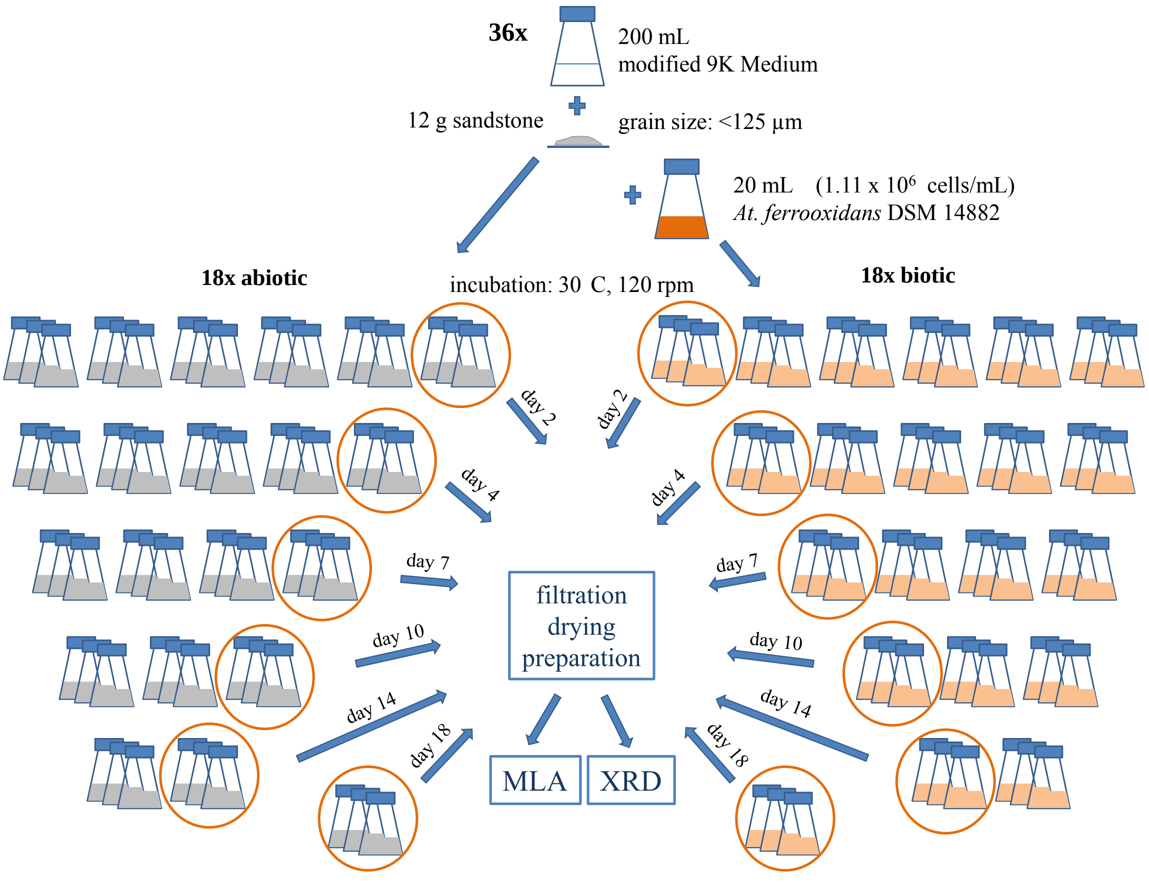

Figure 1 *Experimental setup and sampling scheme of sandstone (bio)leaching*

Chemical analysis

Major element concentrations in sandstone ore (fraction <125 µm) were determined by X-ray fluorescence spectroscopy (XRF) using an AxiosMinerals, PANalytical.

Analysis of copper, ferric and ferrous iron in the leaching solutions was performed using ion chromatography (ICS-5000, 4 mm system, Thermo Scientific). An IonPac® CS5A column (Thermo Scientific) with an eluent flow rate of 1 mL/min Met Pac PDCA (7 mM pyridine-2,6-dicarboxylic acid, 66 mM potassium hydroxide, 5.6 mM potassium sulphate, 74 mM formic acid) separated chelated metal complexes. The metal complexes were detected at 530 nm after postcolumn derivatization with 0.5 mM 4-(2-pyridylazo) resorcinol dissolved in MetPac PAR Postcolumn Reagent Diluent (1 M dimethylaminoethanol, 0.5 M ammonium hydroxide, 0.3 M sodium bicarbonate) at a flow rate of 0.6 mL/min (Cardellicchio et al. 1997).

Mineralogical analysis

The mineralogical analysis of sandstone ore was done by MLA and XRD. For detailed investigation of copper sulphide minerals all 36 leaching samples and the untreated ore were analysed by MLA. Therefore, polished and carbon coated grain mounts, composed of 3 g dry sample in an epoxy resin block (Ø 30 mm), were prepared. A subset of twelve leaching samples, one biotic and one abiotic of each sample point, and the untreated ore were analysed by XRD. Preparation of sandstone ore for XRD was done by milling with ethanol in a McCrone micronizing mill.

The MLA comprised a FEI Quanta 650 F field emission scanning electron microscope equipped with two Bruker Quantax X-Flash 5030 EDX detectors and FEI's MLA suite 3.1.4 for data acquisition. The grain-based X-ray mapping (GXMAP) measurement mode was used, because of similar backscattered electron grey levels of expected copper sulphides (chalcocite, covellite, bornite, chalcopyrite). The operating parameters of MLA are listed in table 1.

***Table 1** Operating parameters of MLA measurements.*

MLA parameters		SEM parameters	
Pixel size	0.6 µm/px	Voltage	25 kV
Minimum EDX	2000 counts/analysis	Probe current	10 nA
Acquisition time	5 ms	BSE calibration	Au 254
GXMAP trigger	25-255		
Step size	6 x 6 px		
Minimum particle	8 px		
Minimum grain size	4 px		

XRD analyses were carried out using a PANalytical Empyrean diffractometer, equipped with a PIXcel3D detector and Co-Kα radiation at 35 kV and 35 mA with a Fe-Kβ-filter. A step size of 0.013° 2Θ in the range of 5 to 80 2Θ and a step time of 800 sec/step were set. The software BGMN Profex 3.5.0 (Doebelin and Kleeberg 2015) was used for mineral identification and Rietveld refinement.

Results and discussion

Bioleaching of copper

Microbial activity was observed indirectly by pH and the ferric/ferrous iron content ratios in solution. The pH increased in all leaching solutions within the first day up to 3.1 due to carbonate dissolution and ferrous iron oxidation, then followed by a gradual decrease of pH (fig. 2-A). A significantly lower pH was measured in the presence of *At. ferrooxidans* from day 7 onwards, indicating microbial activity (production of H_2SO_4).

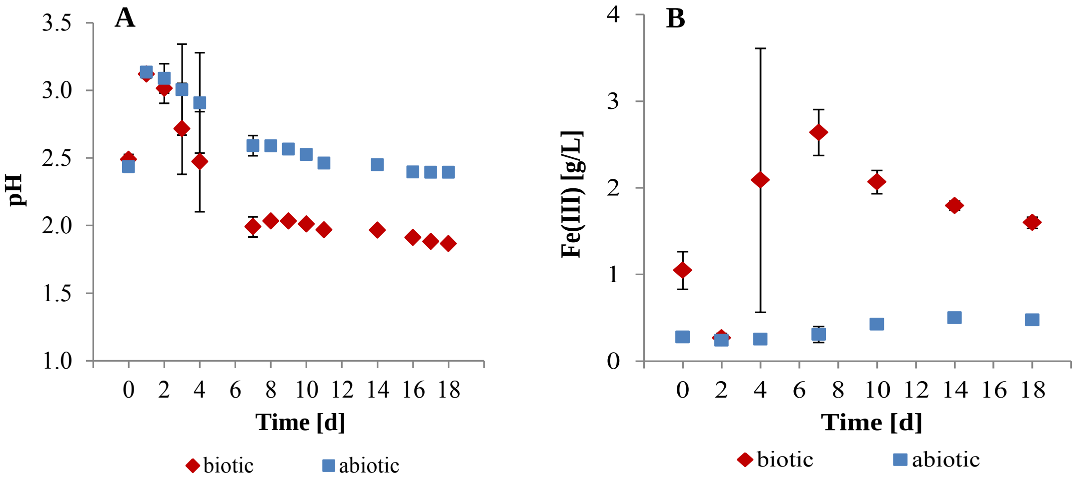

***Figure 2** Results of pH (A) and dissolved ferric iron (B) during bioleaching with At. ferrooxidans DSM 14882.*

Moreover, the amount of dissolved ferric iron increased in biotic approaches from 1 to 2.6 g/L within the first week (fig. 2–B) and thus proved the activity of *At. ferrooxidans*. In contrast, ferric iron increased only slightly from 0.3 to 0.5 g/L in abiotic controls, due to chemical iron oxidation.

The investigated sandstone ore contained on average 2.5 wt.% copper according to XRF analysis. Copper leaching was more efficient in presence of *At. ferrooxidans* DSM 14882 (fig. 3). Significant differences between biotic and abiotic treatment were evident from the fourth day onwards. Within the first week 69% of copper were extracted biotically and 43% abiotically. In the last 10 days only minor amounts of copper were leached so that in total 84% copper were biotically extracted and 52% were abiotically leached.

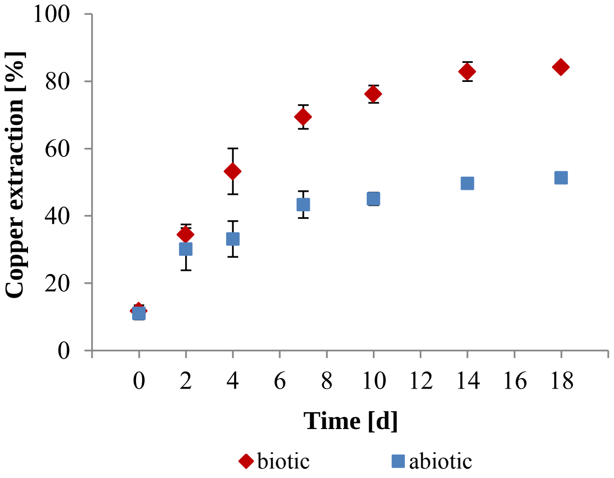

Figure 3 *Copper extraction of approaches with At. ferrooxidans DSM 14882 and abiotic controls.*

Mineralogical effects

The sandstone ore was mainly composed of quartz (70.7 wt.%), clay minerals (12.0 wt.%), feldspar (7.7 wt.%), carbonates (4.2 wt.%) and copper sulphides (3.3 wt.%). The main copper minerals were chalcocite (1.3 wt.%), covellite (1.0 wt.%) and bornite (0.9 wt.%). Due to the low amounts of these copper sulphides, quantification during bioleaching was only possible with MLA.

More bornite was leached biotically than abiotically according to MLA data (fig. 4-A). At day 18 only low amounts of bornite were detectable in biotic leaching residues, while in control residues only half of the bornite was leached. Chalcocite, in contrast, was dissolved completely within 4 days in biotic approaches and within 10 days in abiotic approaches (fig. 4-B). The content of covellite increased simultaneously in biotic and abiotic leaching residues up to day 10 and decreased only afterwards (fig. 4-C). Overall the formation of covellite was lower and dissolution was higher in presence of *At. ferrooxidans*.

Based on the MLA data in fig. 4, dissolution/formation rates for the three copper sulphides were determined by calculating the slope between the points of highest/lowest and lowest/highest content of mineral. During biotic and abiotic leaching chalcocite dissolution rate was 0.04 g/d and 0.02 g/d, therefore significantly higher than covellite (0.01 g/d biotic, 0.005 g/d abiotic) and bornite (0.005 g/d biotic, 0.003 g/d abiotic) dissolution rates. The dissolution rates of all three copper sulphides were approximately twice as high in biotic samples than in abiotic samples. In contrast, the formation rate of covellite was about double in abiotic approaches (0.013 g/d) than in biotic (0.006 g/d). For covellite it has to be taken into account that the formation of secondary covellite interfered with the dissolution, so it is impossible to separate both effects.

The apparent increase in the abundance of covellite during leaching experiments indicates that obviously some of the chalcocite and bornite has been transformed to covellite. Formation of secondary covellite in (bio)leaching experiments has previously been documented in several studies (Dutrizac et al. 1985, Bevilaqua et al. 2010, Lee et al. 2011). It means that copper has been oxidized

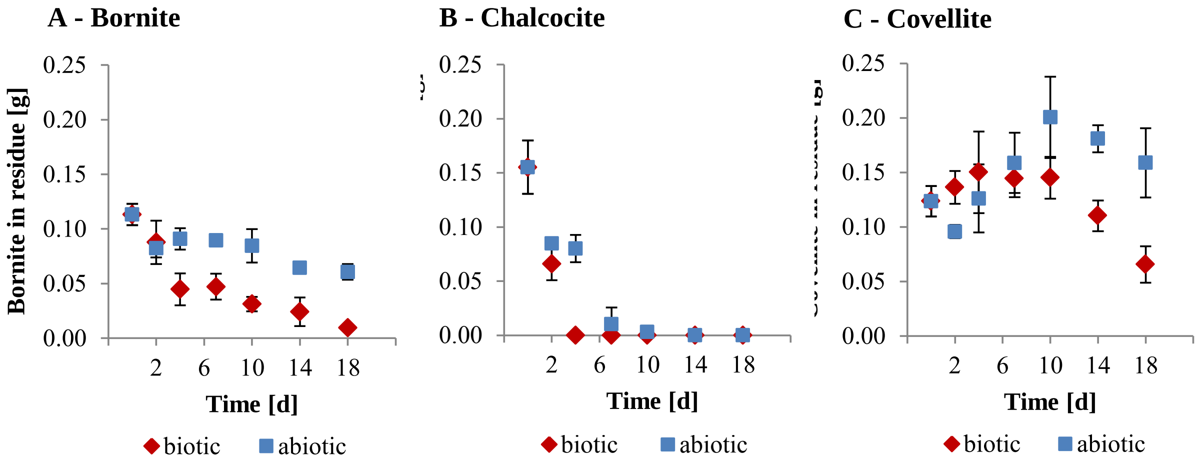

***Figure 4** Content of bornite (A), chalcocite (B) and covellite (C) in leaching residues during (bio)leaching analysed by MLA, average of 3 samples.*

from the monovalent state in chalcocite (Cu_2S) and bornite (Cu_5FeS_4) to the divalent state in covellite (CuS). In this study *At. ferrooxidans* obviously also enhanced the leaching of covellite/secondary covellite, which was also observed in a study by Bevilaqua et al. (2010). Ahonen and Tuovinen (1995) supposed that ferric iron suppresses the formation of covellite in leaching experiments. This hypothesis could explain the lower contents of secondary covellite in our biotic leaching residues. Given that ferric iron does not only accelerate bornite and chalcocite turnover but also covellite turnover, the suppression may reflect an effect of ferric iron on both, covellite formation and turnover.

MLA data also indicated the formation of possible iron-hydroxides during experiments. However, an exact mineral identification and quantification with MLA was not possible due to very fine-grained minerals and mixed spectra resulting from iron precipitations at the rims of different mineral grains. Therefore, XRD measurements were performed to identify and quantify the iron hydroxides and also to verify the MLA data. Based on XRD data the iron hydroxides were identified as jarosite and ammoniojarosite. They formed in biotic and abiotic leaching residues, although significantly more ammoniojarosite was formed in batch cultures (fig. 5-B). The content of jarosite is nearly equal in controls and residues from biotic experiments over the whole time of the experiment (fig. 5-A).

The comparison of copper extraction (fig. 3) with jarosite/ammoniojarosite development (fig. 5) indicates a correlation. The copper extraction decreased in the second week while the formation of jarosite and ammoniojarosite increased. Therefore, passivation of the copper minerals by jarosite and ammoniojarosite can be an explanation for reduced copper extraction during the last 10 days.

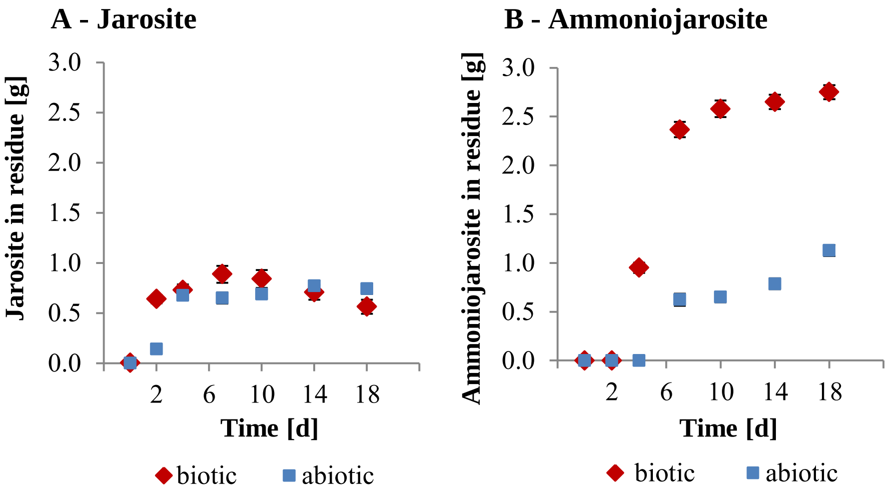

***Figure 5** Content of jarosite (A) and ammoniojarosite (B) in leaching residues, analysed by XRD.*

Conclusions

Mineralogical and chemical data proved that leaching of the Polish Weissliegend sandstone was enhanced by *At. ferrooxidans* DSM 14882. The dissolution of the three copper sulphides covellite, chalcocite and bornite was faster in biotic approaches than in those without bacteria. Obviously the presence of *At. ferrooxidans* resulted in faster transformation of bornite and chalcocite to covellite, but also in a faster oxidation of the latter compared to abiotic controls. As a result a less pronounced increase in covellite content was detected in biotic leaching residues. Passivation of remaining copper minerals by jarosite and ammoniojarosite probably reduced the copper extraction in the second week.

It was possible to quantify mineralogical changes of copper sulphides and iron hydroxides over the entire bioleaching process with combined MLA and XRD analysis. A detailed investigation of leaching residues with low mineral contents is practicable with MLA and thus the latter can be a method to get new insights in (bio)leaching processes.

Acknowledgement

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Microbiology and Chemistry Interactions in a Biological Sulphate-Reducing Process

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Abstract

In this study, we tested the industrial anaerobic sludge as inoculum for biologic sulphate removal from mine water with high sulphate (app. 10 g/L), but negligible metal concentration originating from a subarctic mine. Because of the remoteness of the mine, ethanol was chosen as substrate due to its easy storage and transportation to remote sites. Experiments were performed in three 0.7L reactors at room temperature. The reactors were operated as upflow anaerobic sludge blanket reactor (Reactor 1), and fluidized bed reactors with different carriers.

Physicochemical parameters (pH, redox, sulphate, sulphide) were measured over six months and the microbiology was analysed by high throughput (HTP) sequencing. The pH in the reactors varied between 5.2 and 7 and the sulphate removal varied from -111% (indicating sulphate production) to 48% removed sulphate. In addition, up to 3.5 g L^{-1} acetate was formed at pH 7.2 – 7.4.

The HTP sequencing revealed that the microbial communities changed markedly from that of the inoculum. SBR communities evolved during the experiments. The most common bacteria in the reactors belonged to sulphide- and thiosulphate- reducing Epsilonproteobacteria, the archaeal population consisted mostly of acetate-utilizing *Methanosaeta* – methanogens. 2 – 15% of the bacterial communities consisted of SRB. In addition, the microbial consortium contained a large variety of organic matter degrading species.

A high input sulphate level and a low pH together with undissociated H_2S may inhibit growth and activity of the SRB. Elevated concentration of acetate may also inhibit the SRB. Analysis of the microbial community gives added insight into the processes. Our study also indicated that parameters normally used for following up an SBR process such as redox and pH, is not necessary sufficient for assuring a functioning process.

Key words: SBR, sulphate removal, chemical indicators, microbiology

Introduction

Biologic sulphate reduction is a widely applied method for sulphate removal from mine waters (Bowell, 2004). The technology relies on sulphate reducing bacteria (SRB), which in anoxic conditions use organic compounds or hydrogen gas as a substrate for reduction of sulphate to hydrogen sulphide (Elliot et al. 1998; Kaksonen et al. 2003; Sahinkaya 2009). The sulphate reduction equations when ethanol is used as a substrate are presented in Eq1 – Eq.3 (Sahinkaya et al. 2011).

$$2CH_3CH_2OH + SO_4^{2-} \rightarrow 2CH_3COO^- + HS^- + H^+ + 2H_2O \qquad \text{Eq.1}$$

$$2CH_3COO^- + 2SO_4^{2-} \rightarrow 4HCO_3^- + 2HS^- \qquad \text{Eq.2}$$

$$4HCO_3^- + H^+ \rightarrow CO_2 + H_2O \qquad \text{Eq.3}$$

Eq.1 and Eq.2 show that ethanol degradation is a two-step process where the sulphate to sulphide conversion is first producing acetate and acidity, followed by acetate degradation and production of bicarbonate and sulphide. If both reactions are proceeding completely, the pH rises due to the bicarbonate conversion to carbon dioxide (Eq.3). Moreover, ideally the sulphate to sulphide conversion takes mainly place in the acetate degradation step (Eq.2).

If sulphate reduction is incomplete, i.e. the reaction described in Eq. 2 is very slow, increasing acetate concentration resulting from Eq. 1 can inhibit the growth of SRB (Kaksonen et al. 2003b, Kaksonen and Puhakka 2007, Sánchez-Andrea et al. 2014). Especially at lower pH values (<4.75) acetate is mostly in the form of highly toxic acetic acid. However, with a diverse microbial community, acetate can be used by other species besides SRB (e.g. methanogens) and the likelihood of inhibition is reduced.

Dissolved metals present in the treated solution reacts with the produced sulphides (Eq 2) and precipitate as insoluble metal sulphides, If metals are not present the produced sulphide should be transformed to a non-toxic form. This can take place by oxidizing the sulphide to elemental sulphur, either via a chemical or biochemical process (Eq.4) (van der Zee et al. 2007).

$H_2S + 2O_2 \rightarrow S^0 + H_2O$ Eq.4

Ethanol has been suggested as an easy substrate for use in biological sulphate removal applications due to its relatively low price, easy availability and transport. E.g. Nagpal et al. (2000) used ethanol as substrate for SRB in a fluidized bed reactor achieving 95 % removal of ~2500 mg/l sulphate with a hydraulic retention time (HRT) of 35 h. Nevertheless, in a similar experiment with a down-flow fluidized bed reactor, Celis et al. (2009) obtained only ca 30 % sulphate reduction. Sulphate loading was 830-1660 $g/m^3 \cdot d$ and HRT was 48 h. In both experiments acetate accumulation was detected in the effluent. Whereas this affected negatively reactor performance in the study by Celis et al. (2009), Nagpal et al.'s (2000) results were not affected by the accumulation of acetate. The difference can be explained by differences in the microbial communities operating in the bioreactors.

In this study, ethanol was used as a substrate in biological sulphate removal from sulphate rich water originating from a northern mine. The performance of three bioreactors with different carrier materials was compared by monitoring the physicochemical parameters and characterizing the microbial communities in the reactors with high throughput (HTP) sequencing method.

Methods

Bioreactors. The experimental setup consisted of three anaerobic 0.7 L reactor reactors. Reactor 1 was operated as upflow anaerobic sludge blanket reactor (UASB), while Reactor 2 and Reactor 3 as fluidized bed reactors (FBR). Reactor 2 and Reactor 3 were operated with 10 % fluidization volume and filtralite and activated carbon as carrier materials, respectively. Later, the carrier material for Reactor 2 was changed to 0.5-1.0 particle sized sand, as Filtralite easily blocked the tubes. The sludge blanket and carrier material volume was 0.3 L.

The inoculum for all reactors was anaerobic granular sludge from an industrial waste water treatment plant in Finland. Ethanol was chosen as a substrate, due to proven references (e.g. Nagpal et al (2000) and also because of simple storage and transportation to remote mine site locations. Reactor 1 was inoculated with 300 ml of sludge whereas 60 ml was added to Reactors 2 and 3 together with the carrier materials. The HRT in the experiment was 173 hours, both in the ramp up and actual experimental phase.

The feed solution for the reactors was a mixture of mine water, nutrients and ethanol as substrate, resulting in 8500 – 9000 mg/L SO_4, 56 mg/L KH_2PO_4, 137 mg/L $(NH_4)_2HPO_4$, 11 mg/L ascorbic acid and 11 mg/L yeast extract. The ethanol dosage was calculated based on COD; one gram of sulphate requires 2 grams of COD and the COD of ethanol is 1440 g/L. The ethanol dosage was 15 % of required during the ramp up phase and the first 27 days of the experiment. This was done to prevent any acetate formation in the reactors. On days 28 – 104 the ethanol dosing was increased to 160 % of required to secure enough substrate for efficient sulphate removal. During days 105 – 171 the input sulphate level was decreased to 3000 mg/L by dilution with distilled water. At the same time also the ethanol dosing was decreased to 120 % of required. The reactors were monitored for pH, RedOx, sulphate and sulphide twice per week.

Microbiology. The microbiology of the inoculum and reactors (Day 101 and 140) was determined using DNA based high throughput (HTP) sequencing techniques. Microbial DNA was extracted from

0.5 g inoculum sludge and from 2 mL effluent from the bioreactors using the NucleoSpin Soil DNA extraction kit (Macherey-Nagel) with the SL1 lysis buffer and Enhancer solution. The microbial community composition was determined by amplicon sequencing of the bacterial and archaeal 16S rRNA genes and the fungal ITS region using the Iontorrent platform as described in Rajala et al. (2016). The sequence reads were analysed using the QIIME software version 1.9 (Caporaso et al., 2010) as described in Rajala et al. (2016). Shortly, the sequences were clustered in to Operational Taxonomic Units (OTUs) at 97% sequence similarity and taxonomy was assigned for bacterial and archaeal sequences using the Greengenes database (DeSantis et al., 2006) and for fungi using the UNITE database (Köljag et al., 2013). Principal Coordinates Analysis (PCoA) on the non-normalized OTU data using the Bray-Curtis dissimilarity index was calculated using the PhyloSeq package in R (R Core Team, 2015) and plotted using gplot (Warnes et al., 2016). Abundance profiles of the bacterial, archaeal and fungal communities were visualized using PhyloSeq (McMurdie and Holmes, 2014) in R and plotted with gplot**.**

Results

Performance and chemical aspects. The goal of ramp up phase was to reach negative RedOx-potential values in all reactors. When this criteria was fulfilled, the experiment started (day 0). During the first 20 days, with only 15 % ethanol dosage, the sulphate removal was negative (Figure 1). Then, a drastic drop in the outlet sulphate concentration was observed in all reactors. In reactors 1 and 2 the decrease stopped after a couple of days only and the sulphate removal remained at app. 10 – 20 % and 100 – 250 g/m^{3}d, respectively. The performance of reactor 3 was better; the sulphate removal and reduction rate were app. 45 % and 500 g/m^{3}d. The performance of all reactors improved just before increasing the ethanol dosage to 160 % (day 28). After day 60, in all reactor the outlet sulphate level started to rise strongly, and in reactor 1 the sulphate removal was again negative. Due to technical difficulties with filtratlite in lab scale equipment the carrier material in reactor 2 was changed to sand, and reactor was reinoculated with 200 ml of reactor 3 effluent. Due to the fluctuating sulphate removal rate both sulphate and ethanol concentration in the feed was decreased on day 105. Despite this, the reactors´removal efficiency remained very low.

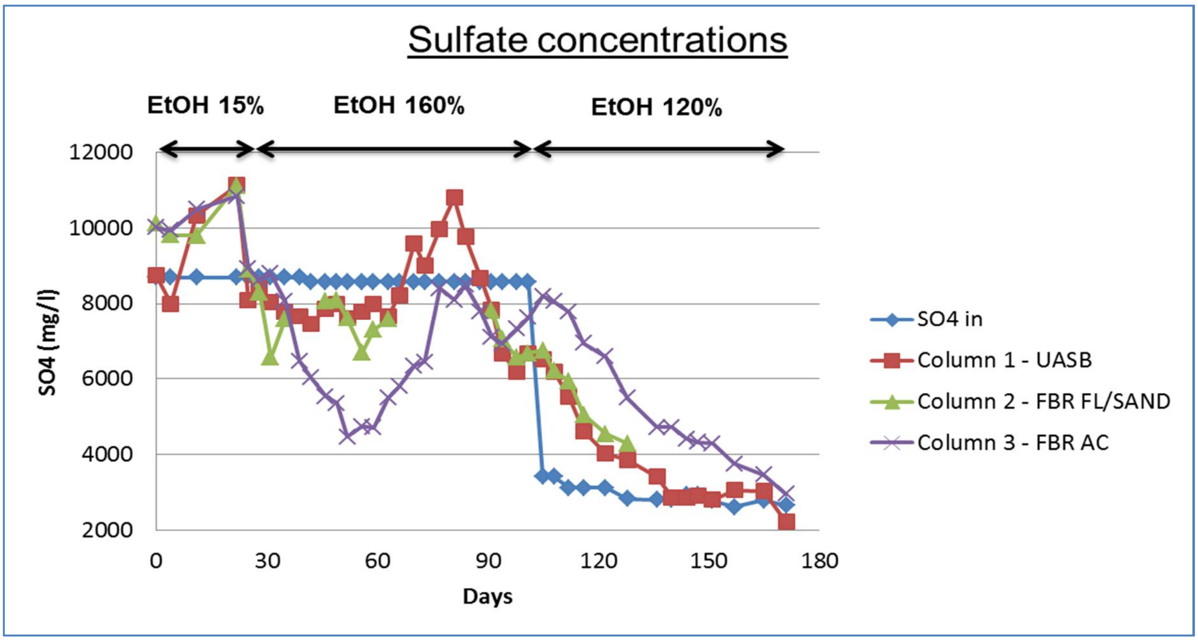

Figure 1 *Sulphate concentrations in influent and effluents during the experiment. Ethanol dosage rate compared to required theoretical need for complete reduction on sulphate according to COD.*

When ethanol dosage was elevated to 160% (day 28), the pH of reactors started to decrease (Figure 2). In reactor 1 the decrease was remarkable, from pH 7.1 to 6.2 between days 28-39. On day 39, the acetate concentration in reactor 1 was 6.8 g/L, indicating that acetate was accumulating to the system and leading to pH decrease (Eq1, Eq2). The pH continued to decrease and therefore $NaHCO_3$ was added to reactor 1 between days 81-88 (total of 3 g) to raise the pH. Simultaneously, the acetate level was 2.2-3.4 g/L. The pH decrease in reactor 3 was less dramatic and increased without $NaHCO_3$ addition to pH >7 on day 84 when the acetate concentration was 100 mg/L.

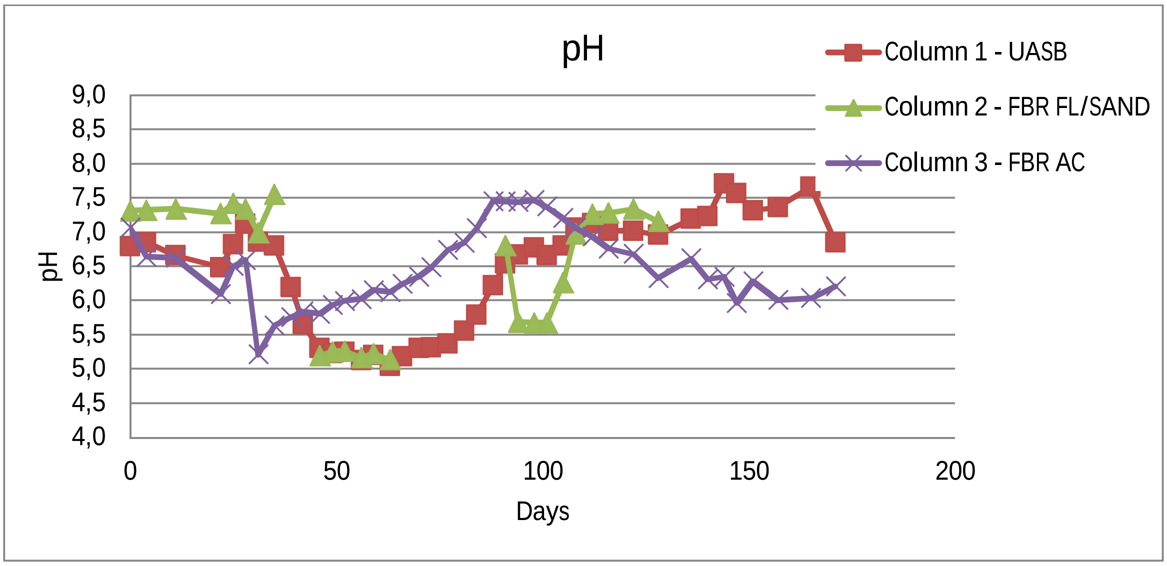

Figure 2 *pH in effluents during the experiment.*

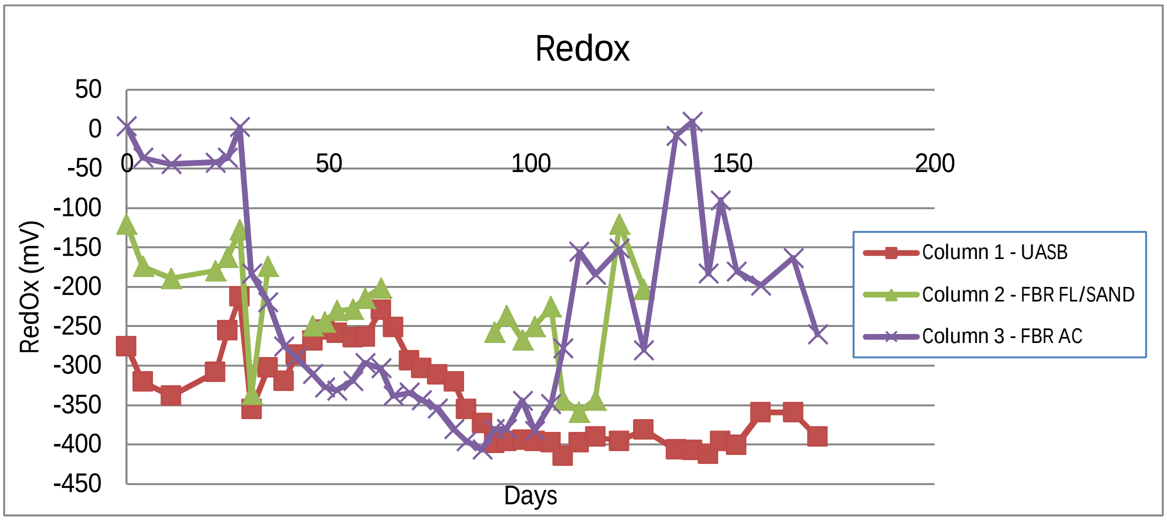

Figure 3 *Redox effluents during the experiment.*

Sulphide formation started practically on day 30 alongside with improved sulphate removal (Fig 4). After day 70, the sulphide level in reactor 1 rapidly increased and fluctuated between 100-300 mg/L; whereas the sulphide level in reactor 3 remained stable at <100 mg/L. Sulphide production did not seemingly correlate with the effluent sulphate level (Figure 1). One possible reason for the lower sulphide concentration in reactor 3 is adsorption to the carrier material activated carbon, but this does not fully explain why sulphide levels decreased over time.

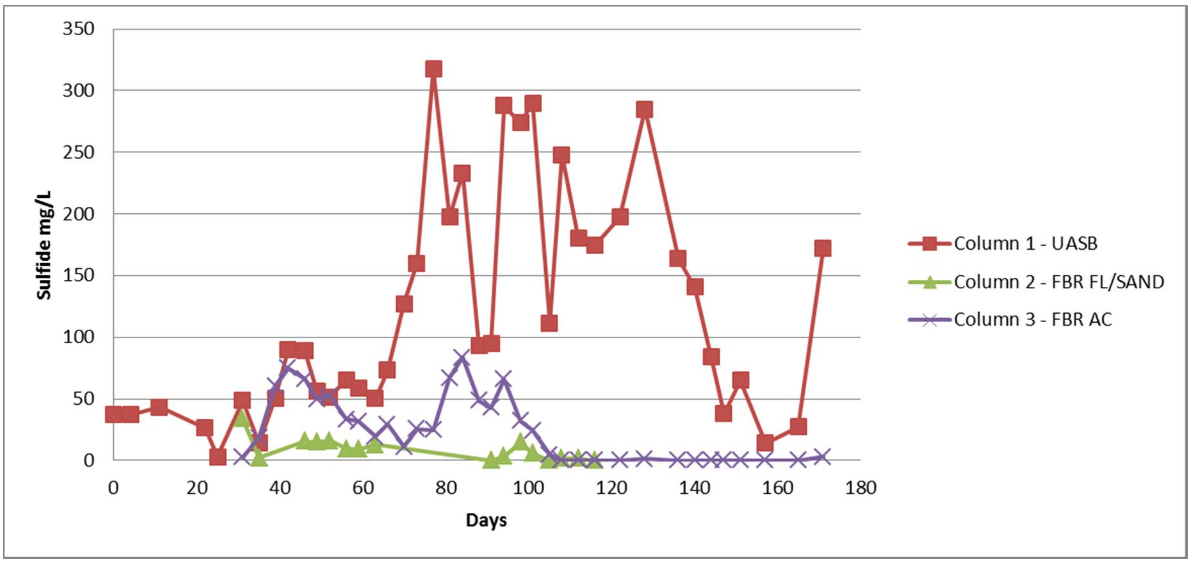

Figure 4 *Sulphide concentration in effluents*

Microbiology. The bacterial, archaeal and fungal communities of the inoculum and of the bioreactors after 101 days from all reactors and after 140 days of operation from reactors 1 and 3 were examined using high throughput amplicon sequencing. In general, the microbial communities changed quite markedly from that of the inoculum over time (Figure 5).

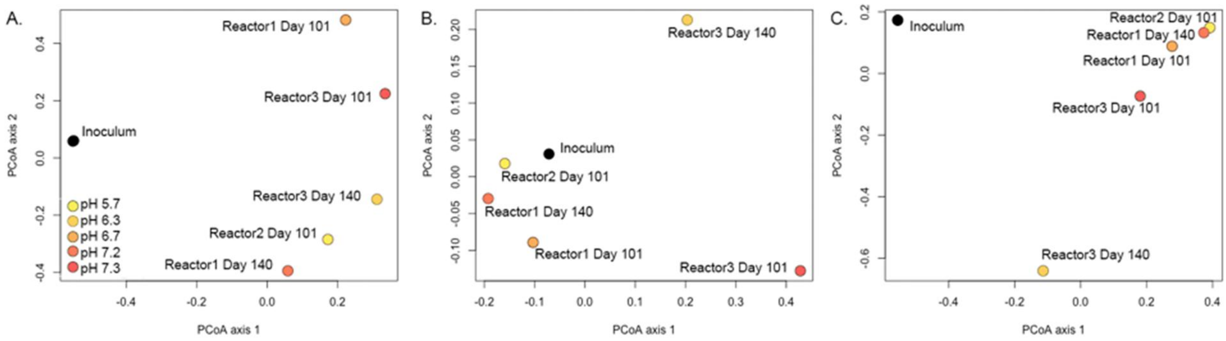

Figure 5 *PCoA plots of the A) bacterial, B) archaeal, and C) fungal communities identified by HTP sequencing from the inoculum and after 101 and 140 days of reactor operation. The reactor samples are coloured according to pH as indicated in the legend in A.*

The most abundant bacteria in the original inoculum were organic matter degrading Aminicenantes (OP8, 49%) and thiosulphate-reducing Caldiserica. In the reactors the bacterial communities changed to contain mostly proteobacterial groups (56 – 80%) and Bacteroidetes (4 – 32%). In Reactors 1 and 3 the proteobacteia belonged to sulfur-oxidizing *Sulfuricurvum*, *Sulfurospirillum*, *Thiobacillus*, *Thiofaba*, and *Thiomonas*, 24 and 80% of the bacterial community (Fig. 6). In Reactor 2 (day 101) the most abundant bacteria belonged to undetermined gammaproteobacterial groups (25%) and the alphaproteobacterial *Ochrobactrum* (20%), which is also known to oxidize reduced sulphur species. The SRB detected in the reactors belonged to the deltaproteobacterial groups *Desulfobulbus*, *Desulfomicrobium*, *Desulfovibrio* and *Desulfuromonas* and contributed between 2 and 15% of the bacterial community. Small amounts of Firmicutes SRB belonging to the *Desulfotomaculum* genus were detected in Reactor 2 after 101 (0.2%) and in Reactor 3 after 140 days of operation (0.5%). The archaeal communities in the inoculum and in all reactors consisted mostly of methanogenic *Methanosaeta*, which uses acetate for its methane production. Reactor 3 at 101 days of operation, however, sported a dominance of CO_2 and H_2 utilizing methanogens belonging to the *Methanobacterium*, which otherwise was present at only low abundance in all samples. Most of the fungi detected in the inoculum and reactors belonged to different groups of Ascomycota (51– 97%). However, Reactor 1 and 2 also contained a considerable amount of Basidiomycota (26 – 47%).

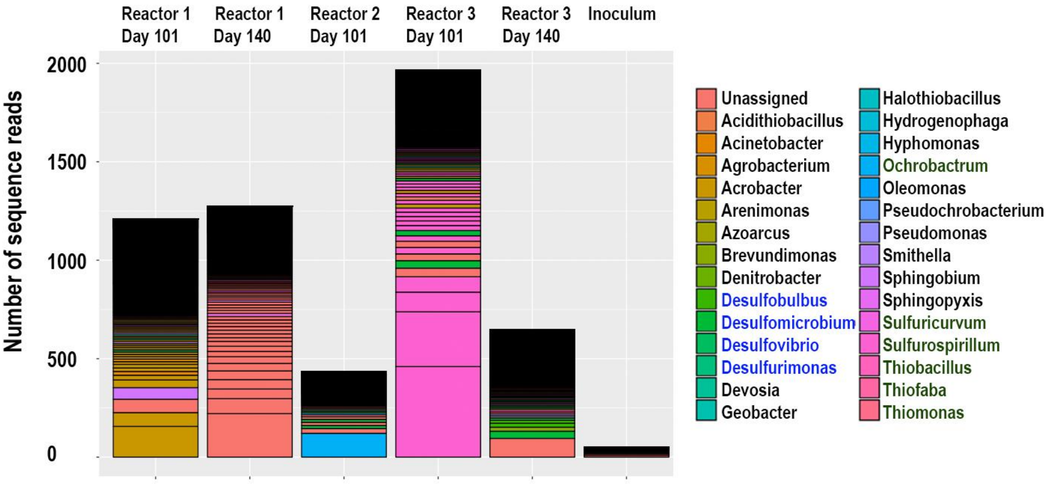

Figure 6 *The abundances of sequence reads belonging to Proteobacterial genera detected by the HTP sequencing. Names of sulphate reducing genera are indicated in blue and sulphur oxidizing genera in green text. The Y-axis show the absolute number of proteobacterial sequence reads obtained from the samples and the OTUs are ordered according to abundance, with the biggest OTUs at the bottom of each reactor. The taxonomic groups are shown by the colour charts to the right in the figure.*

Discussion

In order for SRB to efficiently reduce sulphate, specific environmental conditions need to met. These are low redox potential and availability of suitable electron donors. One such electron donor is ethanol, which has been used with variable results in previous studies (e.g. Napgal et al., 2000; Celis et al., 2009). The down side with using ethanol is the first step of ethanol oxidation (Eq1), where acetate is produced. Napgal et al. reported accumulation of acetate as high as 1.47 – 2.655 g/L without detecting any inhibition in the sulphate removal rate. However, as in our study, Celis et al. (2009) found that the sulphate reduction process was hampered as acetate accumulated.

The initial sulphate concentration affects biologic sulphate reduction. Optimal SRB growth has been observed in approximately 2500 mg/L sulphate concentrations (Al-Zuhair et al. 2008; Sahinkaya et al. 2011). When the sulphate concentration is higher, the reduction rate decreases and acetate accumulation is possible, leading to a risk of increased inhibition and process failure (Sahinkaya, 2009). In our case the sulphate concentration of the mine water was 8500 – 9000 mg/L, which is almost 4 times higher than reported for optimal growth of SRB. Thus, a combination of a high concentration of sulphate and ethanol as electron donor did probably result in the accumulation of acetate and malfunction or the biological process.

SRB need anoxic conditions with negative redox potential of at least -150 to -200 mV for their metabolism to function properly (Postgate, 1979; Gibert et al. 2002). If the redox potential is higher, for example in the presence of oxygen, sulphate remains unaffected and no sulphide is produced (Delaune and Reddy 2005). In our experiments the redox stayed between -400 and -100 mV. The highest value occurred in reactor 3, but there was no obvious correlation between the redox and the reactor performance. In addition sulphate reduction usually works best at pH 7 – 8 (Kaksonen 2004; Moosa and Harrison 2006), although there have been experiences with comparable sulphate reduction even in very acidic (pH 4) environments (Elliot et al. 1998). In our experiments the pH varied between 5.5 and 7.5 which are in acceptable limits. Anyway in combination with elevated acetate levels the lower values seemed to be detrimental to our processes.

High sulphate concentration may result in elevated redox potential and lowered pH and thus diminish the sulphate reduction activity (White and Gadd 1996). These environmental changes may also favour other microbes besides SRB to accumulate in the reactor (Oyekola et al. 2010).This is in agreement with our results, as 2-15% of the identified bacterial sequences belonged to SRB. However, as the current literature on full analysis of microbial communities in SBR is very scarce, it is very difficult to evaluate in detail the process performance vs microbial abundancy. The presence of high amounts of acetate-utilizing methanogens and the relatively low abundance of SRB is consistent with the low sulphate reduction activity observed in the reactors. The growth of SRB that are not able to oxidize acetate is generally inhibited by increasing acetate accumulation. In addition, the high abundance of sulphur oxidizing Epsilonproteobacteria, such as *Sulfurispirillum, Sulfuricurvum* and *Sulfurivorum*, may also have affected the processes in the reactor. These bacteria oxidize reduced sulphur species to sulphate or sulfuric acid.

Oyekola et al. (2010) pointed out that if the sulphide levels are moderately high, the redox potential is likely to be more negative, and thus counteracting the possible inhibiting effect of high sulphate. However, sulphide can also cause inhibition in higher concentration. Depending on the pH, sulphide occurs in as different species with different inhibitory effect. Generally, SRB are less sensitive to total sulphide when the pH is increased from 6.8 to 8.0 and more sensitive to the undissociated sulphide (H_2S) concentration ($pH < 6$).

Mine waters commonly contain only small amounts of organic matter and an external carbon source and electron donor needs to be provided for biological sulphate reduction. Numerous options for substrates are available, and ethanol is one of the commonly used ones, mainly because of relatively low cost and good suitability for a wide range of SRB. However, as in our case the possibility of incomplete oxidation and the production of inhibitory acetate is a risk.

Conclusions

A high input sulphate level and a low pH together with undissociated H_2S may inhibit growth and activity of the SRB. Elevated concentration of acetate may also inhibit the SRB. Analysis of the microbial community gives added insight into the processes. Our study also indicated that parameters normally used for following up an SBR process such as redox and pH, is not necessary sufficient for assuring a functioning process.

Despite the easy accessibility of ethanol as electron donor for biological sulphate removal processes, the ethanol in our case was incompletely oxidized, which resulted in acetate accumulation in the reactors. In future experiments a different source of electron donor may be needed in order to promote growth and activity of SRB.

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Sulfur Cycling in an Oil Sands Tailings Pond

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Abstract

Oil sands tailings ponds are used as the primary storage and settling basins for toxic tailings produced during oil sands processing in northern Alberta (Canada). As a result of microbial metabolism, methane production contributes to greenhouse gas emissions and was shown to affect tailings densification. In particular, sulfur cycling is supposed to play a key role both for the turnover of organic matter and the regulation of methane emissions. Adversely, the activity of sulfate-reducing bacteria (SRB) is likely to generate huge quantities of toxic H_2S, which pose a strong concern for both gas- and water-phase environments in the vicinity of the ponds.

In order to identify reactive zones of sulfur cycling and to assess the impact of microbial sulfate reduction on organic matter transformation and CH_4 emissions, biogeochemical analyses of original tailings from two vicinal pond profiles were combined with a number of laboratory experiments performed under well-defined conditions.

In conclusion, results give evidence that H_2S outgassing from the pond is effectively prevented by the biochemical re-oxidation and primary incorporation of H_2S into iron sulfide minerals. As demonstrated by the long-term incubation of original tailings in anoxic microcosms, considerable volumes of CH_4 emissions may be prevented by the activity of SRB in sulfidic tailings between 3.5–7.5 m in situ. In addition, results show that microbial sulfate reduction is essential for the anaerobic mineralisation of labile organic matter with significance for tailings ponds carbon cycle and gas production.

Key words: Oil sands tailings ponds, sulfur cycling, CH_4 emissions, carbon transformation

Introduction

The Athabasca basin in northern Alberta (Canada) harbors one of the world's largest oil sands deposits, holding an estimated amount of 170 billion barrels of recoverable oil (Alberta Environment and Research Development 2013). Despite short-term economic benefits, oil sands industry is controversially discussed due to considerable environmental impacts, like the large-scale disturbance of landscape, the high operational water demand and the generation of toxic tailings during oil extraction (BGC Engineering 2010). For storage and passive bioremediation tailings composed of sand, clay, metals, unrecovered bitumen and toxic process chemicals are pumped into huge anaerobic settling basis on site. As of 2014, these oil sands tailings ponds already cover an area of 182 km^2 (Alberta Environment and Research Development 2013), representing a large and unique mine water problem. In the ponds, tailings settle to the bottom reaching a density of about 30% solids referred to as mature fine tailings. During densification pore water is released to the surface of the ponds, forming a shallow water layer on top (~ 3 m) which is used to recycle water to the extraction plants (McKinnon 1989). Depending on the initial toxicity and rate of bioremediation, tailings ponds can be integrated into the surrounding environment as prospective aquatic habitats (Westcott 2007).

In oil sands tailings ponds, sulfur cycling is promoted by the presence of sulfate which is added to the ponds in form of gypsum ($CaSO_4 \cdot 2H_2O$) in order to enhance the densification of fine tailings (Ramos-Padrón et al. 2011). Consequently, microbial sulfate reduction is supposed to represent the quantitatively most important electron-accepting processes for the anaerobic transformation of organic matter and may therefore be substantial for tailings detoxification and reclamation (Figure 1) (Holowenko et al. 2000). However, the contribution of sulfate reduction to organic matter decomposition in tailings ponds has not been quantified yet.

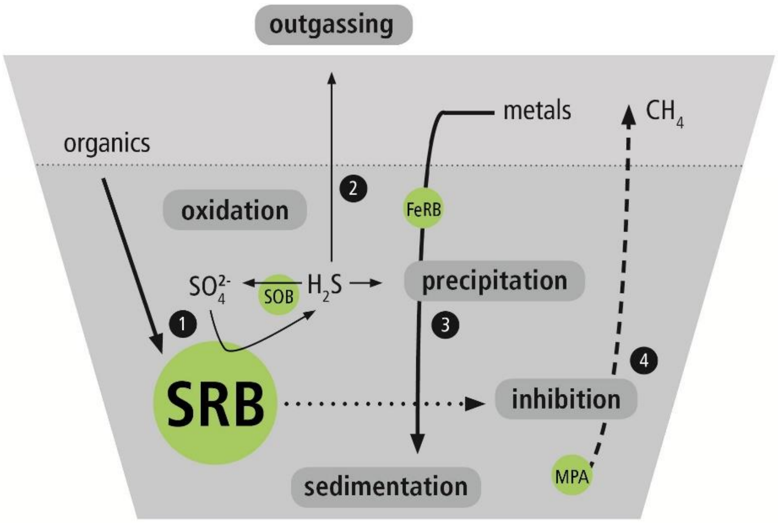

Figure 1 *Sulfur cycling in oil sands tailings ponds (adapted from M. Koschorreck). 1) Transformation of organic matter; 2)* H_2S *outgassing/re-oxidation; 3) Precipitation; 4) Effect on* CH_4 *emissions. SRB – sulfate-reducing bacteria; SOB – sulfur-oxidizing bacteria; FeRB – iron-reducing bacteria; MPA – methane producing archaea*

As a result of microbial metabolism, a distinct sulfidic zone evolved in many ponds, potentially generating huge amounts of hydrogen sulfide (H_2S) or HS^- (Ramos-Padrón et al. 2011). Beside operational challenges regarding eventual adverse impacts of H_2S ebullition on tailings sedimentation (BGC Engineering 2010), H_2S exhibits a high chemical demand for oxygen (COD) and is toxic to many organisms (Reis et al. 2004). In addition, biogenic sulfur gases (e.g. H_2S or dimethyl sulfide) can degas to the atmosphere, eventually contributing to air pollution and acid rainfall in the surrounding environment after re-oxidation to SO_2 and SO_4^{2-} (Howarth et al. 1992). Beside re-oxidation upon contact with oxygen or by sulfur-oxidizing bacteria, H_2S is likely to react with dissolved metal(loid)s (Rickard and Morse 2005) in anaerobic pond layers to form insoluble precipitates like iron sulfides (FeS) (Salloum et al. 2002). With respect to water quality, the formation of sulfide minerals may contribute to the immobilization of both toxic H_2S and heavy metals during disposal of reactive mine tailings. Until now, quantitative measurements examining potential H_2S outgassing and the composition and distribution of total reduced inorganic sulfur in tailings ponds are still lacking. In addition to H_2S, methane contributes to 60–80% of gas flux over oil sands tailings ponds. Beside its contribution to greenhouse gas emissions, methanogenesis was shown to increase tailings densification (Siddique et al. 2014), which is relevant for operational water re-use. In laboratory incubations, methane production significantly decreased in tailings supplemented with sulfate, suggesting an inhibition of methanogenesis by sulfate reduction due to the competition for methanogenic substrates (Holowenko et al. 2000; Ramos-Padrón et al. 2011). However, not much is known about the impact of microbial sulfate reduction on methanogenesis in tailings of different depths, which is essential to predict overall CH_4 emissions from the ponds.

From the previous findings and theoretical considerations outlined above, sulfur cycling in oil sands tailings ponds represents a central elemental cycle with relevance for pond management and eco-toxicological assessment. Therefore the aims of the present study were to assess information on possible factors of sulfur biogeochemistry controlling (i) H_2S outgassing and metal sulfide formation, (ii) methane emissions and (iii) the transformation of labile organic matter. To achieve this, microbial numbers and activities were integrated with wet geochemical analysis and stable isotope geochemistry in material from two vicinal sites of an active oil sands tailings pond. In order to determine the impact of microbial sulfate reduction on carbon transformation and CH_4 emissions, original tailings were subsequently incubated with/without a set of relevant organic acids (lactate, acetate, formate, propionate and butyrate) in anoxic microcosms with/without molybdate as selective inhibitor for microbial sulfate reduction. Over a period of 180 days, we monitored methane production and organic acid transformation.

Methods

2.1. Sampling, geochemical and isotope analysis

Samples were collected on September 2011 from two vicinal (~ 100 m) sites of an active tailings pond. Samples were obtained from the water cap (1, 2, 3 m) and from the tailings zone (4.5, 5.5, 7.5, 13.5 m) using a piston sampler (Penner and Foght 2010). Samples for geochemical analysis, most probable numbers (MPN) and microbial activity were transferred into sterile 500 mL plastic Nalgene® bottles. Subsamples for analysis of sulfur isotopes were transferred into 125 mL Nalgene® flasks containing Zn-acetate. Bottles were shipped within two weeks, cooled and darkened without any headspace. Wet geochemical analysis were performed using standard procedures as described in Koschorreck et al. (2007). Total reduced inorganic sulfur (TRIS) was analyzed according to a sequential extraction after Canfield (1989) and Fossing and Jørgensen (1989).The extracted fractions of acid volatile sulfide (AVS), chromium reducible sulfide (CRS) and elemental sulfur (S^0 extracted as dimethylformamide-extractable sulfur (DMFS)) were measured polarographically. Stable isotopes of sulfur were analyzed according to Knöller and Schubert (2010).

2.2. Most probable numbers (MPN)

MPN to enumerate viable cells of SRB and SOB were performed as serial dilutions in deep-well plates (Wendt-Potthoff and Koschorreck 2002). Selective media were used with modified concentrations of [g L^{-1}] NaCl (1.0), $MgCl{\cdot}6H_2O$ (3.0), NH_4Cl (0.3), KH_2PO_4 (0.2), KCl (0.3), $CaCl_2{\cdot}2H_2O$ (0.15) (Widdel and Bak 1992). All media were adjusted to pH 7.5 and incubated in the dark at 20°C for 6 weeks. MPN and their confidence intervals were calculated using the program of Klee (1993).

2.3. Activity rates

All assays were conducted in duplicate in the dark at 20 °C. For the measurement of microbial gas production, 1 mL of sample was filled into a 10 mL sterile glass vial, sealed with a butyl rubber stopper and immediately gassed with nitrogen. Methane and carbon dioxide production in the headspace was monitored for 30 days, using a gas chromatograph (SRI 8610C, Schambeck) equipped with a flame ionization detector (FID) and a methanizer (SRI instruments, Torrance, U.S.A.). Rates were calculated from the linear regression of CH_4 and CO_2 partial pressure in the headspace. Thiosulfate oxidation potentials were measured in batch slurries containing a 1:1 (v/v) ratio of sample to added liquids. Liquids consisted of a mineral media containing [mg L^{-1}] NaCl (1.0), $MgCl{\cdot}6H_2O$ (3.0), NH_4Cl (0.3), KH_2PO_4 (0.2), KCl (0.3), $CaCl_2{\cdot}2H_2O$ (0.15), a trace element solution SL12 (Widdel and Bak 1992) and $Na_2S_2O_3{\cdot}5H_2O$ with a final concentration of 7.5 mmol L^{-1}. Assays (70 mL) were incubated under aerobic conditions in 125 mL Erlenmeyer flasks on a shaker (100 rpm) with autoclaved controls. Thiosulfate concentrations were measured by ion chromatography (Dionex ICS-3000). Rates were calculated as linear regression of thiosulfate decrease over time. Microbial sulfate reduction was determined by adding 20 µL of a 1.33 mmol L^{-1} $^{35}SO_4^{2-}$ solution to 5 mL of sample. Assays were incubated in 150 mL serum bottles under N_2 for 22 h. Subsequently, 5 mL of a Zn-acetate solution was added to stop the reaction. Extraction of radioactive sulfide was done by passive diffusion (Meier et al. 2000). Radioactivity was measured in a scintillation counter (TRI-CARB 2300TR, Perkin Elmer). Statistical tests were carried out using SigmaPlot version 12.0.

2.4. Microcosm studies

Microcosms were set up as batch slurries in 125 mL serum bottles with an equal ratio of original samples to added liquids (35 mL each). The liquids consisted of an anoxic mineral media containing [g L^{-1}] NaCl (1.0), $MgCl{\bullet}6H_2O$ (3.0), NH_4Cl (0.3), KH_2PO_4 (0.2), KCl (0.3), $CaCl_2{\bullet}2H_2O$ (0.15) and Na_2SO_4 (4.0). After autoclaving and gassing with nitrogen, 1 mL L^{-1} each of a sterile selenite solution, a vitamin solution (DSMZ 148 medium, www.dsmz.de) and a trace element solution (SL10), 30 mL L^{-1} of a 1 M $NaHCO_3$ solution and 1 mL L^{-1} of 1M Na_2S solution were added aseptically (Widdel and Bak 1992). A mixture of carbon sources containing 2.5 mM each of Na-lactate, Na-acetate, formate, propionate and butyrate was added from sterile concentrates to half of the microcosms. The final pH of the media was adjusted to 7.5. Na-molybdate at a final concentration of 10 mM was added to part of the microcosms as specific inhibitor of microbial sulfate reduction. Serum bottles were sealed with butyl rubber stoppers and flushed aseptically with N_2 gas. Autoclaved controls served to account for chemical reactions. All incubations were done in duplicate and incubated at 15°C in the dark. Concentrations of methane, CO_2, sulfate and organic acids were measured every 2–6 weeks. Gas production was monitored by gas chromatography (Section 2.3) after removing 0.2 mL of headspace gas aseptically with a syringe. Concentrations of carbon sources were measured using HPLC (Thermo Separation Products). Sulfate concentrations were measured by ion chromatography (Dionex ICS-3000). Microcosms were replenished with sulfate to 2000 mg L^{-1}, when concentrations dropped below 500 mg L^{-1}.

Results

3.1. Major biogeochemical characteristics and sulfur isotopes of original samples

Both sites contained tailings under a water cap of about 3.6 m. Solids content increased from nearly zero (water layer) up to 40% solids (w/w) at 13.5 m. No oxygen was detected below the water-tailings interface at both sites. Sulfate concentrations dropped sharply from 4 mM in the water to less than 0.5 mM below the water-tailings interface (Figure 2). No sulfide was detected in the water cap. Fractions of AVS, CRS and DMFS increased below the water-tailings interface with highest concentrations (~ 9 mM) between 4.5–7.5 m. Generally, sulfides were dominated by AVS (~ 4 mM), the primary product of microbial sulfate reduction. At 4.5 m, DMFS represented the dominant sulfur species, indicating partial oxidation of sulfides. Beside the concentration, the isotopic composition of sulfur varied with depth (Table 1). In particular, $\delta^{34}S$ of sulfide at 4.5 m was 1‰, which is 6‰ lower than the sulfur isotope signature of sulfate in the water cap, most likely reflecting fractionation during microbial sulfate reduction.

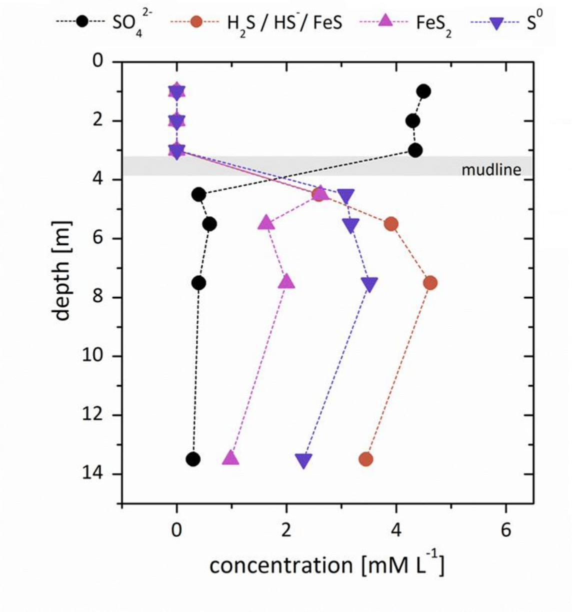

Table 1 *Sulfur isotopic composition*

depth	$\delta^{34}S$–S ‰	sulfur species
1 m	7.37	SO_4^{2-}
2 m	7.31	SO_4^{2-}
3 m	7.43	SO_4^{2-}
4.5 m	**0.91**	**H_2S, HS^-, FeS**
5.5 m	4.41	H_2S, HS^-, FeS
7.5 m	3.72	H_2S, HS^-, FeS
13.5 m	3.91	H_2S, HS^-, FeS

Figure 2 *Concentrations of sulfide and sulfate along the pond profile. The different fractions represent: (●) sulfate, (●) AVS (acid volatile sulfur), (▲) CRS (chromium reducible sulfur) and (▼) DMFS (dimethylformamide extractable sulfur).* (*Data are from Stasik et al. 2014)*

3.2. Cell counts and microbial activity

Highest numbers of SRB (10^4–10^6 cells mL^{-1}) were detected at 5.5–7.5 m (Figure 3a). Accordingly, sulfate reduction rates (SRR) increased below the water-tailings interface, with a maxima at 7.5 m (~ 100 nmol mL^{-1} d^{-1}), before decreasing to 10 nmol mL^{-1} d^{-1} at 13.5 m. Throughout the pond high numbers of viable cells were also detected for aerobic SOB, ranging between 10^4–10^8 cells mL^{-1} (Figure 3b). Thiosulfate oxidation potentials increased below the mudline, with a maximum around

600 nmol mL^{-1} d^{-1} at a depth of 5.5 m. No methanogenesis or CO_2 production was observed in the water cap. Below the mudline CH_4 production fluctuated between 54–76 nmol mL^{-1} d^{-1} (not shown).

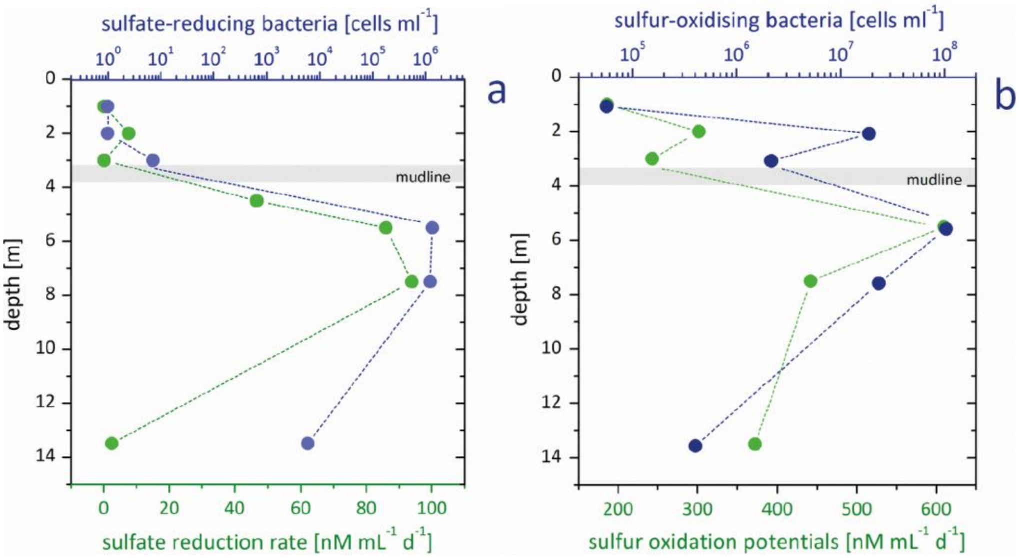

Figure 3 *Microbial cell numbers and activity as a function of depth. a) Sulfate reduction rates and cell numbers of SRB, b) Thiosulfate oxidation potential and cell numbers of SOB* (*Data are from Stasik et al. 2014)*

3.3. Impact of sulfate reduction on CH_4 production

During the long-term incubation of pond material in anoxic microcosms, methane was produced with rates ranging between 2–13 µmol L^{-1} d^{-1} in tailings at 5.5–13.5 m (not shown). No methane was generated in samples of the water cap (1–3 m). The inhibition of bacterial sulfate reduction by molybdate increased methane production in tailings (5.5–13.5 m) by a factor of 2–6.

3.4. Impact of sulfate reduction on the transformation of labile organic matter

In microcosms without molybdate concentrations of lactate, formate, propionate, acetate and butyrate decreased in water (~210 µmol L^{-1} d^{-1}) and tailings (~370 µmol L^{-1} d^{-1}). The transformation of organic acids and the production of CO_2 (not shown) generally decreased in microcosms with molybdate (Table 2), indicating the significance of microbial sulfate reduction for the mineralisation of labile organic matter in the pond material. When sulfate reduction was inhibited, transformation rates of acetate and butyrate decreased to <5% in the water cap and to 4–16% in tailings. SRB also dominated propionate turnover in tailings, but were not essential for formate and lactate metabolism.

Table 2 *Effect of molybdate addition on the transformation of organic acids, expressed as % of transformation rates measured in microcosms without molybdate*

	depth	lactate	formate	acetate	propionate	butyrate
water	1 m	73	71	2*	96	1*
	2 m	74	85	3*	94	2*
	3 m	78	80	5*	93	3*
tailings	5.5 m	101	100	4*	9*	4*
	7.5 m	102	105	4*	5*	7*
	13.5 m	101	109	16*	2*	15*

* significant ($p < 0.05$) difference to rates measured in microcosms without molybdate. (n=4) Differences were analyzed by two-tailed Student‘s t-test and a p-value of <0.05 was considered significant.

Discussion

4.1. Sulfur cycling, H_2S outgassing and metal sulfide formation

Both microbial activities and viable counts of sulfur-related bacteria demonstrated the presence of a distinct sulfidic zone within the first 4 m below the water-tailings interface (Figure 3) that was also evident by a sharp drop of sulfate and a pronounced increase of sulfides (Figure 2). In addition, sulfur isotope signatures of sulfide showed that the sulfidic zone might have persisted for a long time at the respective depths (Table 1). Interestingly, the sum of sulfate (4 mM) and dissolved sulfide (H_2S/HS^-) (<0.1 mM) measured in the water cap was below an expected sum of 7.3 mM that would result from an average dose of 1 kg m^{-3} gypsum ($CaSO_4$) typically added to tailings in order to enhance their consolidation. Similar observations in another pond (Ramos-Padrón et al. 2011) suggest that this difference might be due to the precipitation of H_2S/HS^- into sulfide minerals that prevents H_2S outgassing. Indeed, while dissolved sulfides were absent in the water cap, considerable amounts of AVS (>4 mM) were found below the water-tailings interface in our profiles. Beside H_2S/HS^-, AVS comprises iron monosulfides (FeS) that are generally quickly formed in presence of reactive (HCl-soluble and hydroxylamine reducible) iron (Rickard and Morse 2005). Tailings ponds contain huge quantities (50 mM) of total reactive iron (Fe(II)+Fe(III); Stasik et al. 2014) that enables the precipitation of iron monosulfides. Throughout the pond, FeS_2 (CRS) was a minor fraction of reduced sulfur compounds indicating limitation of pyrite formation (Gagnon et al. 1995) presumptively due to the abundance of reactive iron that reduced the availability of free sulfides. Nevertheless, an average AVS:FeS_2 ratio of ~2 is in the typical range of natural coastal sediments (0.02–7.2) (Gagnon et al. 1995). In addition to FeS and pyrite, the presence of DMFS at the water-tailings interface suggested a partial re-oxidation of sulfides to elemental sulfur (S^0). The re-oxidation of sulfides in the pond can be estimated by comparing rates of sulfate reduction with the accumulation of TRIS. The investigated pond has been in operation since 1995, suggesting that oldest tailings deposited at the bottom (~ 40 m) correspond to an age of about 20 years. However, tailings investigated in our study were obtained between depths of 5.5–13.5 m, representing a zone where initial sedimentation of tailings occurs during the first 2–3 years after deposition (McKinnon 1989). Assuming a tailings age of 2.5 years, integrated TRIS accumulation between 5.5– 13.5 m would correspond to a rate of 3.6 mmol sulfide L^{-1} y^{-1}. Thus, based on a SRR of 18.25 mmol SO_4^{2-} L^{-1} y^{-1} (calculated from an average SRR of ~ 50 µmol L^{-1} d^{-1} between 5.5–13.5 m) approximately 81 % of sulfide is re-oxidized in the pond. This is in the range of sulfide re-oxidation typically estimated for natural aquatic sediments (72–94 %) (Boesen and Postma 1988). However, as no oxygen was detected in situ and reactive iron was mainly Fe(II), it is likely that sulfides were re-oxidised by crystalline iron oxides and (oxy) hydroxides that are typically abundant and associated with clay minerals in oil sands tailings (Kaminsky et al. 2008). Apart from the chemical oxidation of H_2S/HS^-, high numbers of viable SOB and their potential activity also indicated biologically mediated sulfide oxidation throughout the pond. Interestingly, pools of total reduced sulfur (>9 mM) even exceeded concentrations assumed from theoretical considerations (>7.3 mM) in tailings below the water cap, suggesting a gradual accumulation of sedimentary sulfides. With respect to the development of a future lake ecosystem, the permanent precipitation of metals and sulfides in anoxic sediments below the water body may prevent the dispersion of toxic dissolved sulfide into the overlying water. However, FeS_2 may oxidize upon contact with oxic lake water, resulting in the dissolution of SO_4^{2-}, Fe^{2+} and H^+ and consequently the generation of acid mine drainage (Singer and Stumm 1970; Kuznetsov et al. 2015).

4.2. Impact of sulfate reduction on the organic acid transformation and CH_4 emissions

In tailings of all depths, rates of carbon turnover and CO_2 production significantly decreased when sulfate reduction was inhibited, demonstrating the role of bacterial sulfate reduction as the most important terminal oxidative process in anoxic tailings. As a general trend, the relative contribution of SRB to the turnover of butyrate and acetate decreased with depth (Table 2). Contrarily, SRB were responsible for the turnover of propionate in deeper tailings, but not essential for its consumption in the water cap. Interestingly, SRB were not predominantly involved in lactate and formate turnover, demonstrating the presence of other microbial metabolisms. The particular importance of methanogenic biodegradation for hydrocarbon transformation in tailings was recently demonstrated (Siddique et al. 2012). Accordingly, enormous amounts of CH_4 contribute to greenhouse gas emissions and may have both adverse and beneficial effects in oil sands tailing ponds (Fedorak et al. 2003). When competing for the major fermentation products H_2 and acetate, sulfate-reducing bacteria have a thermodynamic advantage over methanogens (Holland et al. 1987). This is in line with slightly increased methanogenesis in molybdate-amended sulfate-rich microcosms, demonstrating a partial inhibition of methanogenesis by microbial sulfate reduction. An inhibition of methanogenesis by SRB was previously shown in laboratory incubations with mature fine tailings from other ponds (Holowenko et al. 2000; Salloum et al. 2002). However, in order to estimate the inhibition of CH_4 emissions by sulfate reduction in situ, the microbial activity in original tailings has to be considered. Based on our measurements, microbial sulfate reduction and methanogenesis coexisted in situ exclusively in sulfate-rich tailings between 3.5–7.5 m, with methane production rates increasing by a factor of 2–3 (~ 10 μmol L^{-1} d^{-1}) after inhibition of sulfate reduction. Taking an estimated pond surface area of about 6 km^2 and a sulfidic layer of 4 m, the activity of SRB would prevent at least ~ 5.37 million litres of CH_4 emissions from the pond per day.

Conclusions

In conclusion, results give evidence that H_2S outgassing from the pond is effectively prevented by the biochemical re-oxidation of H_2S and formation of iron sulfide minerals that may contribute to the permanent burial of sulfide in anoxic tailings. Throughout the pond, rates of carbon transformation and CO_2 production significantly decreased when sulfate reduction was inhibited, demonstrating the role of bacterial sulfate reduction as the most important terminal oxidative process in anoxic tailings with significance for tailings ponds carbon cycle and gas production. As demonstrated by the selective inhibition of SRB, microbial sulfate reduction may have prevented considerable volumes of CH_4 emissions from the pond due to the competition with methanogens. Moreover, findings on sulfur cycling can be regarded as the actual state of an active oil sands tailings pond prior to the conversion to an end pit lake. In combination with ongoing monitoring programs this will help to understand the development of key elemental cycles and geochemical gradients during subaqueous deposition of tailings and ultimately to evaluate the success of a wet-landscape reclamation.

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Characterising Environmental Risks Associated with Sulfide-bearing Gold Wastes

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Abstract

Acid rock drainage (ARD) is one of the most significant environmental challenges associated with the mining of hard-rock sulfidic ores and coal. Environmental hazards associated with ARD generation concern the formation of acidic pollution, which often contains elevated concentrations of deleterious elements and soluble salts. Current characterisation methods tend to mainly focus on the potential for acidity generation under chemical conditions as a proxy for ARD formation, with little initial attention to the risks associated with the elevated elemental concentrations.

This study demonstrates the application of a suite of techniques for the relatively rapid and integrated characterisation of the potential risks associated with acidity generation and the deportment of deleterious elements from two sulfide-bearing gold wastes. The results demonstrate that the novel biokinetic test can be used to validate and compliment the static chemical ARD predictions tests, providing useful information on the relative rates of the acid forming and acid neutralising reactions under conditions of microbial activity. Quantitative information on the mineralogical composition of acid forming and acid neutralising minerals assists in the interpretation of the geochemical test work, with the sequential chemical extraction test provides valuable information on the distribution and potential environmental risks of minor and trace metals.

Key words: Acid rock drainage, environmental risk, mine waste characterisation, metal deportment

Introduction

The extraction of metals from ores generates large amounts of waste material through both mining and mineral processing practice. The environmental effects arising from the disposal of such wastes are far reaching and long-term (Koehnken et al., 2003), with formation of water pollution originating from the runoff of mine waste disposal sites being a major polluting factor. For sulfide-bearing wastes, the generation of acid rock drainage (ARD) is of particular concern. Characterised by low pH values, the highly acidic nature of the solution results in the mobilisation of deleterious elements contained within the mine waste (Nordstrom (2011). The ecological impacts of pollution from gold mine wastes are often cumulative and their true impact may only be felt long after mining activities have ceased (McCarthy, 2011). Most commonly observed, are the immediate effects to the local flora and fauna; however, the contamination of water sources may lead to far-reaching consequences. In a study of the rivers and water sources surrounding the Witwatersrand basin, Durand (2012) reported significant detrimental effects to local communities who use contaminated groundwater for drinking and subsistence farming purposes. The environmental damage is not limited to animals, but may affect the local soils, due mainly to the accumulation of heavy metals and salts (Kitula, 2006). Reliable characterisation of the environmental risks associated with drainage runoff emanating from mine waste, therefore, requires independent assessment of the potential to form acidity and the deportment of deleterious elements.

Evaluation of the ARD potentials of waste samples occurs through the use of standard ARD characterisation and prediction tools which assess the potential of waste samples to generate acidity. The independent quantification of the inherent acid neutralising and acid forming potentials is achieved through the use of laboratory-scale test work, with the difference between the values used to assess overall acidity generation (Price, 1997). Following the classification of the samples, kinetic tests are performed on those which show acid generating potential, or for which some uncertainty in the classification is observed. These tests are aimed at characterising the temporal behaviour of the ARD generation and the composition of the resulting pollution with time (Parbhakar-Fox and Lottermoser, 2015).

Although results from the standard static characterisation tests provide a rapid assessment of the overall acid generating potential, these results are limited to the extreme chemical condition of the test methods. Thus, no information is gained on the potential for ARD generation under microbial conditions most commonly experienced within waste deposits (Hallberg, 2010). The recent development of the biokinetic tests to account for microbial action has been demonstrated on base metal wastes (Hesketh et al., 2010), gold wastes (Dyantyi et al., 2013) and coal ultrafine wastes (Opitz et al., 2015). Furthermore, the exclusive focus on the potential for acidity generation as a proxy for ARD formation results in a lack of information regarding the deportment of deleterious elements from the waste sample during the characterisation step, particularly the environmental consequences associated with the elevated elemental concentrations within neutral drainage (Plante et al., 2010). These samples are classified as non-acid generating and are, as per the standard screening protocols, not subjected to further test work (Parbhakar-Fox and Lottermoser, 2015).

Measurement of the elemental concentrations in solutions resulting from the static characterisation test may provide information regarding metal deportment under severe conditions, with the addition of sequential chemical extractions allowing for semi-quantitative information of elemental deportment under disposal conditions (Opitz et al., 2015). The inclusion of a detailed mineralogical assessment, allows for a fundamental understanding of the geochemical behaviour of waste samples within ARD characterisation tests (Becker et al., 2015). The inclusion of mineralogical analyses of waste samples in the current characterisation toolbox, either as a co-current characterisation step (Maest et al., 2005) or as preceding characterisation step itself (Parbhakar-Fox et al., 2013), has been suggested previously. However, the integration of such analyses within the common ARD characterisation protocols remains limited.

The present study was undertaken to demonstrate the combined application of techniques for the rapid and effective characterisation of the potential environmental risks associated with two wastes from the extraction and primary processing of different sulfide-bearing gold ores.

Material & Methods

Gold waste samples

Two mine waste samples were used in the completion of this study. Sample A was sourced from a greenstone belt gold deposit. The second waste sample (B) was sourced from a historical tailings dam, generated during the processing of a Witwatersrand gold ore deposit. The compositions of the two waste samples are presented in Figure 1 (Opitz et al., 2016). Acid generating minerals consist of predominately pyrite (A:1.2 wt. %, B: 0.3 wt. %) and pyrrhotite (A: 5.8 wt. %, B: 0.1 wt. %), with small (< 0.1 wt. %) concentrations of other metal sulfides. These trace phases consist predominately of chalcopyrite, galena, and pentlandite. Acid consuming phases within the waste samples consist predominantly of fast-weathering carbonates (A: 0.9 wt. %, B: 0.01 wt. %), with intermediate-weathering silicates such as chlorite (A:1.4 wt. %, B: 1.4 wt. %) and slow weathering Fe-oxides phases such as magnetite (A: 33.4 wt. %, B: 1.9 wt. %) also present. The majority of the waste samples, however, consist of non-reactive silicate minerals such as quartz (A:26 wt. %, B: 70.9 wt. %) and plagioclase (A: 13.5 wt. %, B: 23.9 wt. %).

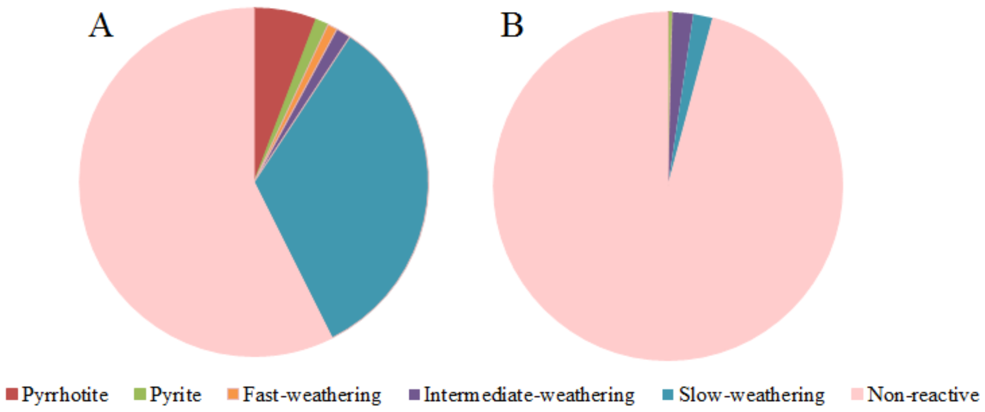

Figure 1: *Results from the mineralogical analysis using QEMSCAN on the two gold waste samples indicating the acid generating minerals, pyrite and pyrrhotite, and acid consuming minerals, carbonates, chlorite and magnetite as fast-, intermediate- and slow-weathering respectively, and non-reactive mineral phases.*

Characterisation of the ARD potentials

The ARD potentials of the waste samples were estimated directly from sample mineralogy in accordance with the method developed by Paktunc (1999) using the difference in the theoretical acidity generated by the acid-forming minerals and consumed by the acid-neutralising phases. Standard acid base accounting tests (ABA, Lawrence and Scheske (1997)) were used to calculate the maximum potential acidity (MPA), on the basis of LECO analysis of total sulfur, and the acid neutralising capacity (ANC), determined empirically, of the waste samples. These tests were performed in conjunction with net acid generation tests (NAG, Miller et al. (1997)) in triplicate. To assess the potential for ARD generation, biokinetic tests were performed according to the method outlined by (Opitz et al., 2016) at 37 °C for 90 days.

Sequential chemical extraction tests

Sequential chemical extraction tests were performed using a method outlined by Broadhurst et al. (2009). In this test, the waste sample is subjected to a sequential chemical leach protocol, to determine the distribution of metals to seven different fractions: water soluble, ion-exchangeable, carbonate, amorphous Fe/Mn-oxide, crystalline Fe/Mn oxide, sulfide and residual/inert.

Environmental risk assessment

The environmental risks associated with the deportment of the deleterious elements were assessed using a ranking and scoring method as outlined in Broadhurst and Petrie (2010). Here, elements are ranked and scored according to their potential environmental significance, as determined from their leachable concentration levels derived from the SCE tests, their acceptable risk concentrations as derived from water quality limits (DWAF, 1996), and their typical crustal abundance. Elements of interest were identified on the basis of common deleterious elements within gold waste deposits (Opitz et al., 2016), with the deportment of As, Cu, Cr, Ni, Pb and U presented. Elemental concentrations were quantified using induced coupled plasma mass spectrometry (ICP-MS) analysis using a Thermo-Fisher X-series II quadruple ICP-MS machine.

Results & Discussion

Characterisation of the potential for acidity generation

- Mineralogical assessment

The results in Table 1 indicate that both samples can be classified as potentially acid generating due to the greater quantities of acid forming phases relative to the acid neutralising phases. The higher acid forming potential for Sample A, as compared to that observed for sample B, can be attributed to the greater quantity of pyrrhotite and pyrite minerals (see Figure 1). Similarly, the higher content of the fast-weathering minerals resulted in a greater acid-consuming potential for sample A, as compared to sample B where the majority of the acid-consuming minerals were intermediate- and slow-weathering phases.

***Table 1:** Theoretical ARD estimates using the mineralogical composition*

Sample	Acid-forming Potential [kg H_2SO_4/ton]	Acid-consuming Potential [kg H_2SO_4/ton]	ARD Estimate [kg H_2SO_4/ton]	ARD Classification
A	83.9	9.1	74.8	Potentially acid forming
B	6.7	0.3	6.4	

- Static ARD characterisation tests

Significant discrepancies were observed in the quantitative acid generating and acid neutralising results between the mineralogical and static ARD tests (Table 2). The observed differences in the AP and MPA calculations were due to differences in the sulfide values obtained from the chemical and mineralogical analysis, with the LECO total sulfur method resulting in lower sulfide sulfur (A: 2.3 wt. %, B: 0.06 wt. %) than that calculated from the pyrrhotite and pyrite contents (A: 2.8 wt. %, B: 0.2 wt. %). In an assessment of different methods for the determination of total sulfur in geological samples, Czerewko et al. (2003) observed significant under-estimations in the total sulfur content for low-sulfur samples using LECO analysis. For the samples in this study, an under-estimation in the total sulfur content would explain the lower MPA values as compared to the AP values estimated directly from the sample mineralogy. The differences in calculated acid consuming potentials may be attributed to the presence of intermediate- and slow-weathering minerals not being accounted for in the mineralogical estimates. Previous studies (Becker et al., 2015) have indicated partial dissolution of these mineral phases under the relatively aggressive ANC test conditions, resulting in a higher neutralising capacity than that predicted from quantification of the fast-weathering acid neutralising minerals.

Although differences were observed between the mineralogical estimates and the static ARD test results, the overall ARD classification was the same for all the tests in the case of sample A. Similarly, the NAPP results suggests a potentially acid generating classification (-20 < NAPP < 20) corresponding to that from the mineralogical estimate in the case of sample B. The elevated NAG pH value (pH 4.0 < NAG pH), however, suggested a "non-acid forming" classification for this sample. The overall classification of the ARD potential for this sample, therefore, remained uncertain due to these discrepancies.

***Table 2:** ARD test results following static characterisation tests performed in triplicate*

Sample	MPA [kg H_2SO_4/ton]	ANC [kg H_2SO_4/ton]	NAPP [kg H_2SO_4/ton]	NAG pH [kg H_2SO_4/ton]	ARD Classification
A	70.2 ± 0.7	53.2 ± 1.8	17.0 ± 1.9	2.5 ± 0.0	Potentially acid forming
B	1.9 ± 0.4	3.9 ± 0.5	-2.1 ± 0.3	6.5 ± 0.1	Uncertain

- Biokinetic tests

The pH profiles within biokinetic tests provided an indication of the relative rates of acid formation and acid consumption under the acidic, microbial conditions (Figure 2). The observed initial rise in solution pH for sample A can be attributed to the dissolution of the fast-weathering carbonate minerals. The rapid decrease in solution pH thereafter, was due to ferric iron precipitation and, below pH 3.5, sulfide mineral oxidation using ferric iron, as (re)generated by Fe-oxidising micro-organisms. The biokinetic test results confirmed the potentially acid generating classification of sample A as characterised by the static tests and mineralogical evaluation.

For sample B, the lack of initial changes in solution pH was indicative of the lack of fast-weathering carbonate minerals within the waste sample, consistent with the mineralogical composition (Figure 1). The subsequent absence of significant changes in solution pH with time further indicated no net acidity generation or consumption within the tests, with any acidity generated from the oxidation of the sulfide minerals neutralised by the intermediate- and slow-weathering minerals. The slight increase in solution pH was attributed to a combination of the addition of distilled water to account for the volumes lost to evaporation, and the acid consumption of the intermediate- and slow-weathering mineral phases as determined from sample mineralogy. The biokinetic test results supported a non-acid forming classification for waste sample B as opposed to the potentially acid forming classification from the acid-base accounting and mineralogical estimates.

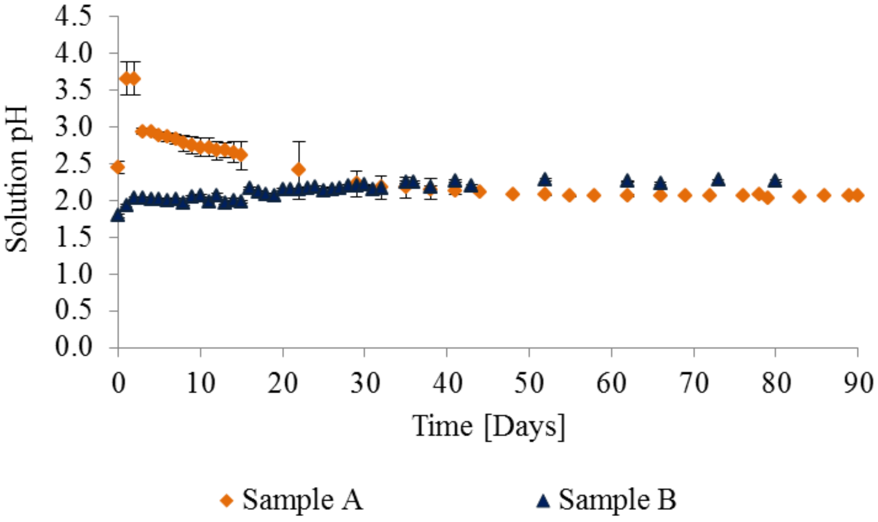

Figure 2: *pH profiles from biokinetic tests performed at 37 °C on waste samples A and B.*

Sequential chemical extraction (SCE) tests

Leachable element concentration levels and relative extents of mobilisation under the SCE tests conditions are presented in Table 3 and Figure 3 respectively. A comparison of results in Table 3 indicates that, whilst leachable concentrations of Cr and the base metals Ni and Cu are higher in sample A, sample B contains higher leachable levels of the toxic elements, Pb, U and, in particular, As. Furthermore, the relatively high mobility of elements in the leach stage 1-5 for waste sample B is indicative of the weathered nature of the sample. This is consistent with the origin of the waste, indicating previous oxidative dissolution of primary sulfide minerals such as arsenopyrite, chalcopyrite, galena, pentlandite and uraninite, and the subsequent re-precipitation of the solubilised metal ions in the form of more reactive secondary minerals and salts. The latter mineral forms are more likely to be readily available for dissolution at circa-neutral pH values and non-oxidative acid leach conditions within the waste deposit.

Although a fairly significant percentage of the As, Pb and U in Sample A is mobilised in the first 5 leach stages, indicating some weathering, leachable concentrations in these stages remain relatively low. The majority of the Cr, Cu and Ni, furthermore, was associated with the primary sulfide phase, and only mobilised under acidic, oxidative leach conditions (stage 6). This was congruent with the sample mineralogy which indicated a significant association of the Cr, Cu and Ni with primary chromite, chalcopyrite and pentlandite minerals respectively.

Table 3: *Leachable elemental concentrations from the SCE tests for sample A and Sample B showing concentrations available for deportment*

Element	Sample A [mg/kg]				Sample B [mg/kg]			
	Stages 1-3	Stages 4-5	Stage 6	Total (Stages 1-6)	Stages 1-3	Stages 4-5	Stage 6	Total (Stages 1-6)
As	2.2	0.7	2.5	5.3	4.5	64.7	27.1	96.3
Cr	5.8	50.0	403	459	1.7	8.7	25.4	35.8
Cu	1.2	12.3	68.3	81.7	70.6	99.5	9.7	180
Ni	15.6	30.0	210	255	7.5	8.7	11.1	27.3
Pb	3.2	3.0	2.3	8.5	13.7	99.6	4.6	117
U	0.1	0.2	0.3	0.7	23.2	5.2	3.7	32.1

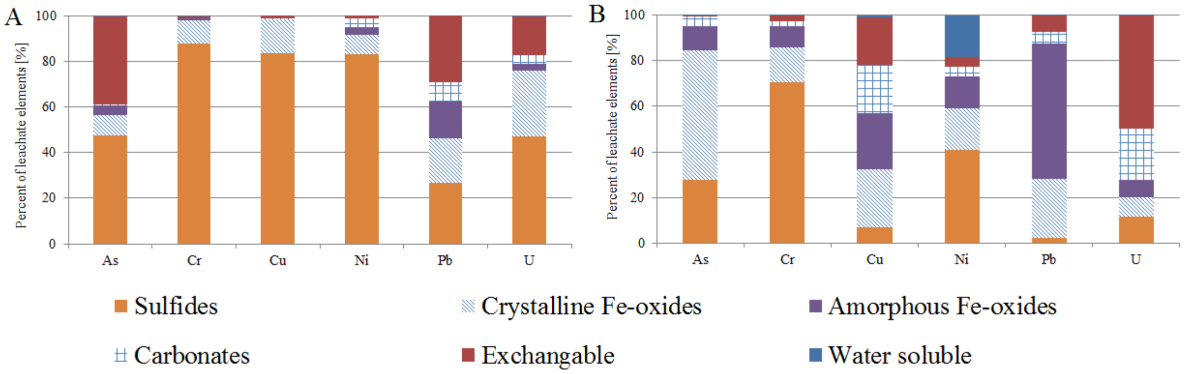

Figure 3: *Relative extents of mobilisation of leachable elements during sequential chemical extraction (where 100% represents the total leachable concentrations over the 6 stages presented)*

Environmental risk assessment

The risks associated with the elemental concentrations from the SCE tests are presented in Table 4. As a result of the relatively low concentrations of leachable elements in sample A, particularly in readily soluble forms (SCE stages 1-5), only Ni and, to a lesser extent, Cr pose a potential risk to the environment, and then only under oxidizing acid leach conditions. As indicated above, this can probably be attributed to the dissolution of primary pentlandite (Ni) and chromite (Cr) under the relatively aggressive leach conditions consistent with stage 6 of the SCE test

The relatively high concentrations of leachable elements and weathered nature of sample B, however, resulted in a significantly higher environmental risk profile, even under relatively mild leach conditions. In particular, a significant environmental risk was associated with the deportment and potential release of As, U and Pb. The relatively high levels of leachable Pb, As and, in particular, U in the water-soluble and carbonates fractions (Table 3 and Figure 3) indicates, furthermore, that this sample may pose a risk to the environment even under circa-neutral and weakly acidic pH conditions. Exposure of the sample to more acidic waters is likely to result in further dissolution of As and Pb at environmentally significant levels, whilst conditions conducive to oxidative dissolution of sulfide minerals may pose an additional risk due to further release of high levels of soluble As.

Table 4: *Environment risk assessment of elemental deportment measurements from SCE tests on wastes samples A and B*

Environmental Significance	Risk factor	Sample A			Sample B		
		Stages 1 - 3	Stages 4-5	Stage 6	Stages 1 - 3	Stages 4-5	Stage 6
High	> 10			Ni	U	As, Pb	As
Moderate	1–10			Cr	As, Pb		
Low	1	Ni	Ni	As		U	Pb, U

Concluding Remarks

The current study highlights the use of a combination of mineralogy, geochemical and chemical leach tests, together with a simple environmental risk assessment method to provide a rapid characterisation of the acid-generating potentials and trace metal deportment risks associated with sulfide-bearing wastes. The integration of the results allowed for an understanding of the minerals responsible for the acid-generating behavior of the waste samples, and the conditions under which the elemental deportment is likely to occur. This information is key in providing guidance for more detailed risk assessment procedures, and to inform relevant risk mitigation strategies.

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Bioleaching of indium-bearing sphalerite under underground mining temperatures

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Extended Abstract

During the process of industrialization, the world-wide demand for resources steadily increases. Significant amounts of crucial metals and metalloids remain in low grade mineral deposits, however using conventional metal extraction methods on these minerals is not environmentally feasible. Minimization the pollution of water, soil and air, caused by conventional mining methods, can be achieved by alternative techniques such as biohydrometallurgy, namely bioleaching. This technique utilizes the activity of iron-oxidizing bacteria to catalyze the dissolution of sulfide minerals, in our case local sphalerite (ZnS) with traces of indium. Microbial metal extraction, especially from low-grade ores, is considered to be more eco-friendly and feasible compared to conventional methods like smelting.

Sulfide ores often contain sphalerite, pyrite or other compounds with complex matrices and mineralogical properties. There are studies reporting successful bioleaching of zinc sulfide in columns or in shake flasks [1,2]. Since different experimental conditions and specimens of ore material have been used in our experiments, the results vary to aforementioned studies. The aim of our project is an *in-situ* leaching site directly in the local mine *Reiche Zeche,* Freiberg.

Realization will facing us with several problems, first working under lower temperatures between 10 and 12°C and second dealing with indigenous microorganisms located in the mining field. This work revealed some preliminary results for leaching zinc and indium under mining conditions and will be fundamental for further approaches.

Commonly acidophilic mesophilic bacteria like *Acidithiobacillus ferrooxidans*, *At. thiooxidans* [3] and *Leptospirillum ferrooxidans* are applied for bioleaching. These iron- and/or sulfur-oxidizing bacteria grow optimally at low pH-values and temperatures around 30°C [4]. *At. ferrooxidans* and *L. ferrooxidans* derive their energy from oxidation of ferrous iron, *At. thiooxidans* and *At. ferrooxidans* are also able to oxidize reduced sulfur compounds like sulfides and elemental sulfur [5]. For the bioleaching of minerals with high concentrations of heavy metals such as copper, zinc, uranium, lead, silver, and gold, *At. ferrooxidans* was successfully used [6,7]. Most of these leaching applications were performed between 30°C and 60°C, e.g. tank or heap leaching. On the one hand the processes are much more effective at higher temperature, and second, the heat is often produced endogenously.

In contrast, our aim will be an *in-situ* leaching application directly in an underground mine site of mine *Reiche Zeche*, where the prevalent temperature is between 10 and 12°C, constantly. Hence, in this work leaching applications were performed at 11°C. Furthermore we didn´t performed our tests with pure cultures, but with mixed cultures originating directly from mine-waters at temperatures of about 11°C.

This gives a competitive edge, to work with indigenous microorganisms, which are adapted to low temperatures and show higher resistances against heavy-meals located in ore-material of this mining site. The objective of the work presented here was to establish the bioleaching of indium and zinc from sphalerite ore und low-temperature-conditions with bacteria enriched from mining effected sites, and to identify the naturally occurring bacterial community in these applications.

In the case of leaching, the main interesting fact is the extraction of important metals from ore-material. We focused on zinc and the socialiced strategic element indium. In this work we compared the results for leaching process at pH 2.6 and pH 1.6. Not only metal release was measured, also pH, ORP, iron content and biomass by cell enumeration were monitored.

The pH values of the approaches starting at pH 2.6 decreased to 2.4 for all tested cultures. In contrast, when using leaching medium with a pH of 1.6, this parameter increased up to 2.2. The redox potential was not affected by pH and increased during the time of leaching from 600 mV up to about 850 mV. In leaching solutions with pH 2.6 no ferrous iron was detectable after 12 days, whereas in approaches running at pH 1.6 it was consumed within the first 9 days. The time-dependent extractions for zinc and indium are shown in Fig. 1(a) and (b), respectively. In approaches starting at pH 2.6 the extraction of zinc from sphalerite ore proceeded nearly linear and ended up at 36 to 40%, whereas only 25 to 28% of indium were recovered. The leaching approaches at lower pH values were much more successful, since 70-77% zinc and 47-54% indium came into solution.

In previous studies, leaching tests at 30°C were performed. Here, in leaching-solutions with pH 2.6 extraction yields of 73% for zinc and 41% for indium were achieved after 34 days of leaching. At this moderate temperature, the advance of the lower pH 1.6 seems to be not that considerable, because just about 81% of zinc and 49% of indium were dissoluted from the ore material.

Next to these physico-chemical parameteres, the composition of the microbial diversity was checked, using the 16S rRNA fingerprint method T-RFLP (terminal restriction fragment length polymorphism) and 16S rRNA metagenome sequencing by Illumina. The evaluation of the results is still in progress.

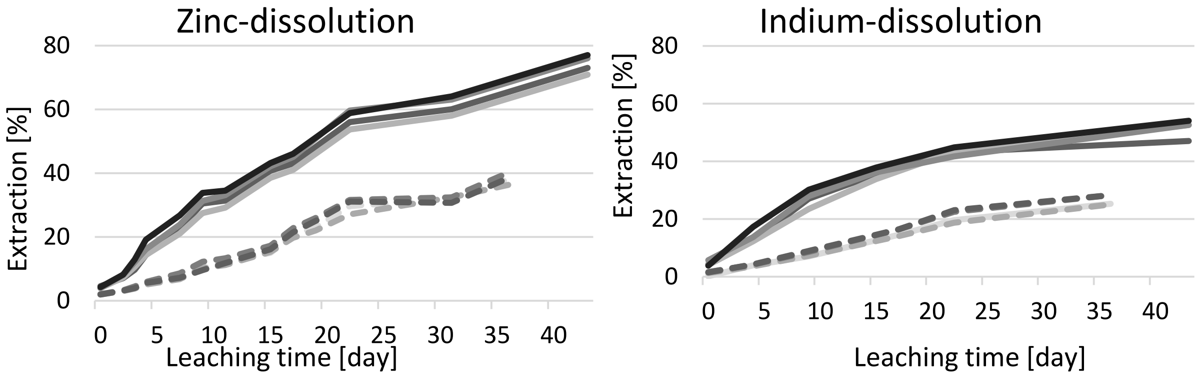

Figure 1: *Dissolution of zinc (a) and indium (b) against time of leaching. The continouus lines show results for applications with start pH 1.6 and dotted lines for start pH 2.6.*

In this work leaching applications in shaking flasks were performed at low temperatures. Thereby it was shown, that bioleaching at 11°C depends considerable on pH and results in higher metal dissolution, if pH of leaching solution is lower. This observation is very important for later applications inside of the mining field, where the temperature is as aforementioned low. Hence leaching should be as efficient as possible. The comparison to leaching approaches at 30°C points out, that the influence of pH under cold conditions is much higher compared to higher temperatures used in heap-leaching for example. Hence, for *in-situ* mining site in the underground the parameter pH becomes very important for successful leaching application.

Key words: IMWA 2016, full paper, writing, tables, figures, reference

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Acid Mine Water Treatment Using Novel Acidophilic Iron-Oxidizing Bacteria of the Genus “*Ferrovum*”: Effect of Oxygen and Carbon Dioxide on Survival

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Abstract

Acid mine waters are characterized by low pH and high loads of iron and sulfate, resulting from the oxidative dissolution of sulfide minerals due to the mining activities. Owing to the effect of these contaminations on the environment, mine waters have to be treated before discharging into the rivers. At the open-cast pit Nochten (Germany) acid mine waters were remediated biotechnologically in a pilot plant by immobilization of ferrous iron resulting from microbial iron oxidation with subsequent precipitation of the iron-oxyhydroxysulfate schwertmannite. The microbial community was dominated by “*Ferrovum*”, which is an acidophilic autotrophic iron-oxidizing bacterium and was not yet been validly described. Since the sub-cultivation of enrichment cultures containing “*Ferrovum*” encountered difficulties and resulted in loss of strains, oxidative stress was considered to be a possible reason for this. Therefore, the culture JA12 containing “*Ferrovum*” and *Acidiphilium* was incubated under different oxygen and carbon dioxide concentrations, as well as under anaerobic conditions. Compared to atmospheric conditions, microaerobic conditions enhanced bacterial survival. Incubation of the culture under increased carbon dioxide and decreased oxygen content affected the bacterial survival positively, while the incubation under anaerobic conditions was not favorable. Information about the novel genus *“Ferrovum”* regarding physiological characteristics will facilitate the handling of the bacteria. The knowledge about optimal storage conditions may make it more simple to provide active cultures for use in mine-water treatment.

Key words: Mine water treatment, acidophilic iron-oxidizing bacteria, *Ferrovum* spp, survival, microaerobic

Introduction

In active and abandoned mining sites sulfide mineral ores are exposed to oxygen and water resulting in effluents characterized by low pH and high loads of heavy metals, especially iron, and sulfate. These acidic mine waters have to be remediated before discharging into rivers to reduce the impact on the environment. The treatment of the waters can occur conventionally by neutralization with subsequent chemical iron oxidation or alternatively by biotechnological processes.

At the open-cast pit Nochten (Lusatia, Germany) mine waters were biotechnologically treated in a pilot plant. Ferrous iron was immobilized by microbial iron oxidation with subsequent precipitation of the iron-oxyhydroxysulfate schwertmannite. Molecular genetic studies of the microorganisms occurring in the mine water treatment pilot plant revealed the dominance of betaproteobacteria of the genus “*Ferrovum*” (Heinzel et al., 2009).

The novel genus “*Ferrovum*” has been detected in several acid mine waters using culture-independent methods (Hallberg et al., 2006; Hao et al., 2010; Kimura et al., 2011). Cultivation attempts of this genus resulted in one isolate (Johnson et al., 2014) and in several cultures containing “*Ferrovum*” and *Acidiphilium* or *Acidithiobacillus* (Tischler et al., 2013). The isolate “*F. myxofaciens*” P3G has been described as an acidophilic, psychrotolerant obligate autotrophic bacterium, which uses ferrous iron as electron donor and oxygen as electron acceptor (Johnson et al., 2014).

Since ferrous iron seems to be the sole energy source of the genus "*Ferrovum*" it is assumed that oxidative stress is increased for the bacterial cell (Ferrer et al., 2016). Due to the presence of ferrous iron and oxygen, reactive oxygen species (ROS), including hydrogen peroxide, superoxide radicals, and hydroxyl radicals, are formed in the cells via the Fenton and Haber-Weiss reactions. ROS damage most cellular component like DNA, RNA, and proteins (Cabiscol et al., 2000).

The long-term storage of "*Ferrovum*" spp. proved to be difficult. The storage as cryo culture, a common method in microbiology, failed (Johnson et al., 2014) . Due to the increased oxidative stress level for acidophilic iron-oxidizing bacteria under atmospheric conditions, it was hypothesized that reduced oxygen concentrations may reduce the stress level. Simultaneously elevated carbon dioxide concentrations may increase the microbial growth, since carbon dioxide, the carbon source of "*Ferrovum*" spp., is only poorly soluble in acidic aqueous solution. Therefore, a culture containing "*Ferrovum*" and *Acidiphilium* was cultivated under different gas phases containing reduced oxygen and increased carbon dioxide levels.

Material and Methods

Culture JA12

Culture JA12 was obtained from mine waters of a treatment pilot plant at the open cast pit Nochten in Lusatia (Saxony, Germany) (Tischler et al. 2013). Analysis using terminal restriction length polymorphism (T-RFLP) revealed the presence of "*Ferrovum*" sp. and *Acidiphilium* sp. in the culture. The bacteria in the culture have recently been genome sequenced (Ullrich et al., 2015; Ullrich et al., 2016). To maintain the culture JA12 it was incubated at room temperature in artificial pilot plant water (APPW, pH 3.0) containing 5 mM ferrous iron and was transferred periodically into fresh medium (Tischler et al., 2013).

Incubation under different gas phases

After the iron concentration, which was determined with the ferrozine method (Lovley & Philips, 1986), had reached approximately 2 mM, 50 µl of the culture JA12 were plated on overlay plates (Johnson et al., 1991; Tischler et al., 2013). After visible growth had occurred, the various overlay plates were incubated at room temperature under different gas phases. Gas phases chosen were (i) atmospheric conditions (21% O_2, 0.05% CO_2), (ii) anaerobic conditions (0% O_2, 0% CO_2), (iii) microaerobic conditions containing 1% O_2, 1% CO_2 (gas mixture provided by PRAXAIR), and (iv) 2% O_2, 5% CO_2 (adjusted by mass-flow regulators). 16 equal-sized small colonies were picked every week and streaked out on new overlay plates. Afterwards the plates were incubated under atmospheric conditions at room temperature. After about 10 days growth of colonies was evaluated to verify the survival under the various gas phases.

Result and Discussion

Members of the genus "*Ferrovum*" have previously been shown to be difficult to sub cultivate for long periods and some strains have been lost (Johnson et al., 2014; Ullrich et al., 2016). Acidophilic bacteria in general face the problem that after use of the substrate and stop of respiration the proton gradient across the membrane is endangered by high external bacterial proton concentrations. Autotrophic acidophilic iron oxidizers in addition face the problem that on the one hand little energy is available from the oxidation of iron, but that on the other hand a lot of energy is needed to reduce CO_2 to generate biomass. In this paper we consider oxidative stress generated by reactive oxygen species as another reason for poor culturability of "*Ferrovum*".

From the plates containing JA12 under different atmospheric conditions every week material from 16 previously untouched colonies was streaked out on new plates. The new plates were incubated under normal aerobic condition for ca. 10 days. Then it was recorded in how many cases of the 16 tests growth on the new plates had occurred. Growth on the new plates showed that at least some cells had survived on the original plates under the respective atmospheric conditions, while absence of growth suggested that many cells had lost the ability to divide (and therefore were considered "dead"). Thus, from the growth or the lack of growth on the new plates a "survival ratio" was determined for each atmospheric condition and each incubation period of the original plates (data between 16/16=1 and 0/16=0).

It was observed that especially under anaerobic conditions "*Ferrovum" sp.* JA12 lost its ability to divide pretty fast i.e. with 4 weeks (Fig. 1). For the colonies incubated under normal aerobic conditions, in contrast, it took about 9 weeks until none of the restreaked colonies resulted in any growth. In colonies kept under 1% O_2, 1% CO_2 or 2% O_2, 5% CO_2 at least some cells could survive until the 11th or 12th week (Fig. 1) and thus survived two or three weeks longer than those under normal atmospheric oxygen concentration (21%). By repeating the experiment six times basically similar results as those shown in Fig. 1 were obtained. Thus, microaerobic condition and/or increased CO_2 concentration seems to be favorable for strain JA12. However, it still needs to be elucidated which effect (decreased O_2 or elevated CO_2) is responsible for the longer survival.

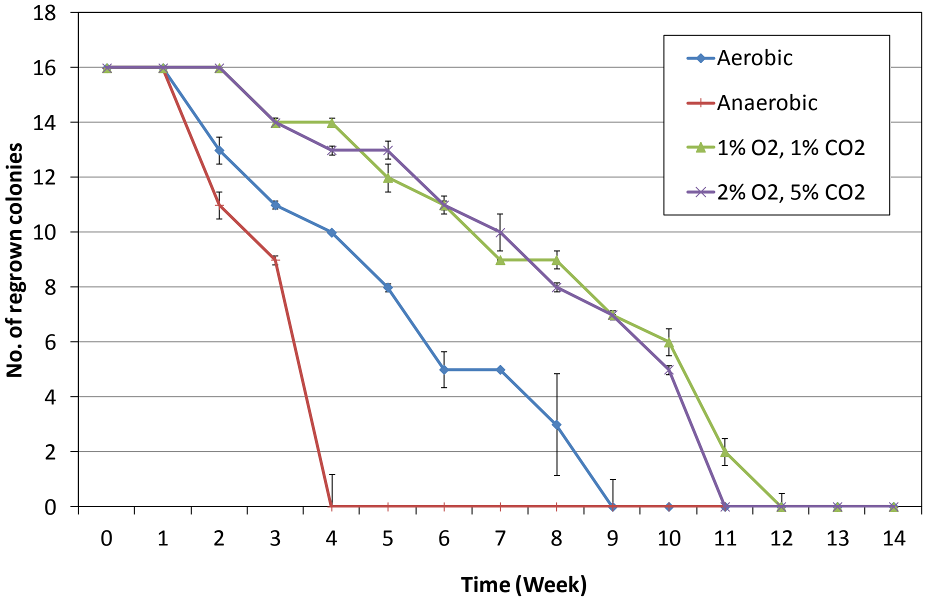

Figure 1 *Effect of different gas phases on the survival of the ''Ferrovum''-containing culture JA12.*

Plates with *Ferrovum* sp. JA12 were incubated under various gas conditions. After the respective time, material from colonies was streaked out on new plates and the number of plates which showed growth was assessed after few weeks.

Conclusions

The experiment described here shows that the survival of "*Ferrovum*" *sp.* JA12 on plates strongly depends on the gas atmosphere. Microaerobic conditions or increased CO_2 concentration seem to have a favorable effect on survival. Accordingly, future studies will be focused on more details on the individual effect of O_2 or CO_2 each in separate experiments.

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Environmental parameters as drivers of bacterial communities responsible for arsenic removal from acid mine drainage

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Extended Abstract

Arsenic (As) is one of the most toxic pollutants commonly associated with mine tailings and Acid Mine Drainage (AMD), with concentration ranging from < 1 µg.L^{-1} to hundred mg.L^{-1} in mine water [1]. Considering the toxicological effects of Arsenic on organisms, it is essential to develop remediation strategies specifically dedicated to the treatment of As-rich AMD. In the former mine of Carnoules (Gard, France), AMD formation coincides with the creek of the Reigous stream. Natural attenuation of As occurs at this site *via* a coprecipitation with iron (III) [2,3]. This natural process, based on bacterial oxidation of iron and arsenic, represents a promising strategy for the development of biological treatment of AMD. In this context, it is necessary to better understand the influence of biological and environmental parameters on the diversity and activity of iron and arsenic oxidizing bacterial populations involved in As and Fe removal.

In the present work, we have hypothesized that the influence of environmental parameters (temperature increase and nutrient supply) will have a significant impact on the composition or activity of bacterial communities and consequently on the processes of iron and arsenic oxidation. To test this hypothesis, we conducted a batch experiment with AMD water collected at the Reigous spring. We have tested three biotic conditions: (i) incubation at 35°C corresponding to optimal temperature for arsenic oxidizing bacteria, (ii) nutrient supply (0.2 g.L^{-1} of yeast extract) used for heterotrophic growth and (ii) control conditions (20°C, which corresponded to summer field water temperature, without nutrient supplement). For each conditions tested, abiotic controls have been performed in parallel with filtered-sterilized DMA water. Dissolved As and Fe concentrations in batchs were monitored during eight days. At the end of the experiment, the speciation of As (As(III)/As(V) ratio) was determined in the precipitates that formed in the batchs and the composition of bacterial community in water was characterized by high throughput sequencing of 16S rRNA ribosomal gene.

No changes in soluble Fe and As concentrations were observed in the abiotic controls, confirming the key role of microorganisms in arsenic and iron removal. At the end of the experiment, 100% of arsenic was precipitated in the batchs heated at 35°C and in the batchs supplied with nutrients, whereas only 68% of arsenic was precipitated in the control batchs. In contrast, iron precipitation was higher in the control (96%) than in the 35°C and nutrient conditions (73% and 23%, respectively). Arsenic speciation in the precipitates also revealed differences, with higher proportion of As(V) when nutrients were added. These findings suggest that nutrient addition stimulated arsenic oxidation by heterotrophic bacteria whereas iron oxidation, mainly due to autotrophic bacteria, was inhibited. To characterize the modifications induced in the bacterial community composition by the treatments (temperature and nutrients), 16S rRNA genes were sequenced using high throupthut approach and *aioA* gene was quantified. In conclusion, our study opened new research perspectives for the development of a biological treatment process taking into account the influence of key parameters (temperature, nutrients) on the composition and activity of bacterial communities involved in iron and arsenic removal in AMD.

This work is part of the ANR project IngECOST-DMA (ANR-13-ECOT-0009).

Key words: Acid Mine Drainage, bacterial composition, iron and arsenic removal

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CHAPTER 10

Geotechnical Aspects related to Mine Water

Coupled Hydromechanical Model For Assessing Land Subsidence Due To Salt Layers Dissolution

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Abstract

Long term evolution of salt mine depends on elasto-viscoplastic behavior of the material but also on specific conditions like the intrusion of water into working areas. Such phenomenon has been observed in the Nancy Basin where brine percolates through access shafts accompanied by significant subsidence at the surface level, bringing about growing societal concerns.

In order to understand the mechanisms and kinetics of dissolution of salt inducing the phenomenon of subsidence, a numerical model is implemented. The model simulates the circulation of water between the salt layer and the impervious layer and the creation of dissolution channels. In active dissolution zones, the channel network constantly evolves: new channels appear with new dissolution zones while others collapse because of their too important dimensions.

Initial porosity and hydraulic conductivity fields, related to each other by a cubic law, are assumed to follow a Weibull distribution. From this initial state, the transient model calculates the evolution of porosity with time, taking into account Darcy's velocity as it was formulated by Yao et al. (2012). Progress in dissolution and transport gives rise to the creation of dissolution channels.

Channels mechanical behavior is investigated through geometrical evolution based on porosity threshold: when porosity exceeds a given value, the channel collapses and the salt layer thickness decreases. Influence of the cumulative salt layer dissolutions on the surface is determined by empirical propagation models.

Key words: Salt mine, Subsidence, Dissolution, Model

Introduction

Salt dissolution induced by freshwater percolation into salt formations (through natural aquifer or mine works) may lead to significant subsidence at the surface level, as it is the case in the area of Dombasle in the Nancy Basin (France). Large salt mining exploitations started there in the mid-19th century and significant subsidence has been noticed and recorded since.

In this on-going study, we aim to numerically model patterns of salt dissolution leading to slow or brutal vertical displacements, using Matlab and Comsol Multiphysics.

Nancy Basin: a 150-year old case study

Dombasle area is heavily constrained in terms of urban development because of past salt mining activities on its territory which are responsible for subsidence and structure damages.

Lorraine subsurface consists in an important Lower Keuper saliferous deposit which is approximately 200 km long, 50 km wide and 100 to 150 meters thick with a dip of a few degrees (Saunier and Courrioux 2008). Under river beds, the saliferous formation roof is only 50 meters deep. The lithostratigraphic section of the Lower Keuper formation is presented on fig. 1. The salt deposit has been industrially mined for 150 years in Nancy Basin (Art-sur-Meurthe in 1861 and Dombasle in 1877), at the confluence of Meurthe and Sânon rivers, 12 km South-East of Nancy City.

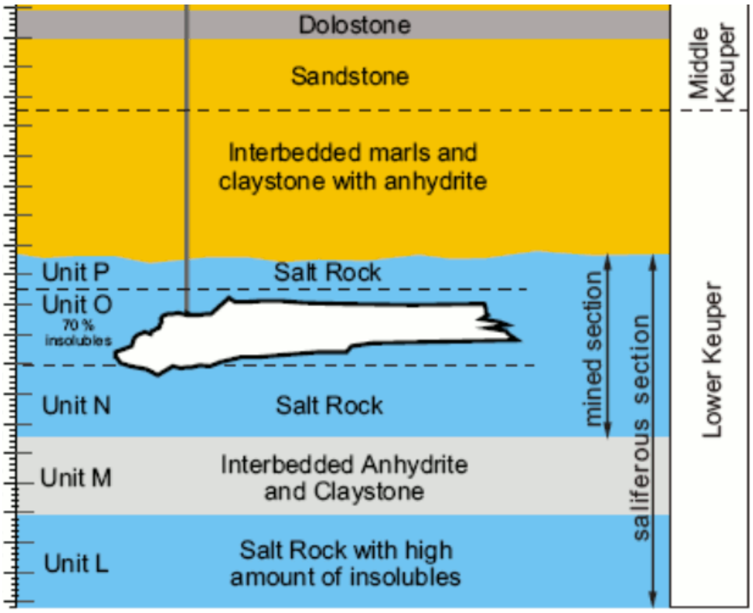


Figure 1 *Nancy Basin lithostratigraphic section.*

The mechanism of dissolution is likely related to rainwater percolation through the overburden towards the salt deposit roof. The latter is impervious to water, therefore groundwater flows towards its outlets (springs or rivers) while leaching the saliferous layers top (fig. 2). It is estimated that 30,000 tons of salt are rejected in the surface water system each year (Lebon 1987).

This mechanism existed prior to mining operations and explains the presence of Dombasle saline aquifer which is actually a network of anastomotic dissolution channels, separated by contact zones between the saliferous deposit and its overburden. During mining activities, the equilibrium of the system has been probably disturbed, allowing the reactivation or the acceleration of the dissolution processes.

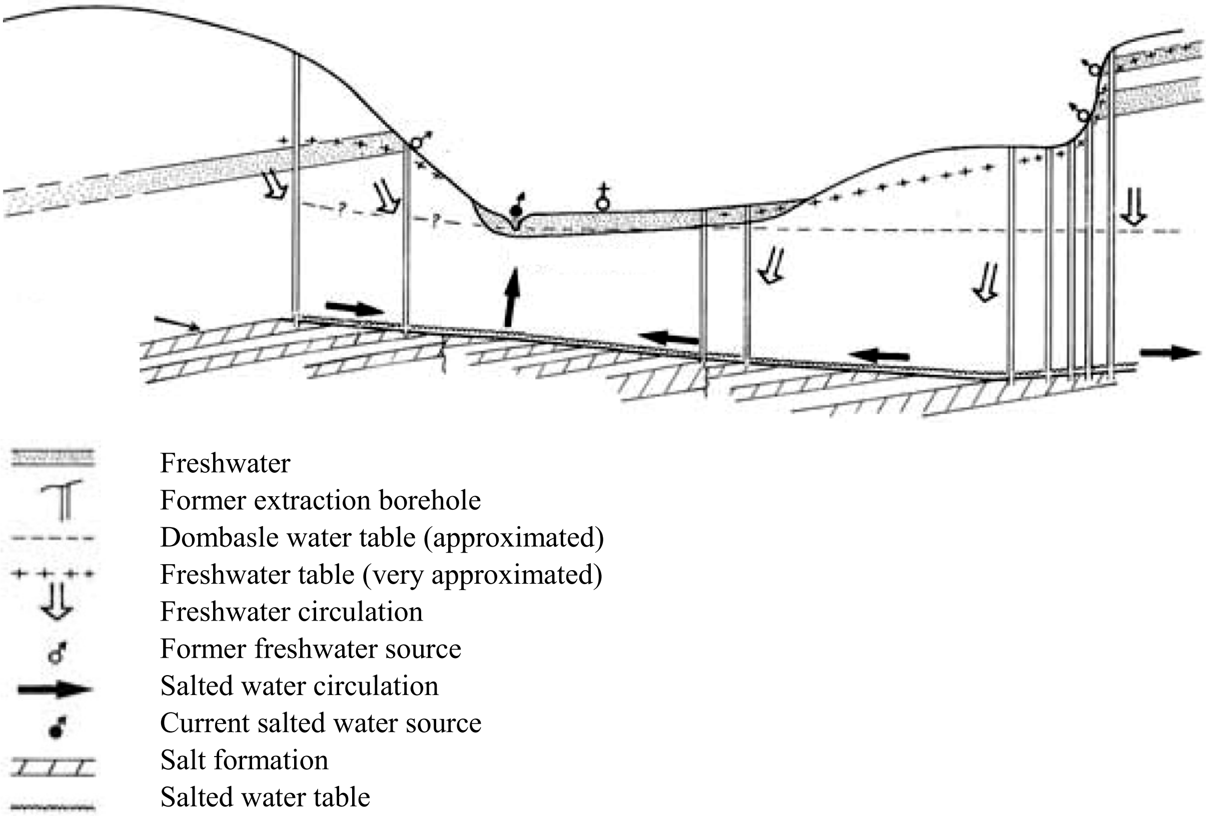
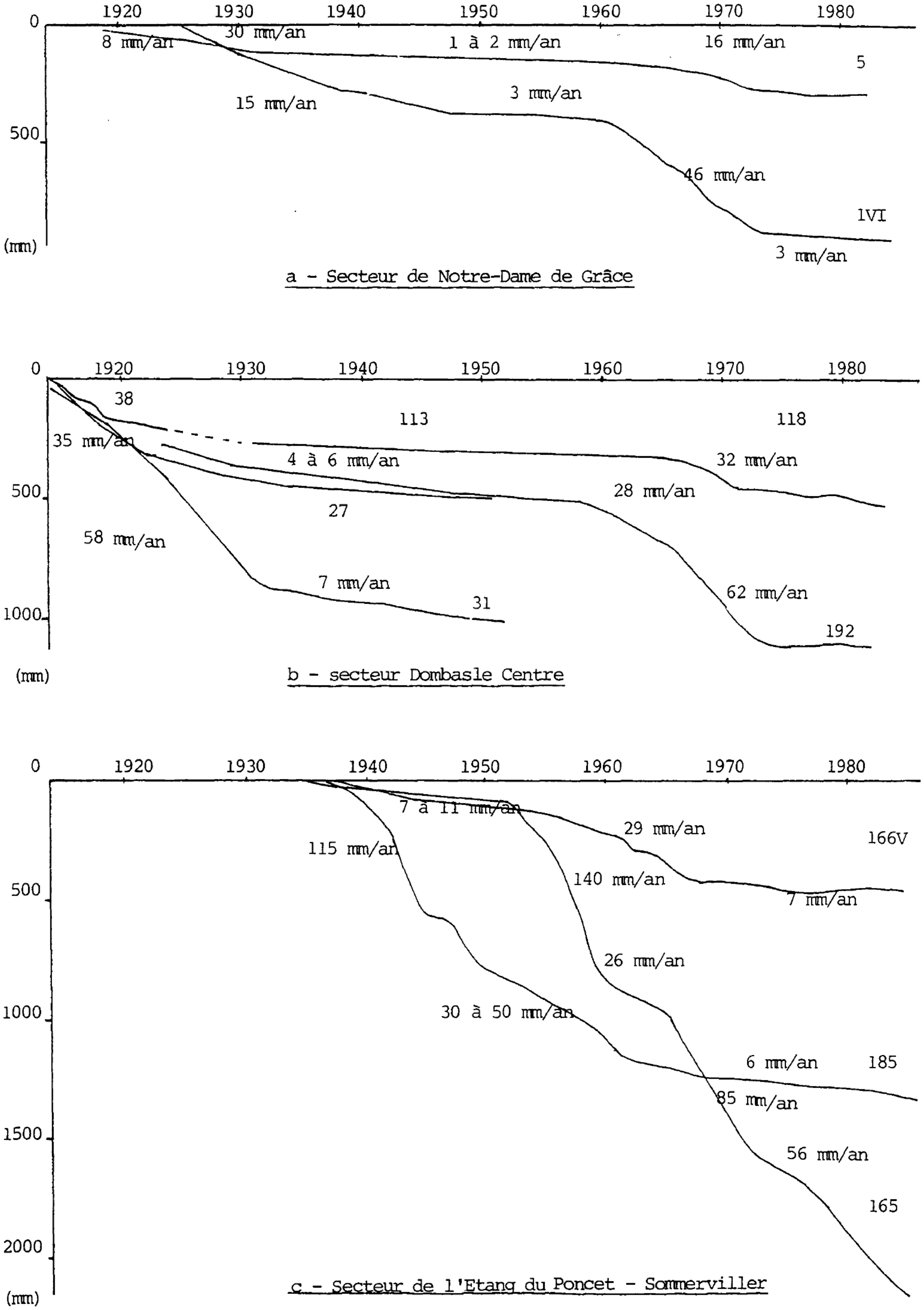


Figure 2 *Dombasle saline aquifer circulations.*

Salt dissolution creates voids which lead to subsidence at the surface. Due to social constraints, the region has been the object of regular and diverse monitoring for a century.


a - Secteur de Notre-Dame de Grâce

b - secteur Dombasle Centre

c - Secteur de l'Etang du Poncet - Sommerviller

Figure 3 Subsidence monitoring since 1914 in Dombasle area.

Subsidence rates have been measured between 30 and 60 mm/year during active dissolution periods (fig. 3), it can reach 140 mm/year in particular sectors. During low dissolution period, the subsidence rate is around 5 mm/year. It has been shown that active/low dissolution periods are correlated to rainfall cycles. Cumulated subsidence after 70 years (fig. 3) is approximately one meter on several sectors and has exceeded two meters on particular points.

Dissolved salt thickness can be locally very important. The intensity of dissolution occurring at the contact between salt deposit and overburden varies according to the location: dissolution is very active where a rich layer is in contact with groundwater.

In active dissolution zones, the channel network constantly evolves: new channels appear with new dissolution zones while others collapse because of their too important dimensions. Several boreholes have been drilled to observe the structure of the dissolution channels: they do not exceed 20 cm in thickness.

In situ experimentations show that this groundwater system presents a high transmissivity. Isotopic dating of groundwater shows that these saline waters are “young”: 1 to 4 years old. They come from natural infiltration of rainwater which percolates later through mineshafts.

Salt channel modelling

Initial porosity field is assumed to follow a Weibull distribution (eq. 1) to take into account the heterogeneity of the salt layer. A random correlated porosity field is initially set in the domain, using the following values of Weibull distribution parameters: $\lambda = 0.15$ (scale factor) and $k = 5$ (shape factor). Initial porosity values (fig. 4a) range from 3% to 25%.

$$f(x) = \left[\frac{k}{\lambda}\left(\frac{x}{\lambda}\right)^{k-1} e^{-\left(\frac{x}{\lambda}\right)^{k}} \; if\; x \geq 0 \atop 0\; if\; x < 0\right. \qquad (1)$$

Porosity (ϕ) and hydraulic conductivity (k) fields are related to each other by a cubic law (eq. 2).

$$k = k_0\left(\frac{\phi}{\Phi_0}\right)^3 \qquad (2)$$

In a regular cartesian mesh, Darcy’s law and an Ordinary Differential Equation (ODE) linking porosity and flow, as it was formulated by Yao et al. (2012), are solved with Comsol Multiphysics (ϕ: porosity; c: salt concentration; v: Darcy’s velocity; K: coefficient). The transient model calculates the evolution of porosity with time, simulating dissolution and transport, giving rise to the creation of dissolution channels (fig. 4b).

$$\frac{\partial \phi}{\partial t} = K(1-\phi)c\|\vec{v}\| \qquad (3)$$

This is a simplification of the geochemical phenomena which occur and which could require more comprehensive (but also time-consuming) investigations by reactive transport modelling means (e.g. with codes such as Phast, Toughreact, Crunch, etc.)

Vertical displacements and collapses

Several mechanisms of vertical displacements occur in the Dombasle area, the prominent one being slow subsidence. We also observe sudden collapse, piping or chimneying. For now in this study, we primarily focus on slow subsidence.

Considering that geochemistry and geomechanics coupling is a highly delicate field of investigation (Liu et al. 2009 and Malvoisin et al. 2015), we make strong assumptions and take a straightforward empirical approach based on porosity and geometry evolution.

Model geometry is regularly updated with Matlab, according to porosity and pressure conditions, in order to simulate fast collapses within the salt formation (fig. 5). Poroelastic strains are considered small and slow compared to collapse mechanisms.

Influence on the surface is determined by propagation empirical models (fig. 6). The conical effect (influence and rupture angles) is expected to be not significant as the salt formation is relatively shallow and topped with significant amounts of clay.

The results of these investigations seem to be consistent with the in situ measurements, notably with the estimation of the subsidence rate, once determined the right parameters values.

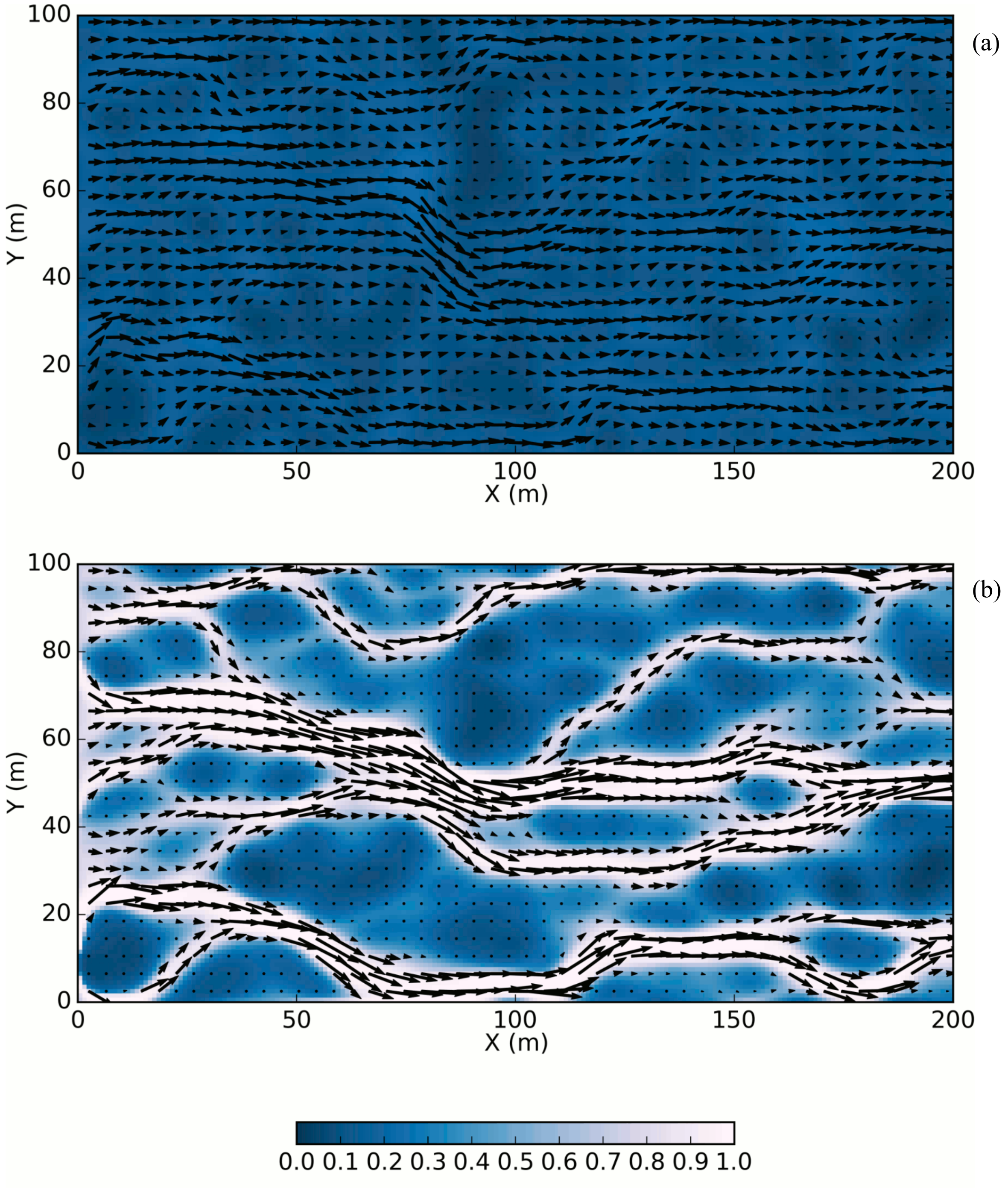


Figure 4 *Example of channels formation modelling in a 2D XY (200 x 100 m) Cartesian mesh (1 m discretization). c is taken approximately constant at salt saturation concentration such as K*c = 0.001. Initial Weibull distribution convoluted with a 5 m radius Gaussian filter. Porosity fields (range from 0% to 100%, color scale dark blue to white) and Darcy's velocity fields (arrows) for T = 0 year (a) and T = 40 years (b). Computed norms of Darcy's velocities range from* 10^{-9} *to* 10^{-5} *m.s*$^{-1}$.

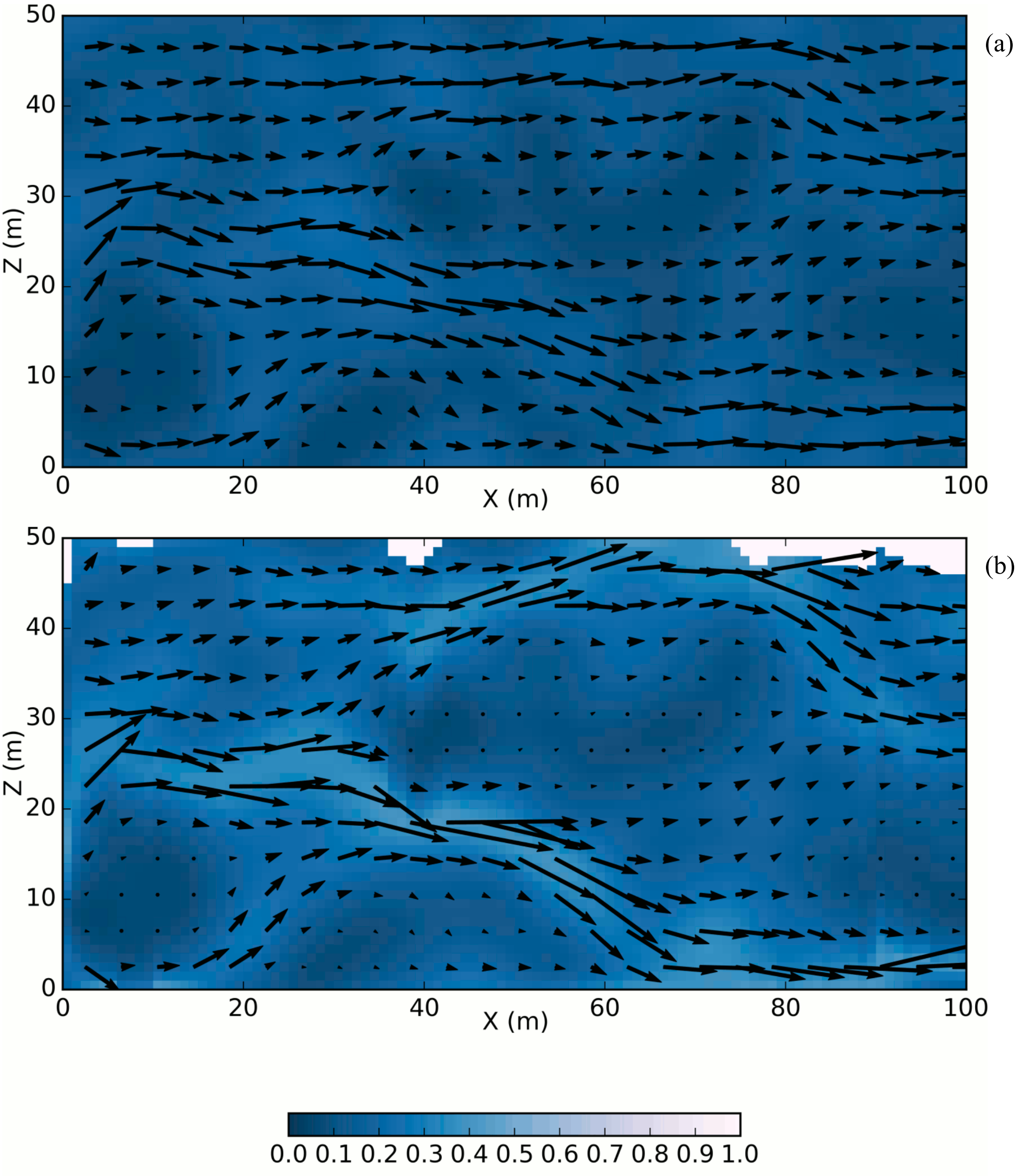


Figure 5 *Example of very fast collapse modelling in a 2D XZ (100 x 50 m) Cartesian mesh. Same flow and initial porosity settings, and same porosity scale, as in figure 4. After each transient flow calculation (0.1 year), geometry and porosity are updated by collapsing columns above a cell where porosity exceeds a threshold of* $\phi = 0.4$*. Results shown at T = 0 year (a) and T = 3 years (b).*

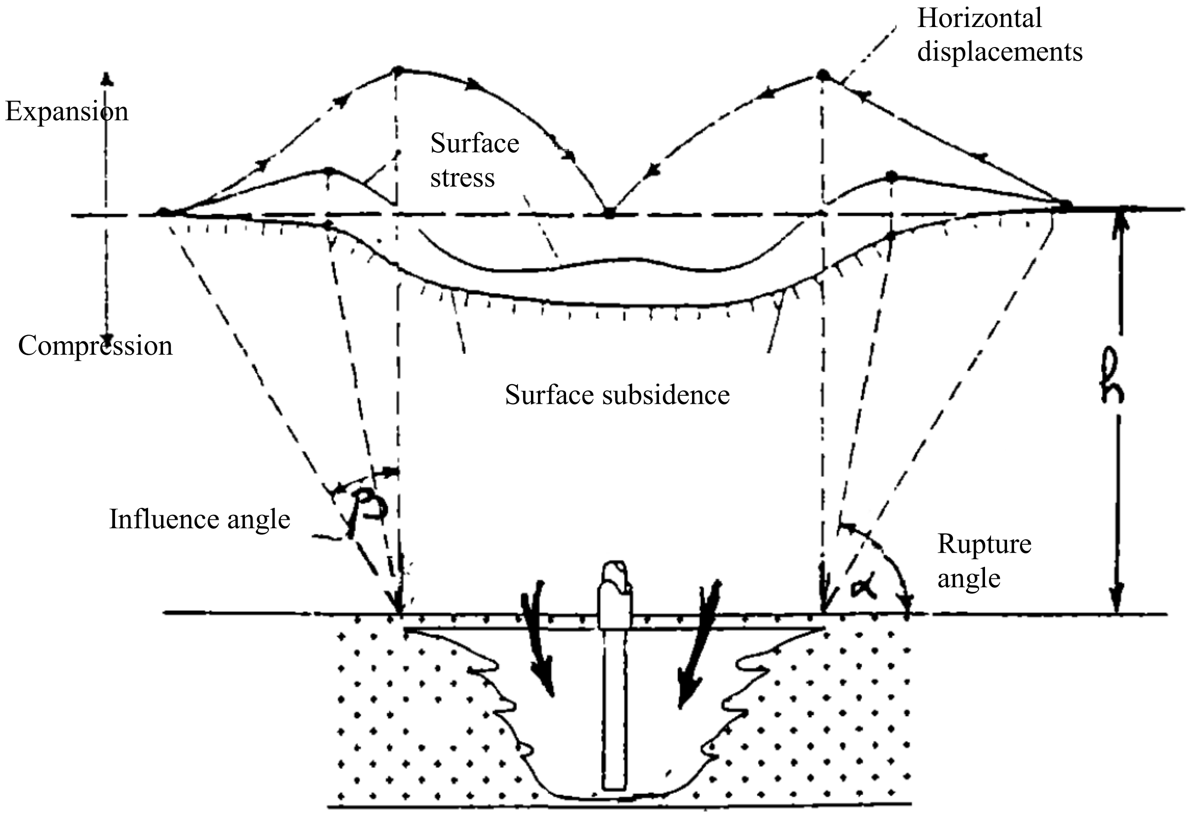


Figure 6 *Model of vertical displacements propagation inducing subsidence at the surface.*

Conclusion and prospects

The loosely coupled hydro-mechanical model currently developed in the frame of this study allows realistic simulation of creation and collapse of dissolution channels.

Once enhanced in its capabilities of modelling several collapse shapes and kinetics, and with improvements on the solute transport representation, it can potentially be a powerful tool for assessing the ground stability around a salt mine. In particular, this model can be used to describe accurately the environmental consequences of salt mine closure on land stability and groundwater quality.

Global performance of the numerical models is expected to be improved in order to refine model geometry and, in the long run, be able to do 3D modelling.

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Graphic Methods for Judging Sources of Roof Water Inrush – A Case Study, China

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Abstract

Water inrush usually is an exposure of hydrogeologic conditions of a coal mine and the characteristics of water-inrush itself could be used as indispensable evidences to quick judge the sources of water inrush. The graphic method is actually a specific application of hydrogeologic analysis. Using the limited data on an unexpected roof water inrush at Yuanbo coal mine (Shansi, China), this article developed a set of vertical and lateral graphic methods to judge the source aquifers, infer the water level of the source aquifers and analyze the reasons of roof inrush accident. It concluded that the sources of roof water inrush were the overlying fractured conglomerate aquifers and the medium-to-coarse sandstone aquifers, which got no direct recharge from the underlying Ordovician karst aquifers. It is advised that more hydrogeologic analysis expertise should be collected and published for wide dissemination, instead of learning the lessons and acquiring the expertise from accidents or hazards again and again.

Key words: roof water inrush; sources of water inrush; graphic methods

Introduction

Inevitably almost all active mines, especially those underground coal mines, always have to be facing a variety extent of threat from water inrush. Most of reported methods used for identifying the sources of water inrush belong to water quality judgement, which depend on how narrowly the quality of inrush water is similar to that of a known aquifer source. Various kinds of mathematical methods were developed over the past decades to measure the “distance” of water quality of the inrush water to the known aquifer water, for example Grey Correlation Analysis (Li 1995), Mahalanobis Discriminant Analysis (Wang 2011), Bayes Discriminant Analysis (Chen 2009), Clustering (Sun 2014), Projection Pursuit Method (Qian 2012), Particle Swarm Optimized Neural Network (Wang 2013), Support Vector Machine models (SVM) (Yan 2007), etc.

However, the inrush water itself often doesn’t show such obviously distinct chemical features at all and the difference between inrush water and the known source water are so entangled that we ourselves are not sure whether the “distance” judgement is really reliable or not. Especially for those hydrogeologically complicated coal mines in East China, the engineers and practitioners thereof always encounter various types of water inrush accidents and they can rarely count on solely using water quality judgement to figure out where the water comes out from. For these experienced engineers, traditional hydrogeologic analysis are their first priority and they always use the chemical features of inrush water to prove their judgement or search implicit clues for their first inference. Traditional hydrogeologic analysis methods play a more preliminary and essential role in engineering practice. Although there had published several collections of mine water inrush cases (Zhao 2006) in China, an issue arising from the situation is that the practical expertise and skills of these practitioners’ are seldom formally developed into systematic methodologies. To more effectively prevent mine water inrush accidents, it is important for us to share and disseminate these valuable expertise, instead of learning the lessons and acquiring the expertise from accidents or hazards again and again.

The aim of this paper is to present a very complicated roof water inrush accident and show how a hydrogeologic analytical method was developed to identify the sources of roof water inrush.

Background

The Yuanbao coal mine is located in the north of Shanxi, China and belongs to the typical semi-arid continental climate region with an annual average precipitation of 384mm and an annual average evapotranspiration of 1847.8mm. Yuanbo mine is also hydrogeologically within the west carbonate outcrop boundary of Shentou Ordovician Karst System.

Owing to being at the west edge of Datong Carboniferous-Jurassic Syncline Coalfield, the Jurassic coal seams is lapped out here. The geologic sequence of Yuanbao coal mine mainly consists of the middle Ordovician Majiagou Formation, the upper Carboniferous Benxi and Taiyuan Formations, the lower Permian Shanxi Formation, the middle Permian Shihezhi Formation, the lower Cretaceous Zuoyun Formation, and the Pleistocene non-consolidated deposits. Majiagou Formation is the base of the late Paleozoic coal bearing sequences, and the mainly minable coal seam called No. 9, with 4m in thickness and 160-300m in depth, bears in Taiyuan Formation. With a simple structure, the overall geologic formations of the coal mine strikes NE-SW and dips at 5～10° to NW. As reported by the authorized exploration company, the hydrogeologic conditions of the coal mine would be fairly simple and the estimated maximum mine drainage would be 80 m^3/h.

The Yuanbao coal mine was designed at an aim annual output of 5×10^6 t/year via longwall & top coal drawing and put into production in 2009. In the beginning year, the successful extraction of the first working face, called Face No.1901, which drained almost no water during mining, seemed to prove that the hydrogeologic conditions of Yuanbao were simple in deed.

However, since Feb., 2012 as the belt gate of Face No. 1916 was western & downwardly driven up to 480m, mine water through roof fissures infiltrated into the tunnel stronger and stronger. The parallel tail gate of the face also suffered heavy room water inrush as it drove near the open-off. By the time the belt and tail gates headed through, the maximum rate of roof water had gone up to 160 m^3/h. Two months later, the inrush stabilized around 120 m^3/h and then last for almost one and a half year until the face was mined out. Such kind of long time and large scale inrush had never happened in this semiarid region and it was against its exploration result. Don't know where the water come from and feared that a near fault, called Fault F1, had conveyed the Ordovician karst water into the roof aquifers, the Face No. 1916 was put aside for almost a whole year.

The limitations and difficulties to judge the sources of roof inrush are (1) the water quality of inrush water was so similar with that of bottom water and underlying karst water; (2) no doubtable fault encountered in two gates when driving; (3) there was no groundwater monitoring borehole and reliable water level data was unavailable; and (4) the nearby Fault F1 was also hydrogeologically unclear. The only available data was a simple inrush description.

Methods

Except for the questionable roof water inrush itself, we collected all kinds of water inrush accidents previously happened within the coal mine together, laid all of them out on the mine's excavation plane map, and drew them respectively on their own sectional maps. Thus, the bulk lateral and vertical water-bearing body were deduced. By post-interviewing the drilling workers and re-constructing a composite drilling geologic column, we further determined the water-bearing aquifers. Addtionaly, we took use of the minute water quality difference, supplementary bottom probe-drilling, etc. to examine other uncertain factor. The scheme of methodologies is as shown in Fig. 1.

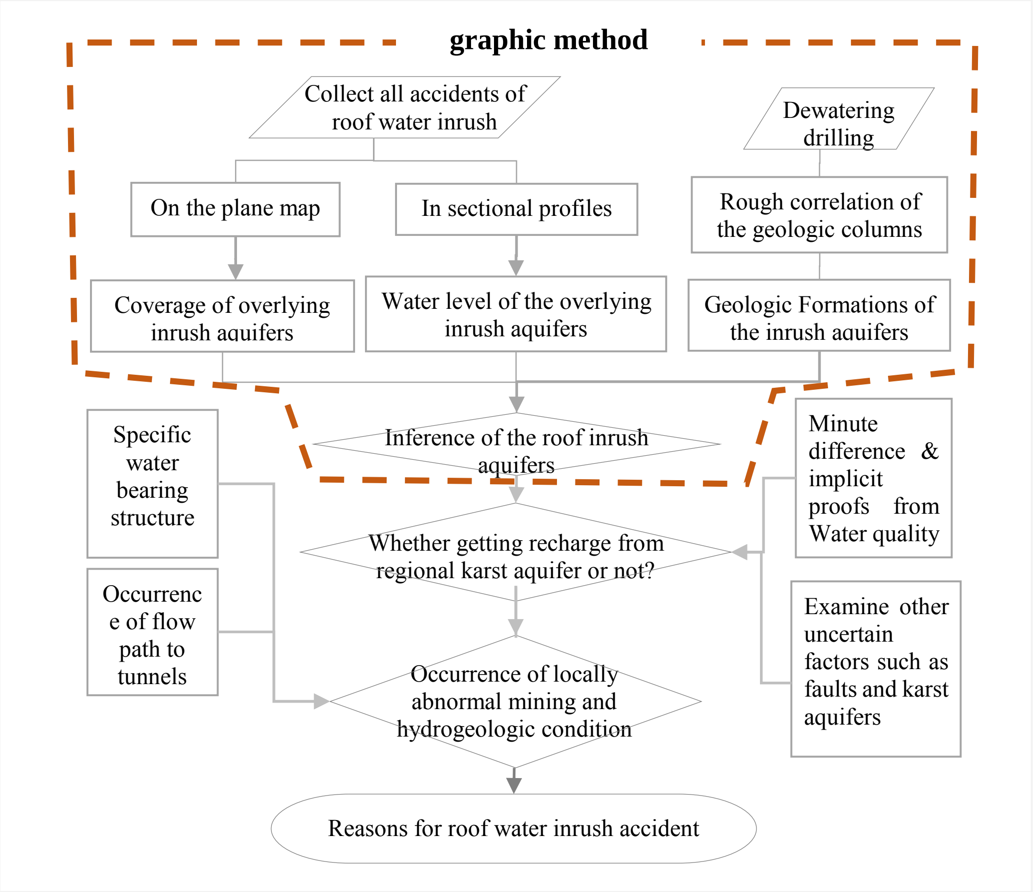

Fig1. Scheme of the graphic methodologies

Results

Totally 76 water inrush accidents were collected and laid out both on the mine's excavation plane map and on the mine's geologic map. It can be drawn that (1) 90% of accidents belong to roof water inrush, (2) the flow rate of most water inrush is less than 5 m^3/h, (3) roof water inrush accidents preferably happened near a fault or syncline, (4) the magnitude of water inrush obviously increased with the depth of the engineering and went up by 4 times up to 20 m^3/h at the bottom of the panel sub-mains, (4) the abnormal roof inrush happen at the lowest site of the coal mine (+1105m) where the Face No. 1916 just went into, and (5) the overall roof water inrush washows an obvious dewatering feature. So it can further deduce that the abnormal roof water inrush at Face No. 1916 is subject to the whole dewatering procedure of the coal mine.

From the plane map of the 76 inrush points, it can be drawn that (1) the highest boundary of water-laden area of the roof aquifers was roughly corresponding to the floor contour line of coal seam No.9 at +1170m, (2) the intensely water-laden area of the roof aquifer was limited at the NW corner of the coal mine and corresponding to the +1140 contour line of the floor, and (3) the roof water-laden aquifers had been dewatered from +1170 to +1140m.

To further infer the water level of the inrush aquifers, we overlapped the section profiles of the belt and tail gates of Face No. 1916 and that of the belt and ventilation of the panel sub-mains. The overlapped section profiles showed that (1) in the panel sub-mains, the roof water inrush initially happened at the level of +1170m and then was getting much heavier up to 8-20 m^3/h at the level of +1140m, (2) in the two gates of Face No. 1916, the roof inrush also coincidently reach its biggest value below the level of +1140m, and (3) to some degree, the Face No. 1916 actually was like a lowest discharging point for dewatering the whole mine.

At the beginning of the roof inrush accident, the mining company had tried to dewater the overlying aquifer via 53 upwardly drilled probing holes and no regular drilling notes were left. By investigating the drilling workers, we re-tracked the information on drilling fluid, water rate, etc. and re-constructed a composite drilling geologic column. By comparison with that of a nearby Borehole 1501, it can be concluded that the water-laden formations are the early Permian Shanxi Formation and medium-to-coarse sandstone aquifers of the medium Permian Shihezi Formation.

The qualities of roof water, floor water and underlying karst water are all neutral, low TDS, low Hardness and could be entitled as HCO_3-Ca、HCO_3-Ca·Mg or HCO_3-Ca·Na water. Judging from the minute difference of these water, we know that (1) the values of TDS, Na^+, Cl- and HCO_3^- of floor water are 1.5, 2, 5~10, 1.5~2 times that of roof water respectively and the values of TDS, Na^+, Ca^+ and HCO_3^- of underling karst water are 2, 2, 1.5, 1.5~2 times that of roof water respectively; (2) the water quality of roof water remained steady and had not been affected by the bottom water and the Ordovician karst water, and (3) it can exclude the possibility that the roof water had got recharge from the underlying Ordovician karst aquifer.

Conclusions

In all, it can be concluded that the roof aquifers had not got direct recharge from the underlying Ordovician karst aquifers, the roof water inrush at Face No. 1916 was subject to the whole dewatering process, and only if the drainage system and security measures be guaranteed could the Face No. 1916 be safely mine out.

From March, 2013 to Dec., 2013, the Face No. 1916 was successfully excavated. In Aug. 2014, when another Face No. 1911, which was located in the same panel as the Face No. 1916 and 200-3000m away to the Face No. 1916, drove to area below +1140m, it got roof inrush as the Face No. 1916 previously did. Both of the practice actually exposed the mine and further proved the reasonability of our method and result.

It is advised that more hydrogeologic analysis expertise be collected and published for wide dissemination, instead of learning the lessons and acquiring the expertise from accidents or hazards again and again

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Mine water outbreak and stability risks: examples and challenges from England and Wales

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Abstract

Although their frequency of occurrence is rare, the sudden outbreak of mine water from abandoned mines, or collapse of waste rock stores can be environmentally significant and represent significant post-closure legacies. This paper reports on a national survey of abandoned non-coal mine sites where concerns over mine water outbreak or stability are apparent across England and Wales. A range of respondents across environmental regulators and local authorities were consulted to populate a geodatabase. Outbreak risk was highlighted as a documented or suspected concern at 19 mine sites. Typical issues were related to adit blockages and associated perched mine water alongside issues of sudden ingress of surface waters into mines under high flow conditions. The majority of the responses concerning stability issues (72 sites in total) were related to fluvial erosion of riparian waste rock heaps. While successful management of such issues is highlighted in some cases, these are generally isolated examples. In both cases, the fact that stability or outbreak issues are often caused or exacerbated by extreme rainfall events highlights a potential future management issue with the predicted effects of climate change in north west Europe.

Key words: Mine water, outbreak, hazards, hydrology, climate change

Introduction

Hazards associated with the sudden, abrupt release of mine water and stability concerns associated with waste rock heaps are common at many abandoned mine sites. Some of the most notorious mine-related pollution events are those where sudden, catastrophic failure of mine structures or waste storage facilities have occurred (e.g. Aznalcóllar, Spain; Wheal Jane, UK: Hudson-Edwards 2016; Younger 2002) and released contaminants into surrounding water systems. Such events often prompt great media attention and require significant, ongoing management, as was typified in the case with the Wheal Jane mine water outburst in southwest England in 1996 (Younger 2002). Given both mine water outbreak and collapse of waste rock heaps can be caused, or exacerbated by multi-day rainfall events (Rico et al. 2008), their frequency of occurrence may be anticipated to increase with the predicted effects of climate change in north west Europe (Hannaford 2015). As such, information on the nature of such potential hazards and the conditions surrounding previous episodes are important for forumulating robust management strategies that can minimise future risks. Inventories of mining wastes have been collected across Europe in recent years as part of reporting requirements of the Mining Waste Directive (European Commission 2006) which should help in that regard. This paper provides a review of occurences of mine water outbreak and stability issues at abandoned non-coal mines in England and Wales.

Methods

This paper reports on part of a national non-coal mine water management initiative in England and Wales (see Mayes et al. 2009 and Jarvis and Mayes 2012 for further details). A national database of catchments affected by non-coal mine pollution, discharge composition and hazards associated with abandoned non-coal mines was collated via an online data response platform. This database was populated by regional experts in the regulatory bodies (Environment Agency, Natural Resources Wales) and local government contaminated land management teams. A total of 99 local authorities responded alongside regulators in the seven River Basin Districts of England and Wales affected by former non-coal mining (Figure 1). The responses requested from local authorities and regulators concerned two key questions: (a) were they aware of any previous or potential mine water outbreak risks in their area / region?, and (b) were they aware of previous or potential stability issues associated with abandoned non-coal mines in their area / region? Respondents were asked to populate responses for the outbreak and stability risk category for individual mine sites. A Yes-Suspected-No dropdown menu provided a simple means for data sorting (null responses are deemed to be unknown), while an adjacent open text field for each question which permitted end-users to provide technical details, case studies and / or data sources.

Results and Discussion

General response and limitations

Specific details about mine water outbreak risk were highlighted at 19 mine sites scross England and Wales while stability concerns associated with waste rock heaps and tailings were documented at over 72 sites (Figure 1). However, as with any survey exercise relying on data return from multiple respondents, the data must be viewed with a degree of caution in terms of completeness and accuracy. For example, of the 387 local authorities approached, responses were received from 99 County, District and Borough Councils, with 26 noting the presence of abandoned non-coal mines within their boundary. Additionally, some of the data show clearly erroneous patterns. For example, the Environment Agency data return for the Severn River Basin District (Welsh-England border) included a number of “Suspected” or “Yes” responses to outbreak risk, which on closer reflection appear to reflect only sites where there currently is a mine water discharge – as opposed to sites where there is a risk of a sudden outbreak. As such, all data returns were reviewed as the database developed with erroneous responses removed.

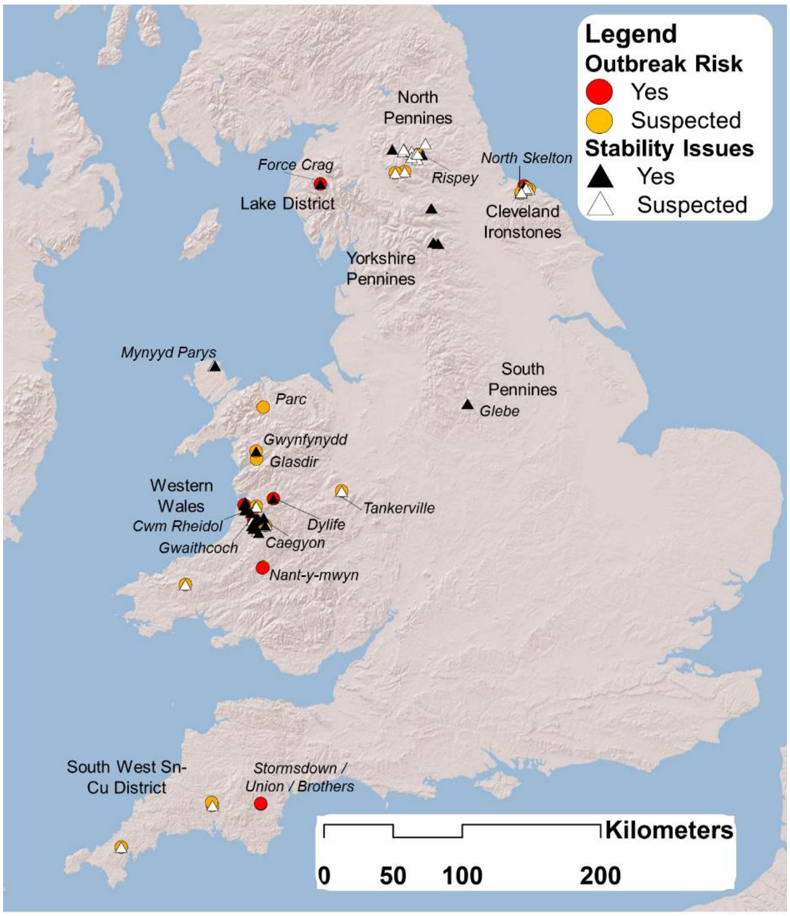

Figure 1. *Non-coal mine sites with reported risk of mine water outbreak and stability issues across England and Wales.*

Mine water outbreak risk

Table 1 summarises some of the outbreak risks identified by the respondents. Typical issues highlighted include flooded shafts with water at higher elevations than recipient water courses and drainage adits (e.g. Force Crag, Cumbria; Cwm Rheidol, Dylife, Nant y Mwyn, all Western Wales), underground blockages (e.g. Glasdir, Gwaithcoch, Parc all in Western Wales), previous history of outbreak in the area and other evidence of instability in shallow workings which could create conditions conducive to breakout. At two sites (Nant y Mwyn and Caegynon, both in Western Wales) issues of upwelling under high flow are explicitly mentioned. At sites with history of outbreak in the south-west of England, the Stormsdown, Union and Brothers mines can be viewed together as they all drain into a tributary of the River Lemon and were subject to a sudden outbreak in 2004 after a suspected mine collapse.

The Rispey site in the Rookhope Burn (northern England) is also mentioned as a site with history of outbreak. The metal mines of the North Pennines have experienced several incidences of recent mine water outbreak which usually follow extreme rainfall events. The Rispey outbreak occurred in December 2006 and was considered to be due to obstruction of the adjacent (and hitherto flowing) Tailrace Level discharge. This forced the collapse of a nearby crown hole from which the discharge newly emerged to the Rookhope Burn. Another comparable incident occurred nearby at Rookhope in April 2005. Following 98.5mm of rainfall in 48 hours (which equates roughly to a 1 in 5 year recurrence interval in that region) and subsequent increase in river flows, former mine workings under the Rookhope Burn collapsed. Large volumes of water subsequently leaked through the workings and emerged from another entry point to the mine on the Boltsburn Old West Level. Diversionary river works were necessary to limit the flow of water into the workings. These incidences are fairly typical in karstified (fissured) and heavily mined terrain such as that found in the Carboniferous limestones of the North Pennines, where workings are susceptible to rapid ingress of waters in high flow which can contribute to conditions conducive to breakout (Gozzard et al. 2011). The former include flooded shafts with water perched at higher elevations than recipient water courses and drainage adits, underground blockages, previous history of outbreak in the area and other evidence of instability in shallow workings which could create conditions conducive to breakout.

The hazards and risks associated with potential outbreak from abandoned non-coal mines depend on numerous factors including:

1. the presence of any infrastructure in the immediate vicinity of the outbreak (e.g. roads, paths, buildings)
2. the time the outbreak occurs (in terms of human activity: e.g. on roads / footpaths)
3. the volume and quality of mine water released
4. the size of the recipient water course(s) and flow rate at time of outbreak (dilution capacity)
5. the presence of potentially sensitive ecological communities in downstream surface waters.

In terms of the risk of occurrence of outbreaks in the future, it is not possible to rule out the possibility of such events occurring, particularly at those sites identified in Table 1. Those sites at which there is an observed head of water above a potential discharge point (e.g. Force Crag, Dylife) probably present the highest risk, and should therefore be priorities for intervention. Indeed, in the case of Force Crag, recent investigative works suggested relieving the mine water build-up via temporary pumping of water from the lowest mine level via a new borehole, to then allow drilling of a new replacement adit entrance which would permit long term gravity-driven drainage of the mine.

In general terms, it is however worth noting numerous factors that are likely to minimise the potential impacts of mine water outbreak at non-coal mines in England and Wales. In most cases, the mines are located in sparsely populated upland areas away from centres of population and major trunk infrastructure. In many of the upland mining settings (e.g. North Pennines, Western Wales) previous outbreaks have occurred following intense rainfall events (e.g. Rispey, Boltsburn Level in Rookhope Burn), or conditions conducive to breakout have been reported under high flow (e.g. Nant-y-Mwyn, Caegynon). As such, outbreaks have tended to occur at times when the dilution capacity of recipient streams is very high due to high flow rates, therefore limiting the measurable short-term water quality impacts. However, the long term residual pollution can be worse than pre-existing states (due to new drainage paths in hitherto dry levels flushing out contaminants) and therefore a cause for concern (e.g. Younger et al. 2002).

Table 1*: Examples of mine water outbreak risk identified across England and Wales*

Issue	Example sites
Flooded workings / perched mine water	Force Crag, Cwm Rheidol, Dylife, Nant y Mwyn
Underground blockages	Force Crag, Glasdir, Gwaithcoch, Parc
History of sudden outburst	Rispey, Belmont, Longacres/North Skelton, Stromsdown/Union/Brothers
Instability in shallow workings	Longacres/North Skelton, Boltsburn Level

Stability risks

A total of 72 mine sites returned an affirmative (’Yes‘ or ‘Suspected’) response for stability concerns. Over half of the ‘suspected’ responses did not provide any details on the nature of the stability concern. In some cases the stability concerns are repeated in the safety and even outbreak risk categories. 42% of the documented Yes responses were associated with areas of riparian spoil which are being scoured by rivers (Table 2). This is a common feature of many former metal mining areas and poses a significant risk also for diffuse contaminant input into surface waters under high flow conditions (e.g. Gozzard et al. 2011; Mighanetera et al. 2009; Byrne et al. 2012). Other stability issues are associated with instability in shallow workings (and associated surface subsidence), ingress of surface drainage channels into workings (see Outbreak Risk) and stability of spoil heaps due to steep slopes (in the absence of fluvial erosion).

The bulk of the mine sites where stability issues have been highlighted fall within the Western Wales and North Pennine orefields (Figure 1), which may be in part a feature of completeness of records in these areas. Stability issues were also noted in the South West (Wheal Andrew, Mount Wellington), Northumbria (Saltburn Gill in the Cleveland ironstone Field), Western Wales (Parys Mountain, Gwynfynydd), Severn (Tankerville) and the Lake District (Force Crag). Some issues relate to historic collapses, such as at the Glebe lead-fluorspar mine in the Southern Pennines where a bund for mine tailings was overtopped after heavy rainfall in 2007. At some of the sites significant geotechnical stabilsation works have taken place to manage the stability issues. One such example is at Nenthead in Cumbria (North Pennine Pb-Zn orefield) where rock-filled gabions and additional rock armour have been used to stabilise the river banks, and the waste heaps immediately adjacent to the river have been capped and vegetated (Figure 2). Artificial rock weirs have also been constructed, in an effort to prevent downstream transport of any contaminated sediments that do enter the river (Figure 2(A)). These works, which extend for a distance of approximately 1 – 2 km, had a reported capital cost of approximately £3 million. Although, unfortunately, no information is available about the resulting improvements in water quality, visual inspection by the authors indicate the intervention has been effective in minimising bank erosion.

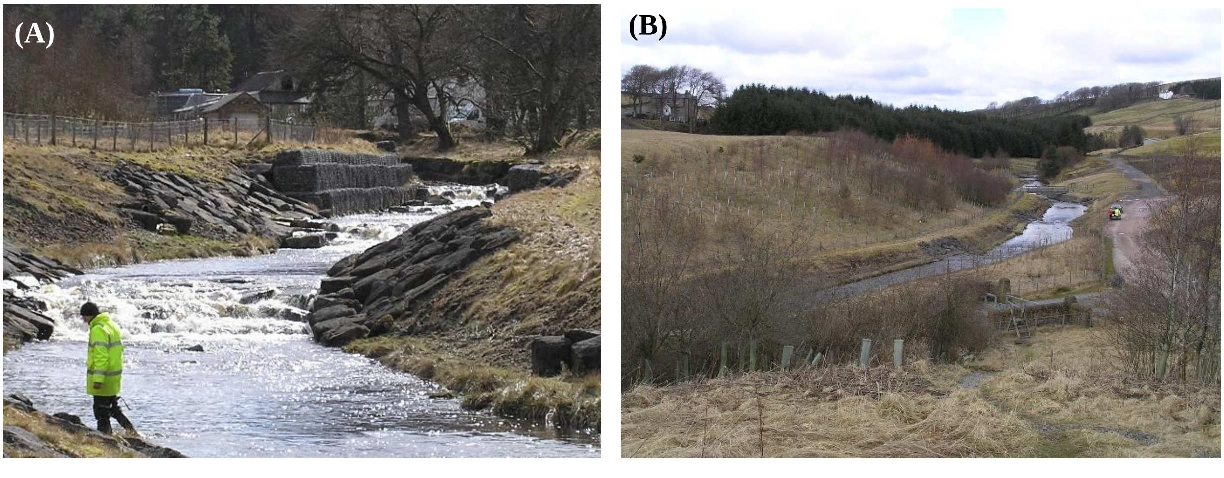

Figure 2. *Use of gabions to stabilise banks of the River Nent, Cumbria (A) and re-grading, capping and vegetation of spoil material along the same stretch of river (B)*

These documented sites represent a snapshot of known issues at a much larger number of mine sites. A recent inventory of non-coal mine-related waste rock heaps across England and Wales found a total of 91 km^2 of material based on archive map analysis (Mayes et al., 2015). Within this inventory 46% were located within 50 m of a major (i.e. first order or above) water course. The documented impacts of diffuse metal-mining pollution have long been recognised in impacting floodplain sediment quality (Lewin et al 1977; Hudson-Edwards et al. 2006) as well as water quality (e.g. Gozzard et al. 2011). There remains some uncertainty over the potential long term impacts of extreme events on waste mining rock at a catchment scale. While extreme high flows can increase delivery of metal-rich material, the balance between input of these potential contaminants and input of freshly eroded uncontaminated material however remains uncertain (NERC, 2016) and requires further attention.

***Table 2**: The number and nature of stability concerns at abandoned non-coal mine sites in England and Wales*

Response	**Yes**	**Suspected**
Total number of mine sites	26	46
No details given	1	25
Spoil heaps / tailings being scoured by river	11	9
Shaft collapse / general instability in workings / fill material	6	6
River flowing into workings	4	0
Concern over stability of tailings dams / spoil heaps	4	5
Steep terrain	0	1

Conclusions

There are a range of documented issues at abandoned non-coal mine sites in the UK surrounding potential risk of sudden mine water outbreak or risk of stability concerns. The latter are primarily related to waste rock heaps in riparian areas. However, the national survey here highlights the uncertainty and incompleteness in the records and future efforts should aim to consolidate records systematically for non-coal mines. Given the forecasted increase in incidence of extreme high flow events in many of the upland catchments of the UK where metal mining activity took place (Hannaford 2015), information about locations and types of hazard are crucial for informing management strategies. Previous outbreak events have been preceded by extreme rainfall events, while anecdotal evidence has suggested stability issues at waste rock heaps are exacerbated by high flows. The initial database collated here provides a basis for future site specific risk assessments, and where necessary, remedial works. Successful management of outbreak risk and stability concerns has occurred at a number of mine sites in the UK provides a good model for future site specific management.

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Integrated Slope Stability and Dewatering Evaluation: Optimizing Slopes to Optimize Value

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Abstract

Many mines have saprolite or laterite soils in their pit walls. These soils, like many unconsolidated or semi-consolidated deposits, are highly susceptible to changes in the moisture content. In order for an open pit mine to have an optimized economic return, the pit slopes must be as steep as possible without risk of failure. This can be done through an integrated study of the hydrogeology, pit slope dewatering, and geotechnical stability.

The Aurizona mine, owned by Luna Gold, is located in Maranhão State, Brazil. The project sits on a peninsula that extends into the Atlantic Ocean, and tidally-influenced water exists less than 5km to the east and west of the mine. The Aurizona mine produced from 2010 to 2015 and is currently in a retooling period to allow for a mine expansion and modifications in the process circuit. The Aurizona mine will exploit gold resources contained in saprolite and an underlying tonalite intrusive rock. Studies performed in 2015 revealed a strong sensitivity between the steepest allowable pit slopes and the project economics.

Global Resource Engineering (GRE) and Crux Engineering Group (CEG) conducted a study to actively optimize the saprolite slopes through an integrated hydrogeologic and geotechnical characterization and modeling effort. The program included a packer testing program to characterize the fractured rock aquifer, an aquifer testing program for the saprolite unit, and a geotechnical testing program to ascertain soil strength properties. Based on this information, groundwater flow models were created to determine not only the total dewatering requirements, but also the moisture content in the pit walls. CEG used moisture content profiles and soil testing data to optimize the pit slopes with the hard rock and the saprolite. The results of the study will be incorporated into the mine plans and upcoming revisions to a Feasibility Study.

Optimized pit wall angles are an essential element in overall project economics for the Aurizona Mine. The study reinforced the value of integrated dewatering and geotechnical studies even at early phases of project development by presenting the best possible stripping ratio (waste to ore) as early as possible in the mine development timeline.

Key words: Slope stability, groundwater modeling, saprolite

Introduction and Background

The project consists of the Main Piaba pit; smaller center and east pits, a carbon-in-leach processing plant, two tailing storage facilities, and two waste dump facilities. Figure 2 shows the future site layout in the vicinity of Piaba pit.

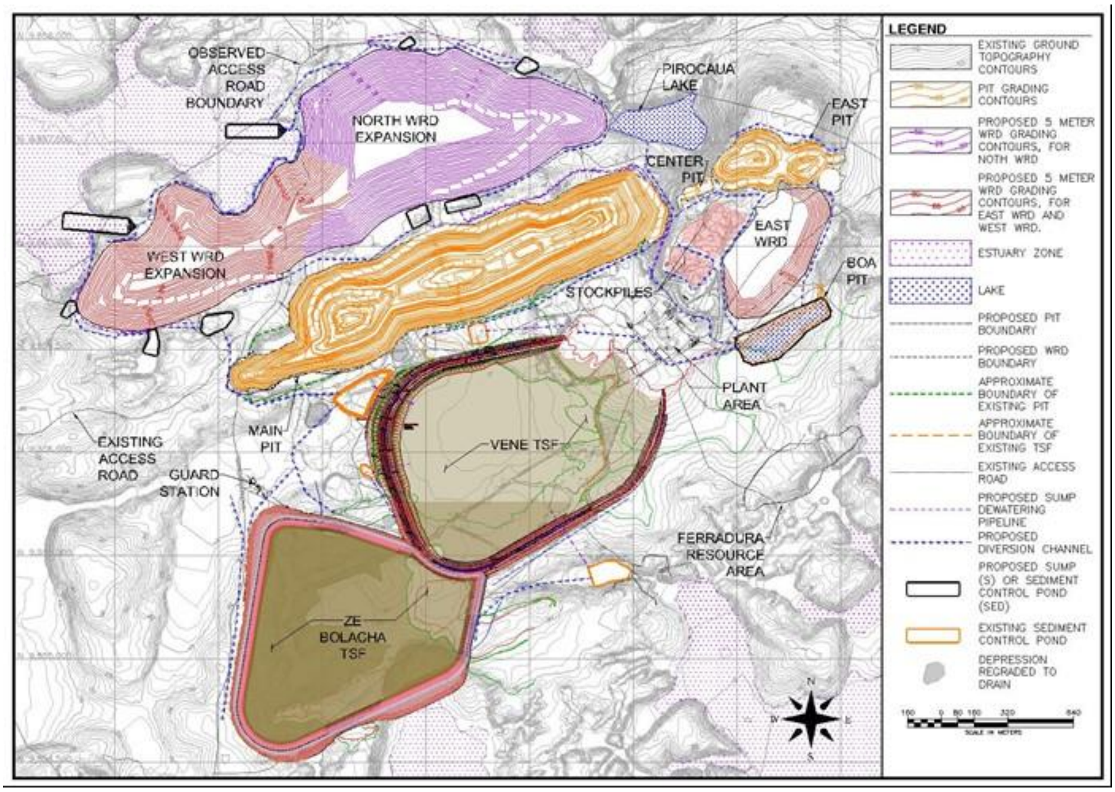

***Figure 2** Aruizona Mine Layout, With Piaba Pit.*

From 2010 to 2015, the mine exploited a laterite-saprolite hosted ore deposit and dug the Main Piaba pit down to the -17 meter (below sea level) elevation. However, in 2015 the reserves within the soft-saprolite were depleted and the mine was placed on care and maintenance pending further mine design and development to allow for exploitation of the hard-rock and transition zone hosted gold resource. The mine currently has a 6-year mine life, and plans to excavate the Piaba pit to -170 meters below sea level. The resource is open with depth and to the west, and with higher metals prices, the pit could go deeper and have a longer mine life.

Pit Geologic Model

The Piaba pit is located within the structurally-controlled epithermal greenstone belt of the Sao Luis Craton. Typical of cratons, it is comprised of meta-sedimentary rocks intruded by igneous bodies. The area is dominated by a series of first-order ENE to WSW trending shear zones with a series of second order faults and shears that are oriented SE to NW. The shear zone system provided pathways for the development of the epithermal mineralization.

The igneous rocks that host the mineralization are bounded on both sides by metasedimentary units to the north and south. Locally, the geologic units resemble ‘layercake’ type with contacts that have been set to near vertical dip. Both the mineralization and lithologic units are oriented east-northeast and southwest. Sub-parallel strike-slip faults are reported along the geologic contacts and dip sub-vertically to the north, making the southeast pit wall the footwall and the northwest pit wall the hanging wall. Figure 3 provides a conceptual geological cross section of the project. Each of the bedrock units shown on the figure are described below.

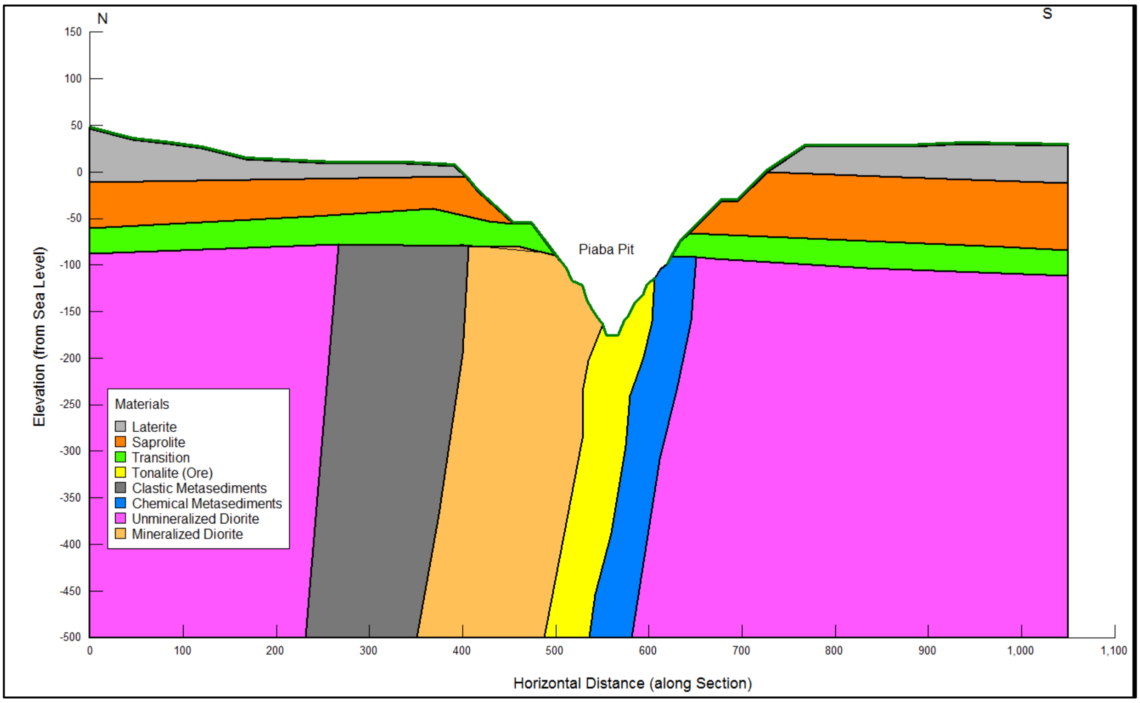

Figure 3 *Conceptual Geologic Model of the Pit Area*

Unmineralized Diorite: This unit is a quartz rich diorite rock with varying degrees of weathering.

Clastic Metasediments (Greywacke): A metasedimentary rock that is highly indurated and poorly sorted. It has been subjected to significant tectonic movements over a long period of time making it highly deformed, fractured, and/or veined.

Mineralized Diorite and Tonalite: The mineralized core is composed of diorite and tonalite. The mineralized tonalite is the ore host of the Piaba deposit. It is characterized by blue quartz and sulfides (primarily pyrite).

Chemical Metasediments (Carbonaceous Metachert): Slightly different metasediments populate the footwall. The chemical metasediments show finer grain size and less-pronounced bedding planes along thin laminations.

Saprolite and laterite: These formations overlie the hard rock formations. Saprolite is the resultant product of in-situ weathering of the parent rock and typically has material properties that improve with depth. The general texture of the saprolite is that of silty or clayey sand or clayey silt. However, the saprolite often retains some of the structures of the parent rock and may contain hard core stones of the parent material making the strength of the saprolite highly variable. Near-surface, the saprolite behaves as a soil, but improves to more rock-like behavior as the transition zone approaches.

Transitions Zone: The transition zone is a layer of mixed weathered rock and saprolite that has significantly higher hydraulic conductivity than the saprolite above or the harder rock below.

Project Challenges

The project economics are very sensitive to the slope angles within the saprolite and laterite formations while understanding the geotechnical strength properties that dictate the slope angles within these deposits is difficult. Aggressive pit slope dewatering is required to enhance the pit slope stability and resulting pit slope angles within the saprolite. This can be accomplished by draining the transition zone.

Methods

Determining the optimal saprolite slope angles involved a two-step process which included 1) determining the maximum possible dewatering achievable by reasonable methods, and 2) determining the resultant pit slopes based on the dewatering effectiveness.

Pit Dewatering

Pit dewatering will be accomplished through in-pit sumps, and horizontal borings (fan drains) drilled 100 meters out into the transition zone from a continuous bench located on top of the slightly-weathered or fresh rock. These fan drains allow for the effective and rapid dewatering of the saprolite formation beneath the pit walls.

In the field, an aquifer test program and a packer test program provided data on the conductivity of the key formations. Based on this data, the effectiveness of dewatering was ascertained with two methods; MODFLOW (Surfact) (HGL 2006) groundwater model to ascertain the regional water level and the saturated flow dynamics of the pit, and a Vadose/W (Geostudio 2012) unsaturated flow model to simulate the seasonal moisture content changes in the laterite and saprolite.

The MODFLOW model simulated the three-dimensional flow dynamics, the impact of regional faults and fractures which act as preferential flow pathways, and the spatial impact of the fan drains. It also simulated the impact pit dewatering will have on local lakes (such as Pirocaua, see Figure 2), and estuaries of the Atlantic Ocean.

However, the MODFLOW model was not sufficiently precise to simulate the impacts of seasonal rainfall on the moisture content within the saprolite and laterite in the pit walls. As a result, GRE created a Vadose/W model for the pit slopes. The Vadose/W model simulated the daily climate conditions falling on laterite and/or saprolite soils. It utilized representative soil water characteristic curve data was that taken from similar sites and applied to the model, and it used the results from the MODFLOW model to define the regional water table.

Saprolite Slope Stability

As mentioned above, the focus of the geotechnical stability study focused on saprolite and laterite slopes.

Ascertaining a Saprolite Weathering Profile

Typical bedrock weathering profiles, with associated weathering categories (ISRM, 2014) for pit slopes in saprolite are shown in Figure 4. Laterite is weathering category VI, Saprolite is IV, to V, and transition is category III

It is assumed that the shear strength of saprolite profiles increases with a decrease in weathering, and therefore, at attempt was made to identify the 'completely' and 'highly' weathered rock at Piaba Pit based on criteria by International Society of Rock Mechanics (ISRM, 2014) standards. Once subdivided, the category IV and V saprolite could be treated separately in the stability evaluations. Unfortunately, a review of the project boring logs suggested that no clear distinction is evident within the saprolite logging that would allow the subdivision of the mass into separate weathering categories. Moreover, weathering and sloughing of the saprolite exposures within the current pit prevented accurate pit wall mapping of the saprolite weathering profiles.

Figure 4 *Conceptual Geologic Model of the Pit Area*

As a result, individual saprolite soil samples collected for the laboratory testing campaign were subdivided during the sampling, testing, and test evaluation process based on weathering and ultimately, a gradational strength profile for soils was developed based on the assumption that the saprolite strength varies linearly with depth.

Relatively undisturbed samples of saprolite were collected throughout the life of the project and tested at reputable testing laboratories in Brazil. Initially, block samples were collected using a backhoe. Additional samples were collected by first excavating shallow test pits within the saprolite of the existing pit walls and then by pushing thin-walled (Shelby) tubes into the soil matrix. Representative samples from the different geological lithologies tested and the samples were distributed throughout existing pit shell.

Consolidated undrained triaxial testing (CUTX) with pore water pressure measurements were completed on all samples, and consolidation pressures were chosen based on the probable change in in-situ stresses during the pit excavation.

Results

Geotechnical Testing

Test results from these studies were grouped and reduced together for the purpose of establishing the saprolite shear strength of the different weathering categories and lithologies (Figure 5). In some cases, the individual tests were deemed invalid based on shearing along a pre-existing plane of weakness within the samples. The Figure 5 shows the p-q plots for the CUTX tests and these plots were used to establish the Mohr-Coulomb shear strength estimates shown in Table 2.

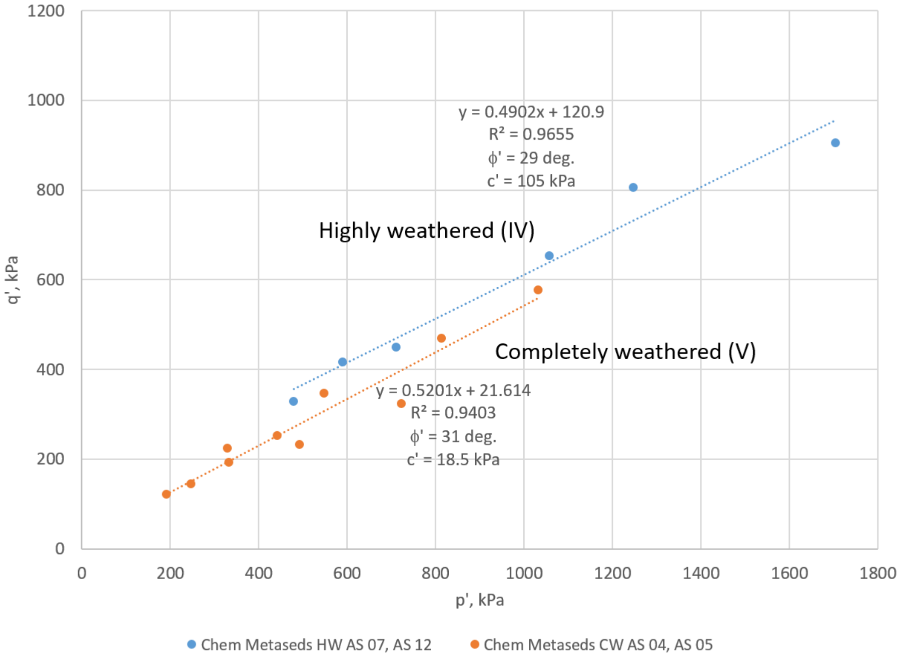

***Figure 5** Example p-q plot for the Saprolite Testing at Piaba Pit.*

Table 2 *'Drained' shear strength parameters generated by the CUTX testing*

Lithology	Weathering	ϕ', deg	c', kPa	Notes
Chemical Metasediments	Comp. Weathered	31	18.5	
	Highly Weathered	29	105	
Clastic Metasediments	Comp. Weathered	31	5	Only one valid sample for testing. Therefore, we assumed and used the strength values from the Chemical Metasediments.
	Highly Weathered	NA	NA	
Diorite	Comp. Weathered	26	27	
	Highly Weathered	33	132	
Mineralized Diorite	Comp. Weathered	32	0	These values are indicative of residual soil and not saprolite. Therefore, they were not used.
	Highly Weathered	28	81	

The testing results confirm that decreased weathering results in a constant friction angle and an increasing 'cohesion' intercept of the materials (overall; greater strength). The increase in cohesion intercept with a decrease in weathering is representative of a stiffer and less weathered soil matrix while a relatively consistent friction angle is the result of a near-constant mineralogy and grainsize of the matrix through the weathered horizon.

Field Conductivity Testing

Aquifer testing and packer testing was required to characterize the aquifer dynamics and dewatering effectiveness. The testing program had the following results by rock type or alteration type:

- Laterite: 10^{-3} to 10^{-4} cm/s
- Saprolite: 10^{-5} cm/s
- Transition Zone: Variable, from 10^{-3} cm/s to 10^{-5} cm/s depending on clay content, degree of weathering.
- Fractured fresh rock: Variable, from 10^{-3} to 10^{-5} cm/s
- Unfractured fresh rock: Consistently $<1\text{x}10^{-6}$ cm/s.

As a result, it appears that, due to its higher conductivity, the transition zone can be used as an "underdrain" for saprolite and laterite slopes. However further testing is required particularly to identify if the fresh rock is sufficiently fractured to act as a preferential pathway for saltwater intrusion into the pit.

Groundwater Modeling

The MODFLOW models predicted that the Piaba pit would receive ~50 L/s of groundwater inflow. This value increases in the 5th year of mine life and decreases in later mine life due to the depletion of hard-rock storativity. Fan drains were found to be effective. They decreased the phreatic surface beneath the pit walls by ~3.5 meters (compared to the case without fan drains). However, the regional-scale MODFLOW model proved ineffective at predicting close-in changes in the soil moisture content in the pit walls.

The Vadose/W model, with a more rigorous management of climate conditions and unsaturated flow, proved effective at predicting the seasonal variations in moisture content that could prove critical to saprolite slope stability. Figure 6 is a screen snapshot of the migrating wet fronts predicted in the Vadose/W modeling.

The moisture content profiles at various times (reflecting worst-case conditions) were provided to Crux for use in the geotechnical modeling.

Figure 6 *Example Result: Perched Seasonal Moisture in Pit Slopes*

Pit Slope Stability Modeling – Inter-ramp Angles

The pit slope geotechnical modeling followed recommendations by Read and Stacey, 2009. In the saprolite, where the rock mass strength controls the pit slope stability, inter-ramp angles were determined by completing a slope stability analysis using design charts and computer simulations. Once inter-ramp angles were established, the combination of bench-face angle and bench widths were varied to achieve the desired inter-ramp angles. Final slopes were determined in conjunction with ramp layouts provided by the mining engineers.

Finally, the overall pit slope angles were confirmed using a limit equilibrium method. The overall slopes encompassed all rock types, the inter-ramp angles, and geotechnical berms. Design assumptions required a factor of safety of 1.3, a fully-drained pit wall, and static conditions (a reasonable assumption in a region with low seismic risk).

Conclusions

Comparatively steep saprolite slopes analyzed and found to be stable. Figure 7 shows representative results (some lithologies could be steeper while others should be shallower) as compared to other saprolite slope angles in recent work and/or published sources.

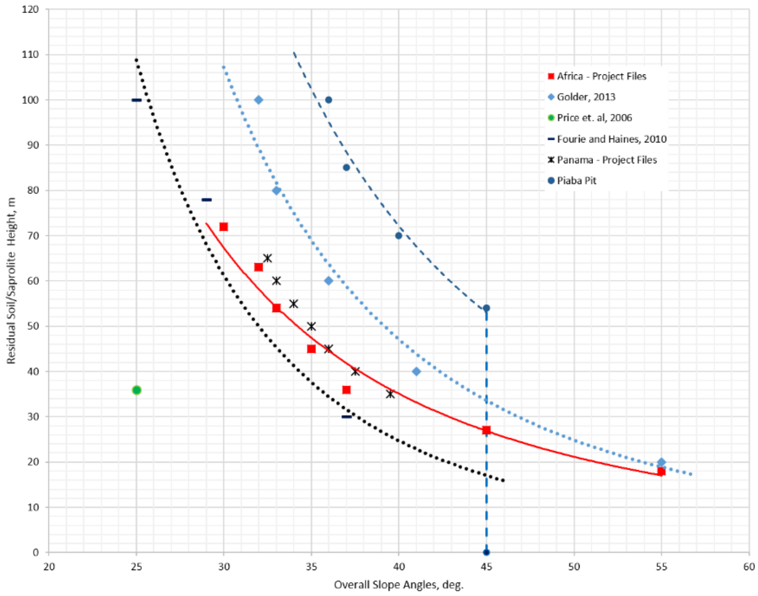

Figure 7 *Comparative Saprolite Pit Slopes*

Results of the stability modeling performed on the fully-drained slopes showed that saprolite pit slopes of modest height, could stand as steep as 45 degrees and meet the project safety factor requirements. As the overall slope heights increase, the corresponding stable slope angles decrease; which is reasonable. Comparison of the Piaba Pit results to those shown in Figure 7 suggest optimistic results. This is due to the following:

1. The project benefited from a relatively large database of strength values at the PFS level;
2. We applied a strength model which increased in depth from the completely weathered strength results to the highly weathered strength results rather than choosing one value for the saprolite which would be sufficiently conservative to represent the entire saprolite thickness; and
3. The pit slopes were effectively dewatered using fan drains; whereas, each of the other case histories shown in Figure 7 included the effects of water within the slope designs.

The project showed that an integrated dewatering and stability model early in mine life can yield significant improvements in project economics, making it an attractive investment for design stage mining projects. As the project proceeds towards design, the dewatering and stability assumptions will be confirmed through more hydrogeological and geotechnical testing and field trials of the horizontal drains.

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Risk Assessment of Coal Mining under Sand Aquifers

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Abstract

This paper presents a method for risk assessment of coal mining under sand aquifers. A case study in a panel of the Quandian Coalmine, Chinese Henan province is proposed to illustrate the application of this risk assessment method. Hydrogeological characteristics of overburden stratums and fractures due to coal mining are considered in the risk assessment as it is essential for preventing groundwater and sand inrush. A risk assessment model is proposed by using a large number of measured data and tests results. Then a mathematical model based on three-dimensional spatial entropy of safety mining area is proposed. The safety mining of coal layer in the study area is assessed by means of three-dimensional spatial multivariate quantitative. Finally, the zoning map of different factors in a superposition way of three-dimensional space of mining suitability is provided for mining reference.

Key words: underground coalmining, sand aquifer, entropy, risk assessment, caving zone, water flow fractured zone

Introduction

Groundwater and/or sand inrush is one of the major safety problems in underground coal mining especially under sand aquifers. This kind of accident is affected by several factors, such as engineering geological and hydrogeological conditions, mining method and mine environment (Sui et al. 2008, Sun et al.2012; Wu et al. 2009). There are various studies that focused on the relationship between the water inrush and geological conditions, overburden failure and the overlying strata thickness (Xu 2012). According to a preliminary statistics, about half of the underground coal mines in China are threatened by groundwater, which means over 250×10^8 tons coal reserves are dangerous to mining.

Sand aquifers is considered as one of the main source for groundwater inrush. Evaluation of mining safety under sand aquifers is usually based on laboratory experiment, numerical simulation and mathematical method (Wang et al. 2008). Since the geological conditions are not predictable, application of these constitutions are not reliable in different coalmines.

A quantitative assessment method which consists of three maps and two interrelated predictions has been proposed by La Moreaux et al. (2014) and Wu et al. (2015). GIS technology enables more automated approaches and accurate methods to evaluate the hazard of coal mining (Malinowska and Hejmanowski, 2010).

Among the factors influencing the water and sand inrush in coalmines, mine layout and cutting height can be controllable by optimizing underground mine design. However, it is more difficult to control the effect of hydrogeological and engineering geological conditions on mining under sand aquifers, since the uncertainty of hydrogeological and geological conditions. Therefore, groundwater inrush is considered as one of the most complicated problems in underground coal mining. In order to overcome the uncertainties and ensure the safety of mining under sand aquifers, a risk assessment method is introduced in this paper.

Three-dimensional spatial entropy is proposed as a risk assessment method for the safety mining under unconsolidated aquifers. Groundwater and sand inrush risks in the Quandian Coalmine are assessed based on the different mining design.

Methods

A risk index method is developed to effectively predict and comprehensively evaluate the safety of mining under sand aquifers. The detailed description of this approach is given in the works of Sui and Yang (2015).

Tab. 1 lists the main indices which consists essential factors for the risk assessment of coal mining under sand aquifers. Five main factors are listed as the first-grade indices; geological structure, sand aquifers, hydrogeological barriers, mining activity and overburden. The second-grade indices contain 12 factors. Among them, the sand aquifers index reflects hydrogeology conditions of the Neogene system especially the specific capacity of its bottom aquifer. Geological structures, including fault and fold, can be considered as the pathway of groundwater inrush. Faults and fractures will be developed in mining procedure. Once the faults or fractures developed to the bottom of aquifer, groundwater and sand would inrush into the panel as an unpredictable accident. Thickness of hydrological barrier in soils and overlying stratum in rock is used to evaluate the possibility of preventing groundwater inrush. It is possible to prevent groundwater inrush if the thickness of the barrier is larger than the fractures. The mining activity can be considered as the trigger of groundwater inrush because of its direct cause of overburden failure.

***Table** 1 Controlling index system of mining safety under unconsolidated aquifers*

The first-grade index	The second-grade index
Geological structure	Faults in fractured zone
	Fold
Sand aquifers	Specific capacity of groundwater of the Neogene
	Hydraulic conductivity
	Thickness of the bottom aquifer
Hydrogeological barriers	Thickness of the bottom clay of the Neogene
	Thickness of the key aquifuge
Mining activity	Cutting height
	Mining depth
	Caving and fractured zone
Overburden	Thickness
	Elevation of bedrock

Information-entropy model is a quantitative method for data analysis and decision making. It is an effective way to determine the different weights of a large number of data obtained from measuring in the field and tests in the laboratory. The concept of information entropy was created by a mathematician named Claude Shannon. It is an effective way to determine the weight. The weight of vector is calculated by a simple spatial entropy method (Sui and Yang 2015), which means how much information there is in an event. In general, any event contains different information. More complicated event contains more information. The comprehensive value is defined in equation (1):

$$CE = \sum_{j=1}^{n} w_j \cdot F_j(x, y) \quad (1)$$

where CE is comprehensive value; w_j is the weight value of the j^{th} evaluation index; F_j is the function of evaluation index factor which attribute to the j^{th} thematic map.

In order to compare the different comprehensive evaluation values, it is necessary to normalize the risk index. The method was given in equation (2).

$$RI = \frac{CE_x - CE_{min}}{CE_{max} - CE_{min}} \quad (1 \le x \le N) \quad (2)$$

where RI is risk index, CE is comprehensive value, CE_{max} and CE_{min} are the maximum and minimum of the grid domain, respectively, x means the x^{th} grid, N is the total number of grid. The risk index will be a value between 0 and 1.

A case study

Site description

The Quandian Coalmine is located in the southeastern part of the Yuzhou Coalfield, 16 km southeast of Zhengzhou. Coal seams are covered by the Cenozoic System with an average thickness of 220m. Panel 11050 is located in the east wing of the 11th District, with a design length of 820m, and a width of 158m as shown in Figure 1. Strikes of this panel is in NEE and SWW. There are two recoverable seams, the seam II_1 and seam II_3. The thickness of the former is from 0 to 10.38m, averaging 4.52m, and the thickness of the latter from 0 to 2.51m, averaging 1.66m. The overlying strata of the coal seam has a thickness ranging from 0 to 150m. The Cenozoic System is classified into seven engineering geological types according to borehole data. Figure 2 shows a cross section of Panel 11050. Tab. 2 lists 10 faults that found in the area according to 3D seismic exploration.

***Table** 2 Occurrence and statistics of the fauts area outcrop belt throw in the 11th mining area*

Fault No.	Throw (m)	Dip angle (°)
DF_{226}	0-15	67
FB_1	0-50	65
DF_{221}	0-6	70
DF_{220}	0-3	70
DF_{222}	0-5	59
DF_{225}	0-13	70
DF_{22}	3	58
DF_{219}	0-13	70
DF_{21}	3	62
DF_{20}	2	43

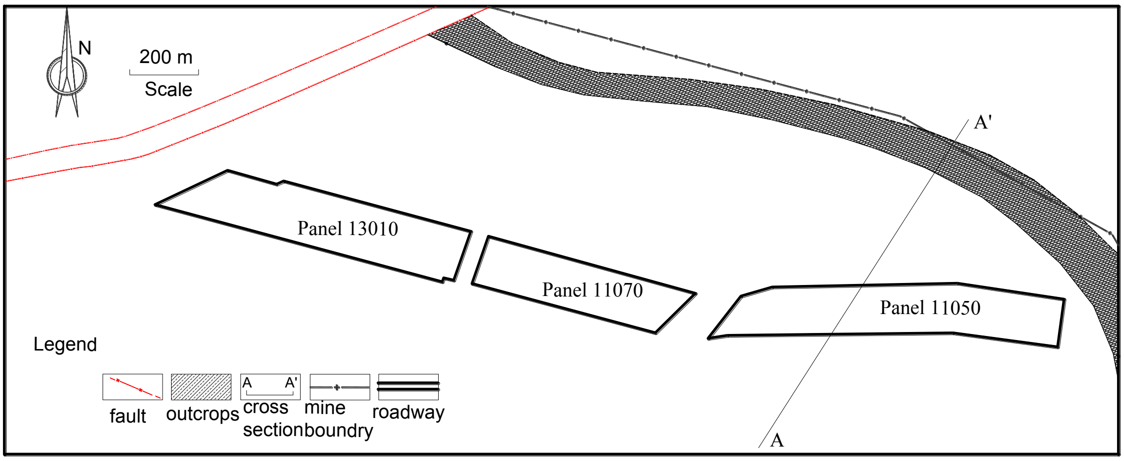
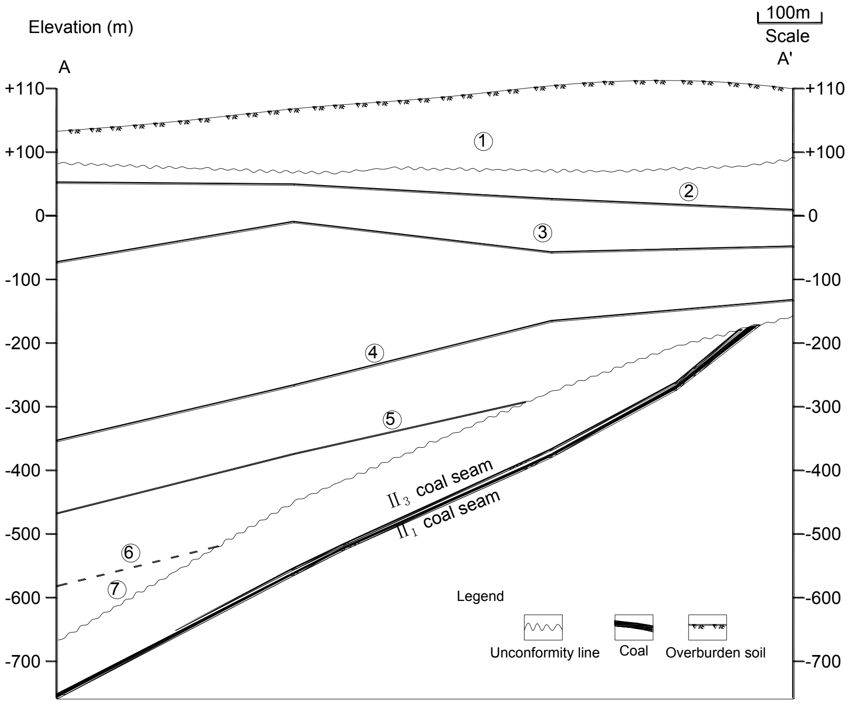


***Figure** 1 Layout of panels in the 11th District of the Quandian Coalmine that shows.*



①The Quaternary clay, sand and gravely sand; ②Clay, sandy clay; ③ Clayey and gravely sand, medium and fine sand; ④Clay, sandy clay with a thin layer of fine sand, interbedded silty clay with fine sand; ⑤Gravel sand, medium sand clay; ⑥Clay, sandy clay and clayey sand and gravel; ⑦Gravel sand, silty clay.

***Figure** 2 A-A' cross section of Panel 11050*

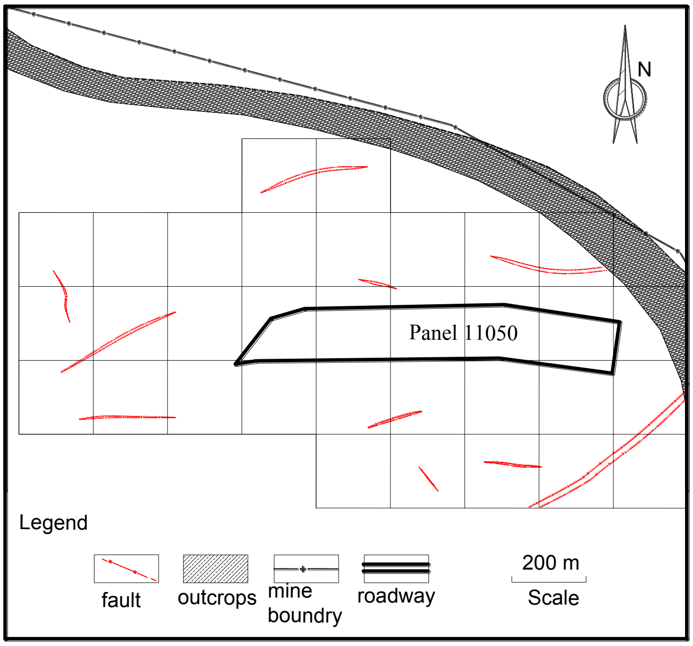


***Figure 3** Faults in the study area*

Nonlinear three-dimensional quantitative analysis of faults

Fault structure in the study area is evaluated by using three-dimensional quantitative method of nonlinearity, an evaluation method which is more reasonable and accurate than the density evaluation method. The fractal dimensions of the fault contains the number of faults, intersect relations and scale, etc.

The study area is divided into 33 square grid with a side length of 100 m as shown in Figure 3. Then, the similar ratio is showed as: r = 1, 1/2, 1/4 and 1/8, respectively. The similarity of dimensions is showed as D_s (Li et al. 2014). The 3D thematic maps of the geologic structures have been analyzed by the 3D Analyst Tools of the ArcGIS as shown in Figure 4a.

$$D_s = -\frac{\log N(r)}{\log(r)} \qquad (3)$$

where the $N(r)$ is the number of the grid crossing by fault trace, r is the similarity ratio of square grid.

Overburden failure height due to mining

Two scale models with a scale of 1:200 were constructed to simulate mining process.

The heights of mining overburden failure zone was calculated by using different methods which are summarized in Tab. 3. Also, the results was compared with the measured data from Xin'an Coalmine where shares the similar geological conditions. Moreover, results from scale models were listed in Tab. 3 for comparison. Recommended results were used to evaluate mining upper limit of coal seams under the sand aquifers.

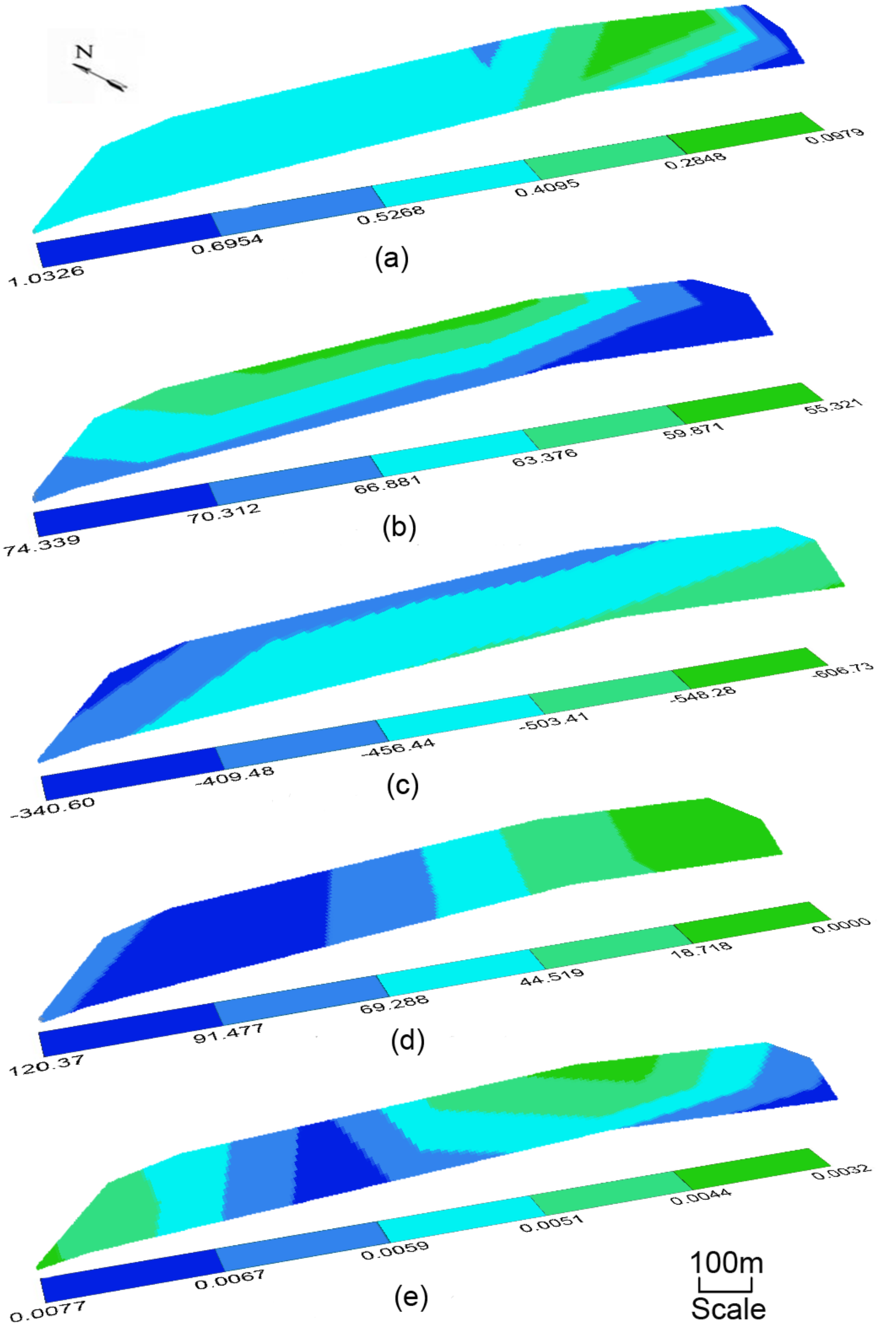
***Table** 3 Prediction of overburden caving zone and water flowing fractured zone*

Cutting height (m)	Caving zone				Water flow fractured zone	
	Code (CCIB)	Xin'an Coalmine	Scale model test	Recommended (m)	Code (CCIB)	Recommended (m)
	H_c/M	H_c/M	H_c/M		H_f/M	
2.0	4.62/6.24		4	12.48	17.58	35.16
2.8	3.90/5.27			14.76	14.38	40.26
3.0	3.75/5.61			16.83	13.77	41.31
4.0		5.46	6.80, 5.50	22.00		47.08
5.0		4.75	3.76-4.63	23.75		50.95
6.0		4.75	3.76-4.63	28.50		54.42
7.0		4.75	4.51	33.25		57.89
7.2		4.75		34.20		58.58
7.5		4.75		35.63		59.62
7.8		4.75		37.05		60.66
8.0		4.75		38.00		61.36
9.0		4.58		41.22		64.83

H_f: height of the fractured zone; H_c: ration of height of caving height; M : cutting height.

Evaluation of Mining feasibility based on 3DGIS

Eleven indices (excluding the index Fold in Tab. 1) as the second-grade evaluation indexes have been analyzed by using 3DGIS. The 3D thematic maps of five main factors as the first-grade indices have been obtained by the model of three-dimensional spatial entropy (Figure 4). An entropy mathematical model was established to quantify the relationship based on the calculation and analysis. Quantitative analysis and dimensionless normalization for the first-grade main factors and their importance degree are determined. Finally, a model of three-dimensional spatial entropy based on GIS is set up, the three-dimensional space superposition of mining suitability zoning map integrated many factors is provided for mining reference as shown in Figure 5.



(a) Geological structure; (b) Sand aquifers; (c) Hydrogeological barriers; (d) Mining activity; (e) Overburden

***Figure** 4 Perspective drawing of each factor's three-dimensional space*

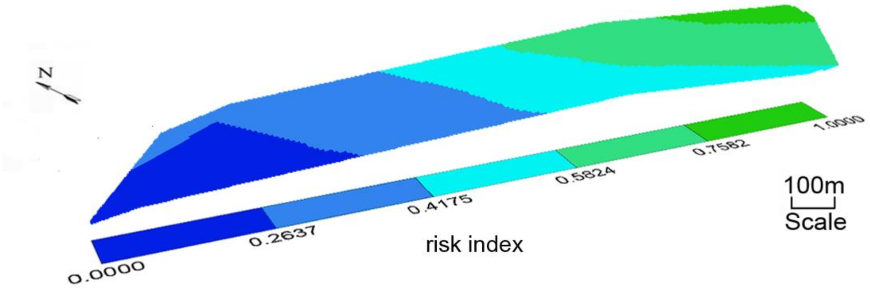


***Figure** 5 Three-dimensional zoning for mining feasibility*

Conclusions

In this paper, a risk assessment method has been proposed for effectively predicting and comprehensively evaluating the safety of mining under sand aquifers. Since analysis of risk assessment of coal mining under sand aquifers has the characteristics of complexity and variability, two or even multivariate mathematical model of three-dimensional spatial entropy is constructed based on GIS, various indices and their relationship have been considered simply and fast, accurate and practical. A panel of the Quandian Coalmine in the Henan province of China was evaluated by using risk assessment model. In the assessment, overburden hydrogeological conditions, engineering geological conditions and overburden failure due to mining were analyzed and several indexes were quantified for the model.

By using a large number of measured data and test results, a mathematical model of three-dimensional spatial entropy of safety mining area is established. And the safety mining of coal layer in the study area is assessed by using three-dimensional spatial multivariate quantitative method. Finally, the zoning map of many factors of three-dimensional space was proposed for determination of mining methods In the region with high risk where $RI \geq 0.7582$, the cutting height of II_1 seam was limited within 2.8m. There was no serious disturbances and accidents such as groundwater inrush and quicksand during mining from September 2013 to March 2015.

Acknowledgements

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Monitoring and numerical simulation of water inrush pathway caused by coal mining above karstic confined aquifer with high water pressure

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Abstract

Mining-induced floor failure and formation of water conducted pathway is the necessary conditions for water inrush in coal mine,which are the basis for monitoring and predicting water inrush. In order to study the formation and evolution of floor failure and water conducted pathway caused by coal mining above karstic confined aquifer with high pressure in Xinyi coalmine,Henan province, China,field monitoring and numerical simulation methods are introduced in this paper. Subsequently,the variations of electrical resistivity, stress and pore water pressure of floor during mining process are analyzed. The result shows that the floor failure caused by coal mining under karstic confined aquifer with high pressure is influenced significantly by advanced supporting stress of coal mining and the failure depth of floor of panel 11011 is about 25 m, which is greater than general empirical value. Based on fluid-solid coupling theory,the established numerical simulation model of mining-induced floor failure can reflect the influencing factors of floor failure more accurately and objectively；and the maximum failure depth is up to 23.75 m,which is very close to field monitoring result. The variations of electrical resistivity,stress and pore water pressure can better reflect the whole process of mining-induced floor failure formation,water inrush pathway evolution and water filling. The conclusion indicates that the above-mentioned parameters can be used as the precursor information for monitoring and short-term predicting the water inrush hazards in coalmines.

Key words: coal mining above karstic confined aquifer；floor failure；field monitoring；numerical simulation, precursor information

1 Introduction

Coal mining operations in China are threatened by various kinds of groundwater during coal extractions. The most serious water disaster affecting the safe operation of coalmines is water inrushes from the coalseam floor in Northern China (Wu and Jin 1995). 8 The confined karst aquifer contains abundant groundwater with a very high water pressure. Furthermore, the aquifuge between coal seams and the aquifer is relatively thin, varying in thickness from 30 to 60 m. Due to these characteristics of the aquifer, in addition to floor aquifuge failure and inherent geological structures (such as water conducting faults, fractures), high pressure groundwater can break through the floor aquifuge and inrush into the working face. Therefore, water inrushes from the aquifer occur frequently, and coalmines often suffer from serious water disasters during mining.

In this case, coal mining above confined water with high pressure conditions which proposed along with the exhaustion of shallow coal recourses in China, the complication of mining conditions, the increasing depth of mining is a high level of difficulty production technology under certain special geological backgrounds. In the water disaster prevention practice of deep mining above aquifer, there is always a basic contradiction between the floor aquifuge with different structures and the water pressure that the aquifuge is subjected to. Therefore, the further study and understanding on the floor structure and mining-induced failure characteristics, the high pressure water inrush models and precursors are significant for efficiently prevention of the water inrush hazards.

2 Research Methods

This paper focuses on the complex structure aquifuge failure in the floor and characteristics of confined water inrush with high pressure over 5MPa induced by deep coal mining. The occurrence and influencing factors of floor water inruch, interaction between water and rock, temporal-spatial distribution were analyzed based on numerous water inruch materials. And then, two basic patterns of floor water inruch, integrated and fractured floor water inrush pattern, were summarized. The floor failure, physical geographic characteristics, changes of floor stress and pore water pressure were also studied according to field measurement and numerical simulation. Three scaled models, including simplex structure, multilayer structure and faultage structure for floor water inruch with high pressure were established based on the high pressure water inruch simulation equipment. The whole procedures of conformation of water inrush pathway and after that the high pressure water inruch during the coal mining were simulated. Furthermore, the basic characteristics of floor water inruch under different floor structure conditions were summarized.

3 Numerical Simulation

The deep mining-induced failure features under different floor aquifuge structure were revealed. The Flac^{3D} numerical simulation model is based on the geological and mining conditions of Xinyi coalmine, and the size is 300×200×180m，mining depth is 900m，thickness is 2.5m，the width and length is 100m and 160m，the thickness of aquifuge is 58m.According to figure 1 and table 1，under the same aquifuge structure and mining conditions，water pressure has a great influence on the failure depth. In addition， the failure depth and range is increasing with greater water pressure. And under the working face，the shape of aquifuge failure range transits from “inverted saddle” to “ inverted trapezoid”

Table1 *Failure depth varies with water pressure values*

Water pressure（MPa）	0	2.5	5	7.5	10
failure depth（m）	14.15	17.36	23.75	29.56	35.73

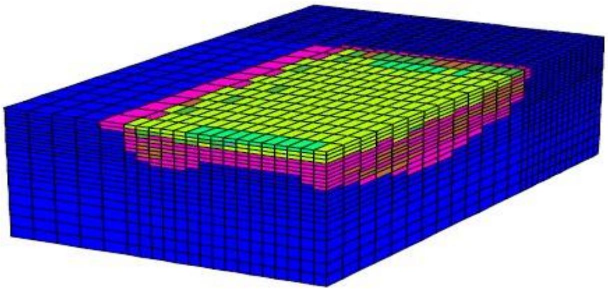
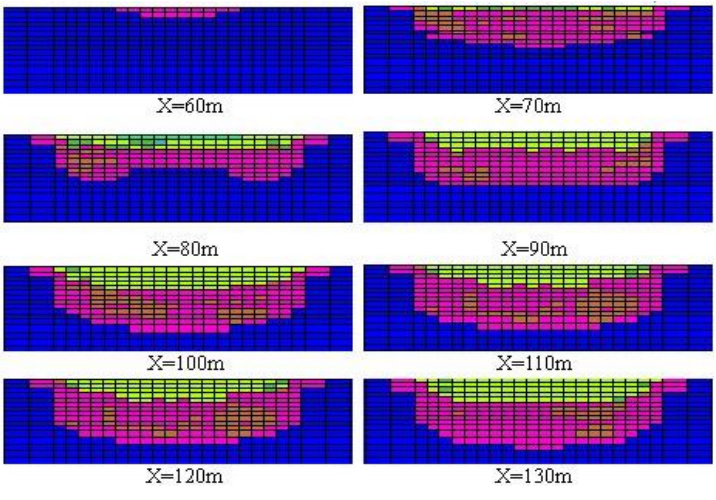


Figure 1 *Numerical model diagram in FLAC^{3D}*



X=60m X=70m

X=80m X=90m

X=100m X=110m

X=120m X=130m

Figure 2 *The aquifuge damage depths under the working face floor*

The results show that, with the condition of confined water pressure over 5MPa that the aquifuge is subjected to, the floor failure is influenced significantly by advance stress and the failure depth is about 23.75 m. The failure depth and range are enlarged with the increasing of water pressure under the same floor structure and mining conditions. There are some differences of the failure range exist from the area under the working face to the goaf, the ranges change gradually from "inverted saddle shape" to "inverted ladder shape".

4 Field Monitoring

In order to test the variations of electrical resistivity and stress in floor during the mining process, field monitoring is tested under the floor of Panel 11011(Fig.3).

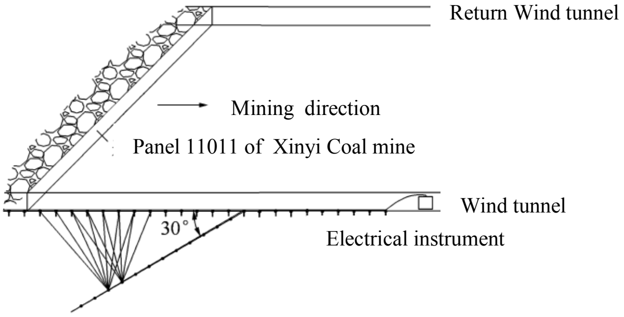
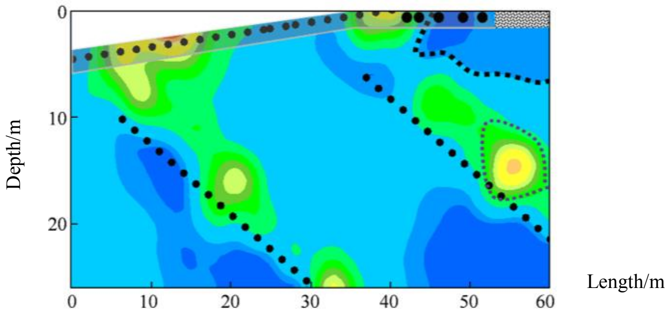
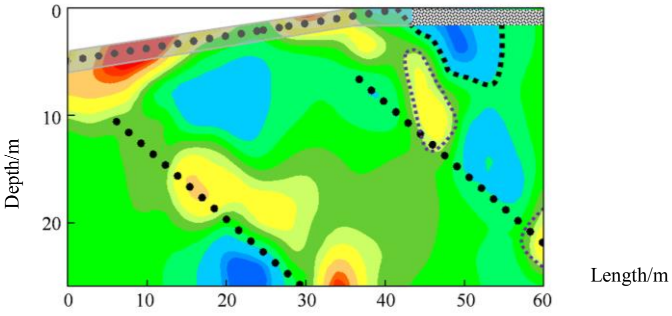


Figure 3 *Sketch of field monitoring for floor failure*

Fig.4 show that the floor aquifuge failure was systematically studied according to field measurements from the point of view of efficient monitoring and "gradual change process" of floor aquifuge failure induced by coal mining. Also, the failure depth of floor of Panel 11011 is about 25 m, which is greater than general empirical value.



(a) Monitoring result of 2009/11/10



(b) Monitoring result of 2009/11/30

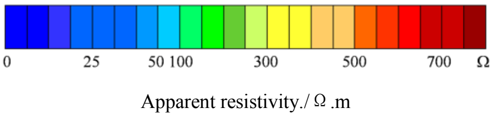


Figure 4 *Detection results of floor failure*

5 Laboratory test

Three scaled models with different floor structures were designed and accomplished to study the precursors of floor water inruch with high pressure.Three scaled models, including simplex structure, multilayer structure and faultage structure for floor water inruch with high pressure were then designed and established based on the high pressure water inruch simulation equipment, which can be used to carry out overburden and floor water inruch simulation experiments using a size of 1.4 ×1.6 m rock sample and can provide 3 MPa vertical load.

Figure 5 *Laboratory test device*

The laboratory test show that: the basic characteristics and laws of stress and pore water pressure variation during the water inruch process with high pressure induced by coal mining under different floor aquifuge structures were also systematically summarized on the basis of the experimental results. The periodic fluctuation of the floor stress and pore water pressure due to coal mining are closely related to the mining progress. During the conformation of mining-induced water inrush pathway, all the parameters increase sharply and fluctuate violently. When the water inrush into the working face, all the parameters decrease considerably and then at a certain range of a low level for a long period. It can be deduced from these results that the floor stress and pore water pressure can be significant precursors for monitoring and forecasting the water inrush hazards in coalmines.

6 Conclusions

(1) The result shows that the floor failure caused by coal mining under karstic confined aquifer with high pressure is influenced significantly by advanced supporting stress of coal mining and the failure depth of floor of panel.

(2)The variations of electrical resistivity, stress and pore water pressure can better reflect the whole process of mining-induced floor failure formation, water inrush pathway evolution and water filling. The conclusion indicates that the above-mentioned parameters can be used as the precursor information for monitoring and short-term predicting the water inrush hazards in coalmines.

(3) The conclusion indicates that the above-mentioned parameters can be used as the precursor information for monitoring and short-term predicting the water inrush hazards in coalmines.

The achievements of this paper lay an important basis for monitoring and forecasting the water inrush disasters in deep underground coalmines, and for safety coal mining above aquifer with high pressure.

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Use of tensiometers to determine the Moisture Characterization Point in ores

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Abstract

The Moisture Characterization Point (MCP) of an ore is based on the moisture behavior in the unsaturated pores, close to but below the field capacity of the ore. The MCP is an alternative method to determine safe moisture limits for the shipment of ore as compared to geotechnical test methods used to determine the Transportable Moisture Limit (TML) in ores, such as the Proctor Fagerberg test.

In this study a soil tensiometer (Hensley 2009) was adapted to measure the suction pressure (pF) as function of the moisture content in the ore. The Moisture Characterization Point (MCP) was defined as a suction pressure of -0,25 bar. This point is below, but relative close to, the field capacity of the ore. The MCP was correlated with the physical and chemical properties of the ores, like particle size, specific surface area and mineral composition of the ores.

The results showed a wide variation in the MCP's for nine different ores, varying between a MCP moisture content of 3.8% up to 21.5 %. The results where compared with the TML limit based on the Proctor Fagerberg tests. For most ores the MCP and TML levels are close (on average a relative difference of 10% between the TML and MCP). For ores with a substantially larger difference then 10%, the ores mineralogy is a dominant factor. The ore mineralogy could be linked to the ore surface area, leading to the conclusion that shipment of ore with goethite content above 35% is not liable to liquefy.

A better understanding of the moisture behavior in ores has assisted in the development of safer cargo schedules (IMO 2013) to ensure the safe shipping of bulk cargoes.

Key words: IMWA 2016, moisture, ores, suction, shipping

Introduction

In 2010, 44 seafarers lost their lives when a number of bulk carrier vessels capsized due to liquefaction of the cargo. These and later incidents have triggered the International Maritime Organization to review cargo schedules defined in the International Maritime Solid Bulk Cargoes Code (IMO 2011). Group A cargoes are liable to liquefaction, while Group C cargoes are not prone to liquefaction. The safe carriage of Group A cargoes is possible by ensuring they are shipped at moisture contents below their Transportable Moisture Limit (TML).

One aspect that determines if liquefaction might occur is the degree in which pores are saturated. As long as pores are unsaturated (below the ores field capacity) pore water pressure buildup due to ship roll cannot occur, and a wet failure mode is not possible. The Moisture Characterization Point (MCP) is based on the moisture behavior in the unsaturated pores, close to but below the field capacity of the ore. A suction pressure of -0.25 bar was chosen as reference point for the MCP. The MCP is an alternative method to determine safe moisture limits for the shipment of ore as compared to geotechnical test methods used to determine the TML in ores, such as the Proctor Fagerberg test.

The MCP adds information by characterizing how moisture is bound within the pores of the ore for what can still be described as a drained (unsaturated) ore. At low moisture contents, the pore water is bound to the mineral matrix as hydration water. This water is irreversibly bound and will not drain. With increasing moisture contents, the pores in the ore are filled with water. The smallest pores have the highest capillary binding force (soil moisture potential, or suction pressure, expressed in KPa) and will be filled first. With increasing moisture contents the larger pores are filled. As long as the moisture content is below the field capacity, the ore will not drain. Above the field capacity of the ore the pore suction is less than the gravital forces, and the ore can drain (Brouwer 1985). For soil sciences this is known as the three soil moisture states describing unavailable water, plant available water and drainable water (O'Geen 2012). Figure 1 illustrates these three soil moisture states.

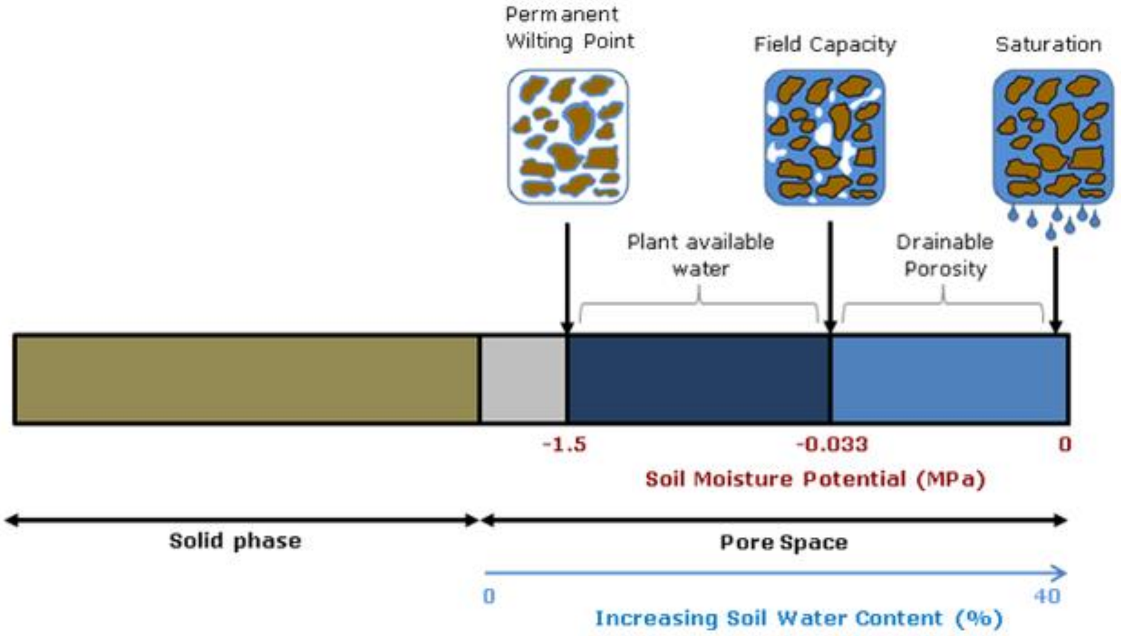

Figure 1: *Water content and water potential at saturation, field capacity and permanent wilting point. The difference in water content between field capacity and permanent wilting point is (plant) available water. Drainable porosity is the amount of water that drains from macro pores by gravity between saturation to field capacity typically representing three days of drainage in the field.*

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As long as the ores are below the field capacity, suction is greater than gravity. Moisture will not migrate (seep) due to ship roll and pore water pressure cannot build up. Hence the ore behaves as a drained ore.

Soil tensiometers are designed to measure the pore suction under static conditions in hydrostatic equilibrium (Klute 1962). The response time to changes in moisture content is on a daily scale. More recent developments in miniature tensiometers shorten this time interval to hours (Cui, 2008). To establish the moisture versus suction relation for different ores and different grain sizes, a step wise small increase in moisture content is needed to determine the slope of the pore suction pressure versus the moisture content. Therefore a smaller miniature tensiometer was developed to measure changes in pore suction pressure at given moisture content on a timescale of minutes. By a step wise increment of the moisture content in the ore a moisture versus pore suction pressure response curve was measured, similar to a soil pF curve (Blaskó Lajos 2011).

Characterization of the ore mineralogy, the ore pore size distribution and the ore surface area was carried out. These supportive measurements correlate to the water adsorption properties of the ore due to the binding of hydration water, capillary suction and the storage capacity based on pore volume.

Methods

The used ore samples were iron ores, bauxite and sand. The ores where characterized by their; bulk density using a pycnometer, initial moisture content (as total mass percentage), grain size distribution for particles between 6.3 mm and 0.063 mm by wet sieving (NEN 2006) and for particles smaller than 0.063 mm by laser diffraction (Vdovic 2010). The ores were characterized on their surface area (in m2/gram) by mercury and nitrogen intrusion (Zong 2014). The meso pore size distribution was calculated by means of the Barrett-Joyner-Halenda (BJH) pore size model (Lowell 2012), using the Brunauer, Emmet and Teller (BET) theory for surface area estimation (Kreysa 2000).

The tensiometers used were from RHIZO INSTRUMENTS in Wageningen, the Netherlands. Each tensiometer has three essential parts:

- An air permeable / water impermeable plastic hollow fiber (pore size 0.03 μm). The fiber is protected by a ceramic cup (pore size 0.45 μm) with a diameter of 3.0 mm.
- A flow through pressure transducer (12 mV/bar output at 3.0 V input, resolution 0.001 mV, -1.0 to +1.0 bar range).
- A vacuum chamber source: for single point measurements a syringe with spacer, for the titration setup a membrane vacuum pump (Baltalab N86KN.18).

Figure 2 illustrates the different tensiometer elements.

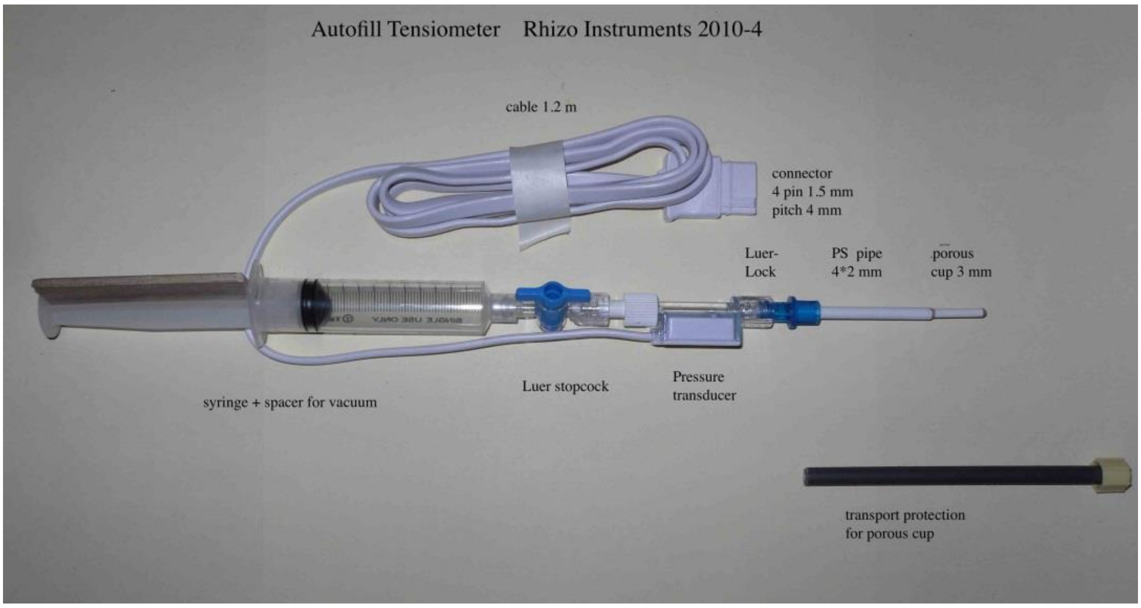

Figure 2, *tensiometer setup. On the right the porous plastic hollow fiber protected by a ceramic cup. In the middle the pressure conductor with a range of plus or minus 1 bar (12 mV/bar output at 3 V). To the lift the vacuum chamber, in this case a syringe.*

By applying a vacuum the pore suction pressure in the tensiometer drops to -0.95 bar. When the suction pressure in the pores increases to a value above -0.95 bar water flows into the tensiometer. The suction pressure in the tensiometer decreases. If the pore suction pressure equals the suction pressure inside the tensiometer, the flow of water stops and the tensiometer is in equilibrium. The tensiometer response curve as function of moisture content can be divided in three regimes:

1. At a moisture contents above the field capacity the tensiometer response drops to zero. The tensiometer completely fills up with water and there is zero pore suction pressure. This is reflected by a quick drop to 0% signal.

2. At moisture concentrations close to, but below, the field capacity, the tensiometer reaches equilibrium with the pore suction pressure (range -0.00 to -0.95 bar).The tensiometer response represents the actual pore suction pressure.
3. Closer to the wilting point the applied vacuum (-0.95 bar) inside the tensiometer is not strong enough to compete with the pore suction pressure. The signal stays close to 100%.

This divides the tensiometer response curves into three types of response curves, which are illustrated in Figure 3 for one of the nine ores (ore C) at different moisture contents.

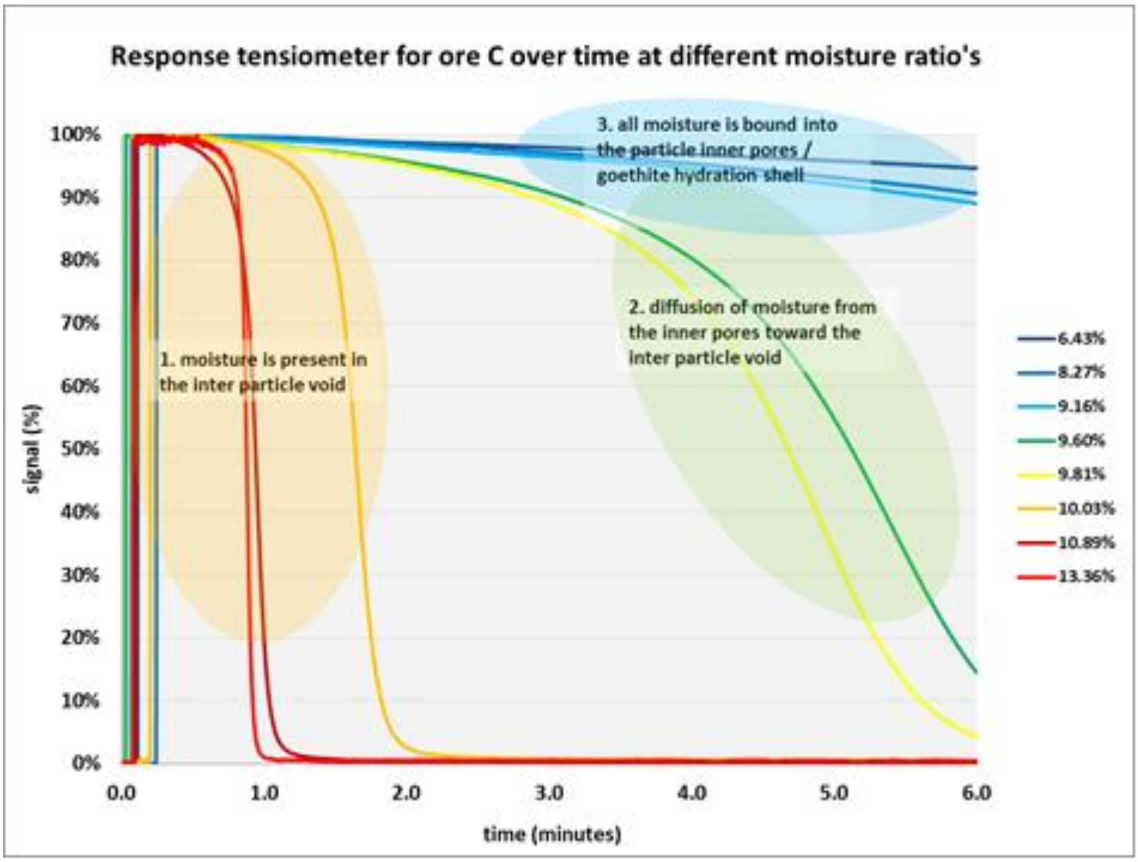

Figure 3, *Tensiometer response near full saturation (in orange/red), near the field capacity (in yellow/green) and near the wilting point (in purple/blue). The x-axis plots the response after closing the vacuum from 0 to 6 minutes. On the y-axis the signal (%) is plotted*

Results

The soil permeability, or hydraulic conductivity, relates to the pore size distribution (Burdine 1953) and soil texture data (Ghanbarian-Alavijeh 2010). Table 1 summarizes the ore texture characteristics, the ore surface area and the MCP and gives the calculated regression coefficient between the parameters and the measured MCP based on a first order fit.

Table 1, *Ore texture characteristics for nine ores and sand (grain size distribution per class (d10, d50 and uniformity coefficient d60/d10), the ore surface area (BET)) and the MCP (75% loss of signal, pore suction pressure -0.25 bar). Calculated correlations between different ore texture characteristics and the MCP based on a first order fit.*

		Uniformity Coefficient d60/d10	d10 mm	d50 mm	SBET m2.g-1	MCP (%)
ore A	iron ore	200	0.01	1.00	13	14.0%
ore B	iron ore	97	0.02	0.73	4.4	8.5%
ore C	iron ore	292	0.01	1.26	5.5	9.8%
ore D	iron ore	68	0.03	0.68	6.6	7.3%
ore E	iron ore			0.18	0.7	6.8%
ore F	iron ore	2.7	0.07	0.16	0.5	3.8%
ore G	iron ore	38	0.12	3.23	20	15.0%
ore H	iron ore	54	0.05	1.68	46	12.0%
ore I	aluminium ore, pre-dried	2.3	2.95	5.86	72	21.5%
sand	sand, pre-dried	2.5	0.25	0.45		9.3%

first order fit	R^2
Correlation between particle size uniformity coefficient (UC) and the MCP	0.015
Correlation between d10 particle size and the MCP	0.15
Correlation between d50 particle size and the MCP	0.83
Correlation between BET and MCP	0.82
Correlation between d10 and BET	0.21
Correlation between d50 and BET	0.89

In addition to the properties listed in Table 1, XRD measurements where done to characterize the mineral composition of the ores. The minerals detected by XRD are given in Table 2.

Table 2 *Minerals detected by XRD for all nine ores and sand, including the mineral formula. The data was not quantified.*

XRD detected minerals	
Quartz	SiO2
Calcite	CaCO3
Gypsum	CaSO4
Gibbsite	Al(OH)3
Goethite	FeO(OH)
Hemathite	Fe2O3
Magnetite	Fe3O4
Siderite	FeCO3
Muscovite (mica)	KAl3Si3O10(OH)1.8F0.2
Dickite (kaolinite)	Al2Si2O5(OH)4
Illite	K0.6 (H3O)0.4 Al1.3 Mg0.3 Fe2+0.1 Si3.5O10 (OH)2

The MCP was established for nine ores and sand. Figure 4 gives the percentage of signal loss as function of the moisture content. The MCP as defined by a pore suction pressure of -0,25 bar (a 75% loss of signal) is plotted as a dotted red line.

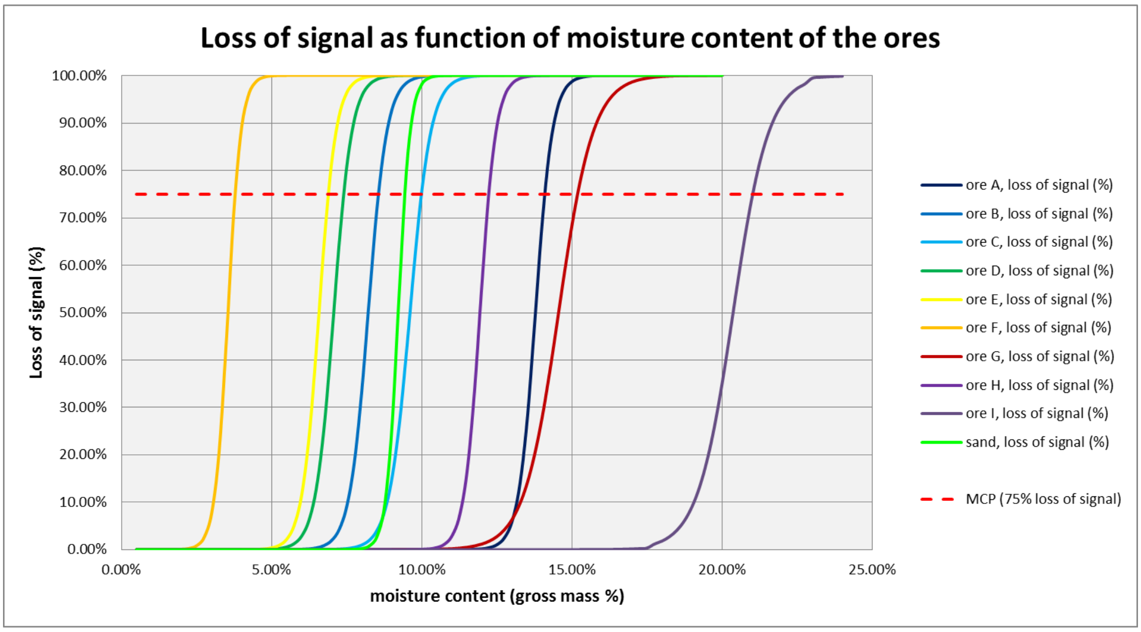

Figure 4 *Signal loss (pressure potential drop) for nine ores and sand as function of the moisture content. The x-axis gives the moisture content (% gross weight). The y-axis plots the percentage loss of signal at a given moisture content for each of the nine ores. The MCP is plotted horizontally as the point of 75% signal loss.*

The TML has been determined according to the IMSBC code (IMO 2013). The TML, with a 70% degree of moisture saturation, is plotted in Figure 6. For comparison the MCP, as defined by a 75% loss of signal, is also plotted in Figure 5.

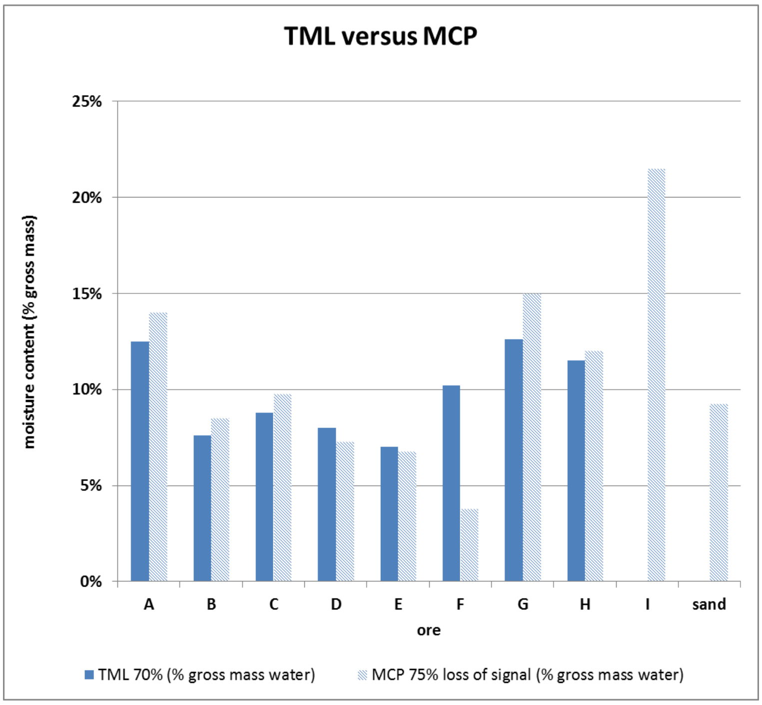

Figure 5 *On the x-axis the nine ores and sand. On the y-axis the TML moisture content (% gross mass) for eight of the nine ores as determined by the IMSBC code (IMSBC 2015). The results are compared to the MCP for all nine ores and sand.*

Conclusions

Based on the (Van Genuchten 1980) closed-form equation for predicting the permeability of an unsaturated soil, it was expected that there would be a positive correlation between the increase in MCP and a larger amount of smaller ore particles (as expressed by an increase in the UC), and between the MCP and the ore surface area (as expressed by the BET). Small particles tend to have a larger surface area (Lecloux 2015) and the micro pore volume between small particles has a lower suction pressure as compared to the macro pores (Mancuso 2012). The relation between the MCP and the amount of smaller particles (as expresses by a low value for the d10 and d50 and a high UC value) could not been found in the tested ores, as is illustrated by the low regression coefficients in Table 5. However, the correlation between the MCP and the ore surface area and the correlation between the MCP and larger ore particles (high BET, high value of the d50) was good (R^2 of > 0.8). Since the ore surface area is not correlating with the amount of smaller particles, the ore mineralogy plays a role.

The ore mineralogy plays an important role when it comes to the mineral surface area. In general goethite tends to have the largest surface area (Hiemstra 1998), although the surface area of goethite varies as function of the formation conditions (Villalobos 2003). The correlation between the goethite percentage of the ore and the ore surface area is moderate (a R^2 of 0.7). For hemathite this correction is weak (a R^2 of 0.4). On average goethite has a 3.5 times as strong contribution to the ore surface area as compared to an equal mass percentage of hemathite. With an increase in the mass percentage of goethite, the MCP also increases.

The goal of this research was to ensure safe moisture standards for shipment of ore based on the transition of the ore between the drained and undrained state of an ore (the field capacity). Ores in a drained state cannot build up excess pore water pressure due to ship roll. The relation between the ore moisture content and the pore suction pressure was determined, leading to the ore specific field capacity. The Moisture Characterization Point (MCP) is based on this relation and defines a safe shipping standard with a safety margin (remaining pore suction pressure of -0.25 bar) with regard to the actual field capacity (the transition from an undrained to a drained state) of the ore. The field capacity and the curve describing the loss of suction pressure as function of moisture content is primary dependent on the type of ore minerals, and to a lesser extent on the ore grain size.

The MCP gives additional information based on ore mineralogy as compared to Transportable Moisture Limit (TML) standard, which is based on the ores compaction behavior versus moisture content (Proctor/Fagerberg Test). In general the TML and MCP correlate well, with a relative difference of around 10%.

Acknowledgements

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Geogenic Caverns in Rock Salt Formations – A Key to Genetic Processes and Hazard Potential

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Extended Abstract

Geogenic caverns are typical geological phenomena in large-scale rock salt formations which occur with a spatial dimensions of a few decimeter to several decameter. They are filled with natural brine, gas or recrystallized salt minerals. Generally, evaporitic rocks, especially rock salt, sylvinite and other potash salts are prone to dissolution or diagenic alteration. Major processes which are linked to the origin of intrasaliniferous caverns include the recrystallization of salt minerals, the dissolution of evaporites by intruding groundwater, or volcanic intrusions from the Earth's mantle. Those processes may form large intrasaliniferous caverns, which may collapse and potentially affect the landscape above and underground mining operations.

Despite their common appearance, geogenic intrasaliniferous caverns remain a significant issue in underground salt and potash mining safety. Many studies have focussed on the occurrence, geochemistry and hydrology of intrasaliniferous brines (Herbert and Schwandt, 2007). However, the origin of geogenic caverns has not been studied yet in detail.

In this study we present an overview of the known types of intrasaliniferous caverns. We establish a classification with respect to the existing tectonic regime, the brine type, as well as the hazard potential for underground mining and above ground. We focus on own field data from the Upper Permian Zechstein formation, data and reports from former and present-day potash and rock salt mines as well as interdisciplinary studies with respect to dissolution processes, brine hydrology and tectonic conditions in evaporites.

The observed examples indicate two general types of intrasaliniferous caverns. On the one hand, atectonically formed caverns are related to post-depositional intrasaliniferous processes regarding the metamorphism of carnallite rock to sylvinite (Pippig, 1992). This process is linked to a significant reduction of rock volume, which creates small-scale caverns. On the other hand, tectonically-formed intrasaliniferous caverns demonstrate a more complex origin, which is strongly linked to present or fossil solution paths (open or closed hydrological system), the saturation and dissolution potential of the intruding brine and the number of the existing tectonic lineaments.

A risk analysis of the studied caverns and dissolution scenarios indicates that atectonic intrasaliniferous caverns show a very low hazard potential, because of the limited space and brine volume in a closed hydrological system. The brine is mostly saturated in potash and salt minerals and has no or a very low potential for dissolution of the in-situ salt rocks and pillars. In contrast to atectonic caverns, tectonically-formed intrasaliniferous caverns show a higher hazard potential. They are formed at fossil or present solution paths and demonstrate open hydrological systems with a hydraulic connection to aquifers under and above the evaporite formation. The hazard potential increases with lower saturation of the involved brines or saline formations waters and the existence of multiple tectonic elements.

Despite the general geogenic hazard potential of caverns in rock salt formations, the hazard potential in underground mining is uncritical, due to close meshed exploration. Safety-related exploration in rock salt and potash mines include horizontal drilling, drill hole radar and seismic surveys in order to identify potential brine migration paths (basement faults, protective layer faults), areas of brine penetration and brine-related alteration of potash and rock salt beds.

Key words: Geogenic brine, rock salt, mining, caverns

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Vulnerability analysis on potash mining dumps using tomographic measurements, modeling and petrophysical investigations

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Extended Abstract

Germany is one of the largest conveyors for potash and rock salt in the world. Over time and during the process of production, more than 100 m high mining dumps of unexplored structure and material have formed. These dumps sites are now in the research focus, as they can become a hazard to human and environment. Especially the stability of these dumps has to be explored as vulnerabilities could occur through processes linked to subsidence, leaching and material conversion. Hazardous sinkholes, fissures and cavities are developed similar to the carstification processes in natural rocks.

Recently analysis include combined geophysical and petrophysical investigations for non-invasive characterization of the dumps. The measuring concept contains tomographic methods such as geoelectrics and seismics as well as grounds penetration radar (GPR), spectral induced polarization (SIP) and nuclear magnetic resonance (NMR). Within laboratory experiments (NMR, ultra-sound, electrical resistivity), rock and mineralogical properties were estimated. Using P-wave velocities and electrical resistivity's potential zones of weakness with probably decreased strength, increased permeability and water content are identified. Additional material properties as water solubility and rock material (e.g. solid or loose rock) were considered in the model developed with the software BERT [1]. An example of the resistivity distribution of one test site is shown in Fig. **1**. The loose material at the hillsides of the waste dump have a very high resistivity compared to the immediate underlying zone of very low resistivity, which has a high concentration of Halite. Furthermore, zones of high and low resistivity have been found in greater depths, which could indicate weak areas of for example washed out material. In conclusion, with the seismic survey the detection of the location of possible sinkholes is more explicit.

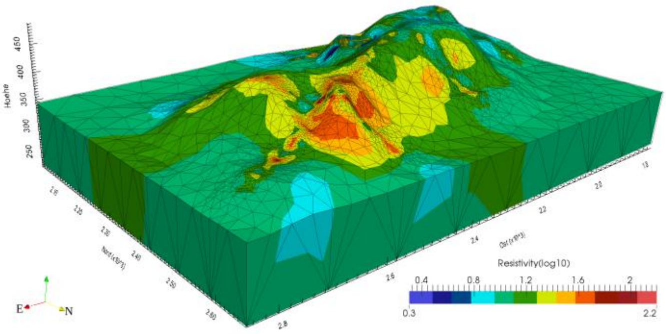

Figure 1: *3D Electrical tomography across the potash mining dump, Inversion using BERT [1]*

Key words: Mine dump, modeling

References

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Seismologic long-time monitoring of the inner burden dump in Schlabendorf/South with hazards of soil-liquefaction causing deformations of the terrain surface

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Extended Abstract

In the area of the former open brown coal pits in the Lausitz, there exist a number of prohibited inner burden dumps. These areas are always tens of square kilometers large, which are not accessible for the forest, agriculture or other use. The reasons for the prohibition are the slip hazards of the overburden. The seismologic monitoring is one possible solution how to detect mass movements in real time and give the operator of an inner burden dump the chance to observe the slip contemporary.

Beginning in 2013 to 2014 a seismologic network with 20 seismologic stations was installed around and on the inner burden dump Schlabendorf/South. The seismologic stations were supplied by solar power and work with a LTE(4G) mobile phone data link. Since the starting time a number of seismologic events have been monitored. Not all of the seismologic events could be observed from the surface because of the considerable depth of the events. During operation time, a number of parameter and correlations from seismologic events were discovered.

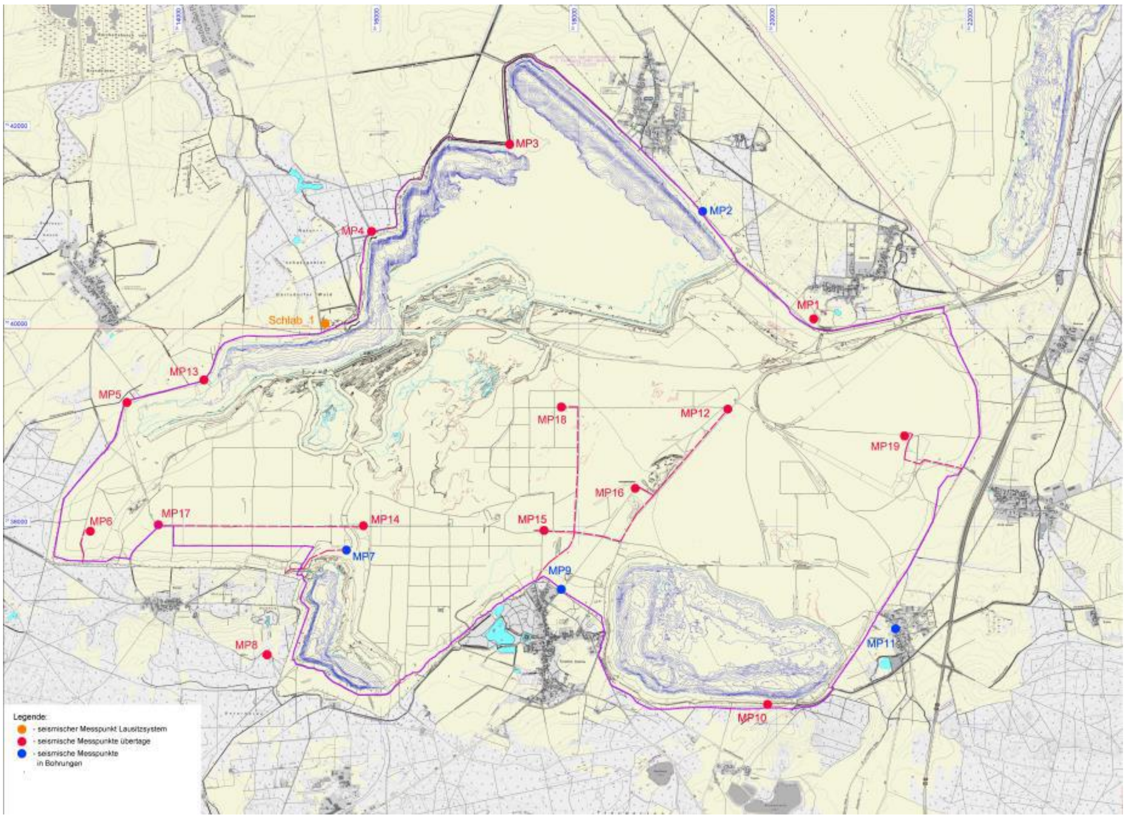

***Figure 1**: Seismologic monitoring Network*

During the monitoring time, a number of seismologic events occurred with visible mass move-ments. Some of the seismologic events took place in subsequent events to each other, which could be interpreted as connected events bursts from the underground to the surface. The geotechnical impact on the surface could be a sinkhole or a surface displacement.

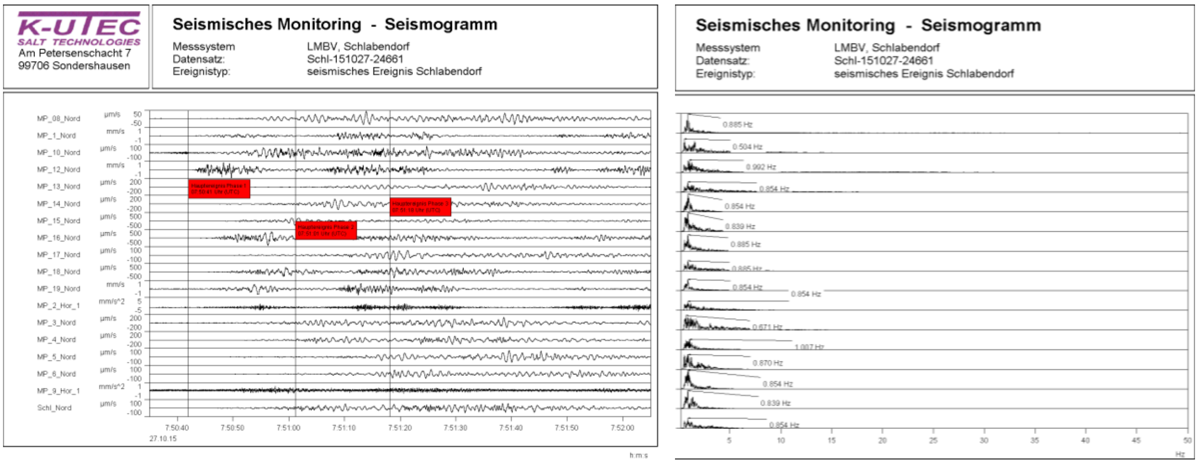

Figure 2*: seismic events and frequency parameter causing the geotechnical event*

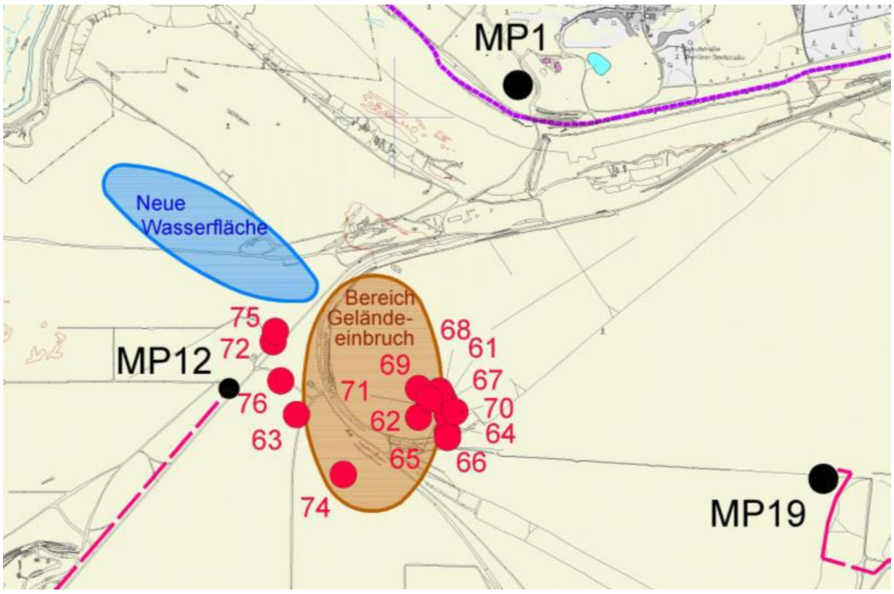

Figure 3*: seismic localization compared to the slides residues on the surface*

With help of the discovered parameters, it should be possible to support the geotechnical model of the inner burden dump as well as to help to understand the processes, which lead to such slides. After almost two years of seismologic monitoring, it seems that the accompanied weather conditions have a great influence on the potential for such slide hazards (Terrain Deformation Hazards). Most of the events occur during the "wet" seasons in spring or autumn. During this time the groundwater level rose which could have supported the slide hazard.

Key words: inner burden dump, groundwater level, slide hazards (Terrain Deformation Hazards), seismo-logic events, soil-liquefaction

Forecasting the water disaster for coal mining under sea area in the Beizao Coalmine, Shandong Province, China

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Abstract

This paper presents a case study of risk assessment for coal mining under sea area in the Beizao Coalmine, Shandong Province, China. The coalmine is facing the risk of sea water inrush hazards because most of its panels under the Bohai Sea. To forecast water disaster, three important factors, including efficient aquifuge, water flowing fractured zone and the water pressure bearing capacity of aquifuge, are considered to assess the mining safety situation for Panel H2301 in the Beizao Coalmine. The efficient aquifuge is identified by lithological analysis and water chemical comparison between sea water and groundwater. The water flowing fractured zone under different mining conditions is obtained by statistically analyzing the field measurements, physical and numerical simulation. A formula is derived to calculate the height of water flowing fractured zone and a forecasting model is built with the aid of GIS. On the basis of these research, the safety mining condition is assessed and the upper mining limit of Panel H2301 has been proposed.

Key words: mining under sea area; risk assessment; water disaster forecast; underground water inrush

1 Introduction

There are over 2.5 billion tons of coal resources located under surface water bodies in China. In recent years, China has been a rich experience of coal mining under water body such as lake, river and reservoir (Compilation Commission 1997), (Sun YJ et al. 2008, 2009), (Xu ZM et al. 2010), (Liu CY et al. 2010), (Wu X et al. 2009), (Peng K et al. 2011). Coal mining under surface water has been successfully done in some locations but there have also been many water-inrush disasters caused by the surface water when the overburden strata were damaged by the coal mining.

In addition, there are six countries having the experience of coal mining under the sea area all over the world, they are Britain, Australia, Chile, Japan, Canada and China. At the early 1980s, nearly 60% of the coal production from 15000 of the underground coalmines in Britain was extracted from the sea area. Coal production from the sea area of Japan and Australia also accounts for a large proportion of the national coal production. In these countries, due to the special coal mining under the sea, mining activities were managed strictly by the government regulations and orders (John W et al. 1982), (Holla.Laxminarayan 1987), (Niskovskiy Y et al. 1996), (D.Robert Gill 2000), (Singh R N et al. 2001), (Singh R N et al. 2001), (Gandhe A et al. 2005), (Winter T C et al. 2008), (Winter T C et al. 2008), (Sun YJ et al. 2008, 2009), (Xu ZM et al. 2010).

Beizao Coalmine, which involves the first practical example of coal mining under the sea area in China, located in the northern part of Longkou city, Shandong Province, is facing a great risk of sea water inrush hazards. The situation of Beizao Coalmine is shown in Fig. 1.

Previous studies have elucidated the occurrence of overburden-rock failure and of water conduction through pathways arising from coal mining activities. The distribution of the “three zones” and empirical formulas for predicting rock failure height, as well as safety measures for mining under water bodies, have been discussed by different researchers (Liu TQ 1995). Current prediction methods for water flowing fractured zone have: field measurements, simulation experiments (physical simulations or numerical simulations) and theoretical analysis.

At present, there are many theories and methods: Neural Network Method, Four-Zone Theory, Multi-sources Information Fusion Method, Vulnerable Index Method and so on, which concerning the risk assessment for mine water inrush including water inrush from the surface water bodies. However, the water inrush assessment method from the surface water bodies has its own limitation because it considers few factors. Geographic Information System (GIS), is a multivariate method, which could study and management of spatial data. Supported by computer software and hardware, it can deal with geo-spatial data by geographical coordinates or spatial location for a variety of processing (Compilation Commission 1997), (Sun YJ et al. 2008).

This paper presents a case study of risk assessment for coal mining under sea area in the Beizao Coalmine, and deals with three key scientific problems: features of efficient aquifuge, height of the water flowing fractured zone and the water pressure bearing capacity of aquifuge, to present the water disaster forecasting results. On the basis of these researches, a forecasting model is built with the aid of GIS, and the safety mining condition under the Bohai Sea is aseessed and the upper mining limit of Panel No.H2303 has been proposed.

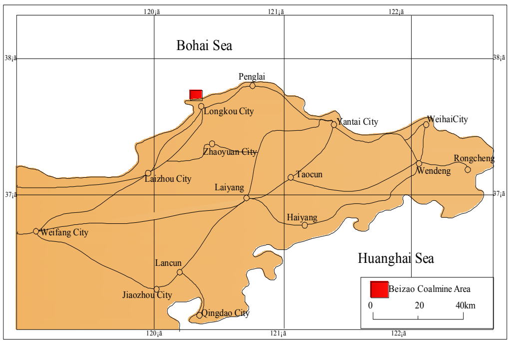


***Figure 1** The situation of Beizao Coalmine in Shandong Province*

2 Geological Background

The major coal seam to be excavated in Beizao Coalmine is number 2 located in the Lower Tertiary System and the thickness ranges from 3.84 to 5.93 meters. The overburden rock consists of mudstone, sandy mudstone, calcareous mudstone, oil mudstone and oil shale, which are easy to be expanded when mudding and have perfect water insulation. The inflow of mine water ranges from 25 to 30 m^3/h, among which the maximum is 42 m^3/h when the aquifer was exposed in Beizao Coalmine.

The thickness of the overburden rock of No.2 coal seam is about 100 meters, which can usually interrupt hydraulic connection between coal measure strata and Quaternary water. According to the marl water observation results in Beizao and Liangjia Coalmine, the marl water level is decreased by almost 30 meters slowly, while the water level in Quaternary isn't change. This result shows that there isn't any significant hydraulic connection between Quaternary water and marl and marl-inter-bedded water.

3 Efficient Aquifuges

The effective aquifuge is an impermeable seam which can prevent sea water from infiltrating into the coal mine. The effective aquifuge from top to bottom determines the infiltration limit interface of the sea water. In order to make sure of the reliability of the infiltration limit interface, a rock-phrase analytical method was applied and data from all boreholes were analyzed. As a result, the impermeable mudstone of the first aquifuge of Quaternary was determined to be an effective aquifuge (see Fig. 2).

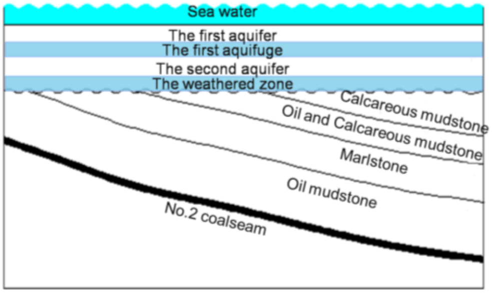


***Figure 2** The effective aquifuge in Beizao Coalmine*

After that, the characteristics of the Hydrochemistry for aquifer on the No.2 coalseam at Beizao Coalmine were described by Piper diagram (see Fig. 3) based on the Ion millinormal percent.

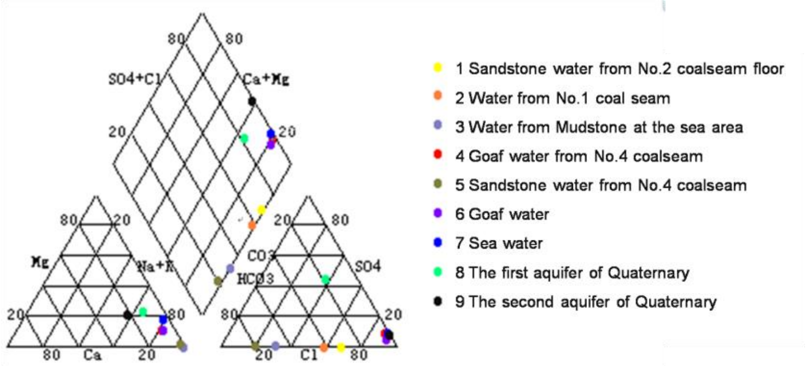


Figure 3 *The Piper diagram of Hydrochemistry*

Fig. 3 shows that, the water quality of aquifers near the coalseam locate at the lower right of the diagram, with the decreasing millinormal percent of HCO_3^- and increasing millinormal percent of Cl^- respectively. The Runoff conditions become worse and worse with the increasing depth of the aquifer. However, the goaf water from the No.4 coalseam roof and the sea water locate at the high right of the diagram. The Cl^- and Na^+ of these samples account for 80% of millinormal percent. Although the differences of Ion millinormal percent between goaf water and sea water were not obvious, the salinity of goaf water and sea water show a huge gap. The salinity of three samples were 17 g/L, 20.6g/L and 30.7g/L. The water quality of Quaternary water, coal seam water and sea water were different from each other. The first aquifer of Quaternary and the second aquifer of Quaternary also indicate different deposit conditions.

The first aquifuge, with the lithological composition of mainly clay and sandy clay ,and a thickness about 20 metres, effectively obstructs hydraulic connection between the first and the second aquifer. However, no sea water was found in the rocks below the first aquifuge, indicating that the effective aquifuge is reliable.

4 Water Flowing Fractured Zone

To obtain reliable data of the height of the water flowing fractured zone, we first established a numerical simulation model and calculated the heights of the fractured zone for the Beizao Coalmine. Secondly, field measurements were used to verify the calculated results and to acquire more data of the water flowing fractured zone.

Studies of the failure process and range in the overburden rock after coal mining have been done. Numerical simulations are often the first choice for these studies. The plastic zone and the stress, which are often chosen when estimating the range of water-flow fractured zone. The Fast Lagrangian Analysis of Continua (FLAC) (Sun YJ et al. 2009), (Xu ZM et al. 2010), developed a few years ago, has been parametrized and used with some success.

A numerical model was created following the known structure of the overburden stratum of panel No.H2301 of Beizao Coalmine. The model for the panel No.H2301 is 1000 m×660 m×270 m in size and had 11 overburden strata (Fig. 4). The specific physical parameters associated with each stratum are listed in Table 1.

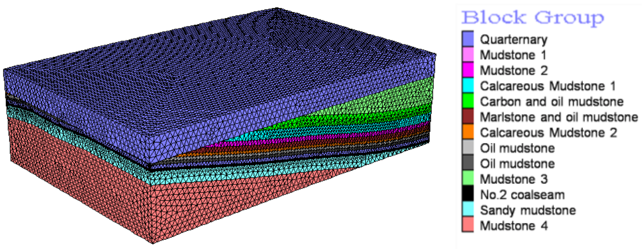
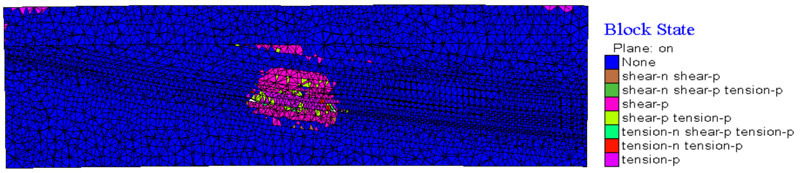


Figure 4 *Simulation model*

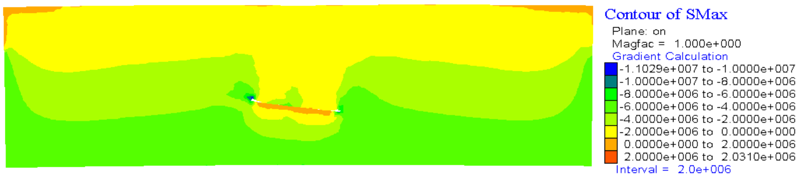
***Table 1** Physical and mechanical parameters of the overburden rock of panel No.H2301*

Rock	Thickness (m)	Tensile strength (MPa)	Compression strength (MPa)	Density (N/m³)	Elastic modulus (MPa)	Poisson's ratio	Friction angle (°)
Quarternary	65	0.002		20000	10	0.3	34.5
Mudstone 1		0.1	1.5	20100	160	0.28	33.2
Mudstone 2	30	0.2	16.72	20250	2300		32
Calcareous Mudstone 1	25	0.66	20.4	23000	1400	0.13	37.0
Carbon and oil mudstone	13	0.88	9	20000	1200	0.22	30.5
Marlstone and oil mudstone	13	0.08	1.4	26000	75	0.13	36
Calcareous Mudstone 2	8	0.75	15	25000	1000	0.3	28.4
Oil mudstone	8	0.47	4.7	18000	800	0.15	38
Oil mudstone	8	0.56	35.8	18000	900	0.28	40.3
Mudstone 3	8.5	0.02	22.8	20250	200	0.34	26.3
Oil mudstone	1.5	0.4	30	18000	350	0.26	27
No.2 coalseam	6	0.4	4	15000	40	0.33	29.5
Sandy mudstone	40	1.5	25	24000	1900	0.32	33
Mudstone 4		0.66	20.4	20250	2300	0.29	37.0

The simulation concentrated on the failure of the overburden rock. The height of the water flowing fractured zone was obtained by analyzing the plastic zone and the stress distribution.



***(a)** Plastic zone distribution*



***(b)** Stress distribution*

***Figure 5** Plastic zone and stress distribution*

Figs. 5a and b show that the changed plastic zone in the overburden rock, subsequent to coal mining, visually indicates the range of disturbance in the overburden. The plastic zone increases as the mined area moves when mining to 150 m the plastic zone increases continuously to reaches a maximum of 55 m.

Then, the field measurements are used to validate the height of the water flowing fractured zone in this research. The field measurements method and the actual data showing the failure range under specific conditions in the four Coalmines, which have the similar geological and hydrological condition, at Longkou coalmining area are shown in the manuscript of ISCEG-Shanghai 2012 (Xu ZM et al. 2012).

5 Water Pressure Bearing Capacity

The water pressure bearing capacity of the overburden rock was assessed with a certain thickness and properties, especially the bearing characteristics of the protective layer, by collecting the physical and mechanical parameters of the over-burden layer of the No.2 coalseam in Beizao Coalmine. As mentioned before, the first aquifuge, with a thickness about 20 metres, in Quaternary was determined as the effective aquifuge under the sea area. According to the evaluation method of security barrier thickness under confined roof in 'Handbook of mine geological work', the rock between water flowing fractured zone of panel No.H2303 and the first aquifuge in the lower sea water interface can look as water barrier, with a thickness about 39metres. Then compared with the required minimum thickness of the security barrier under seawater head pressure to decide whether the practical effective thickness meets the requirements for bearing seawater head. Evaluation formula is as follows:

$$H = \frac{AL}{4K}(\sqrt{r^2 L^2 + 8KP} + rL) \tag{1}$$

where H is the safety thickness of the aquifuge (m), P is water pressure (MPa), L is the width of the panel (m), K is the tensile strength of rock (MPa), r is the density of rock (kg/m^3) and A is the safety coefficient (ranges from 1.2 to 1.5).

The parameters of the panel No.H2303 are substituted into Eq.1, the required minimum thickness of the security barrier under the current sea water head pressure is 7.6 metres, which is much smaller than the thickness of the effective water barrier (39 metres).

According to the evaluation of water pressure bearing capacity of aquifuge, the leaving water barrier in panel No.H2303 is safety and can ensure safe mining.

6 Assessment for the Upper Mining Limit

The concept of the model for water inrush while mining under surface water is that water conducted fissures or cracks destroy the aquifuge and water percolates into coal mines through these fissures or rock cracks. On the other hand, mining under surface water will be safe if there is an effective aquifuge with a sufficient thickness between the lower limit interface of surface water infiltration and the upper limit interface of rock cracks resulting from mining.

Therefore, the upper mining limit assessment model from the basis of these researches (Xu ZM et al. 2012) and the National Regulations can be built by applying GIS as follows:

$$H_{sx} = H_Q - 3m - 58.26 \cdot (1 - e^{-0.3m}) \tag{2}$$

where H_{sx} is the level of the upper mining limit (m), H_Q is the level of the Quaternary bottom (m), m is the mining thickness (m).

According to the overburden rock structures of panel No.H2303, the level of the Quaternary bottom is -76m. On the basis of these researches, the safety mining condition the Bohai Sea is aseessed and the upper mining limit of Panel No.H2301 has been proposed as shown in Fig.8.

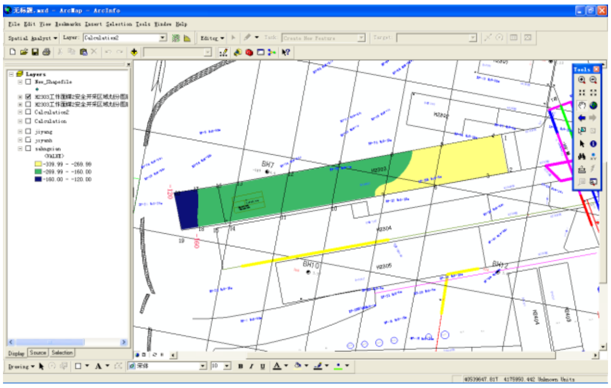


Figure 8 *The section map of the upper mining limit for panel No.H2303*

Fig. 8 shows a schematic map indicating the upper mining limit for panel No.H2303. An indication of the mining condition shows that the upper mining limit for 6 metres' mining thickness is -160m and the upper mining limit will up to -130m when the mining thickness decrease to 3 metres.

Lastly, the predicted result has been successfully applied to decision making at the panel No.H2303 in Beizao Coalmine when coal mining under the Bohai Sea. This is the first practical example of coal mining under the Bohai Sea in China and it provides a successful experience for evaluation and application of coal mining under large surface water body.

7 Conclusions

1) The effective aquifuge of sea water infiltration is the first aquifuge, an impermeable layer of mudstone of Quaternary, which effectively obstructs hydraulic connection between the Bohai Sea water and the overburden rock of the No.2 coalseam. Its reliability is verified by hydrochemistry analyzing.

2) The results of our field measurements and numerical simulation show that the range of the overburden rock failure zone shows an exponential relation with the coal thickness to be excavated. A new formula has been derived and used to calculate the maximum height for the water flowing fractured zone.

3) On the basis of these researches, a forecasting model is built with the aid of GIS, and the safety mining condition under the Bohai Sea is aseessed and the upper mining limit of Panel No.H2303 has been proposed.

Acknowledgements

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Advances in Techniques and Equipment of Mine Water Prevention and Control in China

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Extended Abstract

In China, under the effective supervision and management of state administration of Coal Mine safety, coal mine water disasters decline sharply. However, shallow coal resource is dried up gradually, so coal companies turn to deep coal resource. Generally, the deeper the coal mines locate, the more complex the hydrogeological condition is, and the harder water hazard prevention and control work is. In such conditions, large coal mine water inrush disasters still occur frequently in some coal mine areas. In order to control mine water hazard thoroughly, mine water researchers still have a long way to go.

The aim of this study was to illustrate the features of coal mine water disasters, identify the problems of present water hazard control technology and equipment, as well as introduce some new techniques and equipment of mine water prevention and control. To achieve this goal, the investigation of mine water disasters was conducted, the advances of mine water control was analyzed, and the strategies for improving water hazard control were developed.

In this paper, the features of coal mine water disasters were elaborated based on some statistical data, which include: 1) extremely large mine water disasters still occurs a lot; 2) the main sources of water inrush are goaf water and karst water; 3) mine water disasters mostly occur in private or township coal mines; 4) mine water disasters mostly occur in the process of driftage.

In addition, advances in techniques and equipment of mine water prevention and control, which include geophysics techniques and equipment, drilling techniques and equipment, hydrogeochemical detection techniques and equipment, mine water disaster control techniques and equipment, etc., were introduced.

In order to solve the peoblems caused by mine water hazard, some science and technology countermeasures were developed to prevent and control mine water disasters, which can be briefly summarized as studying basic theories, developing key technology and equipment, constructing research and development platform, and strengthening safety management.

Key words: Advances in Techniques and Equipment; Mine Water Hazard; Mine Water Prevention and Control; Geophysics; Drilling

CHAPTER 11

Hydrogeological and Hydrogeochemical Modelling

Diagnosis of Operating Mine Dewatering Wells Efficiency through Groundwater Modelling

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Abstract

Pumping wells are used to dewater operating mines at various sites around the world. The usual objective of the pumping from dewatering wells is to intercept most of the groundwater flow such that only a small amount of residual inflow would reach the mine.

Decrease of pumping wells production usually occurs over time [1] either due to the extent of the groundwater level drawdown around the mine and depletion of the aquifer storage, or to decline of the well efficiency because of deterioration of the well installation. Therefore, decrease in the pumping rate in a dewatering well does not necessary means that the latter requires rehabilitation or replacement. Borehole rehabilitation or replacement is often costly and should be carried out only if justified upon diagnostic of the reasons behind the decline in the pumping rate.

In ideal world, dewatering wells are designed taking into account the hydraulic and physical properties of the target geological formations, and their efficiency estimated upon installation and commissioning. During the mine operation the efficiency of dewatering wells is (or should be) estimated/reassessed regularly to enable better planning of borehole maintenance and replacement where necessary. However, such procedures are not usually implemented and in some cases even measurements of pumping rate and water level in the wells are not collected.

Assessment of dewatering wells efficiency during the mine life is usually carried out using pumping tests and down-hole surveys. In some circumstances such costly field tests, which may also interfere with the dewatering operation, are not necessary for all dewatering wells. This paper presents an alternative desktop-based approach for an initial diagnostic of the dewatering wells efficiency and a case study is given for an operating pit. The method consists of using groundwater models to simulate the pumping potential of dewatering wells over time. The estimated achievable pumping rate from a dewatering well is then compared to the actual/observed rate to verify if the well is operating at the expected level. The results of the model can be used by the mine managers to decide if there is need or not for down-hole surveys and borehole rehabilitation or replacement. The results enable more efficient planning of the field work based on the predicted pumping potential of each well, and the priority areas identified by the model as potential source of the residual inflows of groundwater into the mine.

Key words: Mine dewatering, numerical groundwater modeling, pumping well efficiency

Introduction

For many operating mines around the world, active dewatering wells are required for one or more of the following reasons:

- To reduce residual inflows into the mine to manageable level;
- To reduce cost of water treatment and discharge constraints;
- To improve mine stability and steepen the slope angles to save cost;
- To improve the productivity of the mine (e.g. improve blasting and loading efficiency);
- To improve safety of the mining operation.

One of the common methods of mine dewatering is the use of vertical pumping wells. Therefore in order to achieve the desirable objectives of dewatering, the pumping wells efficiency must be kept at acceptable level. However, it is evident that the pumping rate of dewatering wells declines over time for various reasons, some of which are not related to the borehole condition or efficiency.

Water well pumping efficiency is defined as the ratio of aquifer loss (drawdown) in the well to the total loss (total measured drawdown) in the well during pumping ([2], [3], [4]). It reflects the capability and resistance of the well installation to transmit water from the surrounding aquifer to the pump. The total drawdown is the sum of linear aquifer losses and the linear and non-linear well losses. The pumping well efficiency is estimated from step pumping tests data with the help of equations such as the Hantush-Biershenk [5] and Rorabaugh [6] equations.

In principle, pumping tests are (or must be) carried out regularly in dewatering wells to estimate the efficiency of the dewatering wells over time. This is a reliable method to quantify the well efficiency and thus assess the degree of its deterioration over time. However, pumping tests are costly, especially in projects where many wells exist, and may interfere with the dewatering operation itself. Furthermore, in some circumstances, the tests may not provide accurate results due to interference between the dewatering wells and the potential effect of other boundary conditions.

Considering the cost and complication related to pumping tests, as highlighted above, groundwater modeling can be used as an initial tool to assess the efficiency of the dewatering wells, before any field work is undertaken. The model results may help reduce the number of dewatering wells to be tested, rehabilitated or replaced. This is due to the fact that in some cases the decline in dewatering well productivity is due simply to aquifer drawdown, or other natural factors such as heterogeneity in the geological formation(s) or anisotropy in the aquifer thickness.

In this paper a case study is presented in which groundwater modeling was carried out to simulate an operating mine dewatering system. The results corroborate some of the assumptions above and highlight the importance of groundwater flow modeling in guiding the planning of dewatering wells rehabilitation and replacement and reducing cost.

Discussion

Mine hydrogeological setting and dewatering system

The site is located in a former-soviet country, and consists of an operating pit around 1 km wide and 2 km long (**Fehler! Verweisquelle konnte nicht gefunden werden.**). The mine has been operating for seven years and the operating depth is 120m, with the target final depth being 500m. The ore body is covered by a sedimentary overburden material of thickness varying between 50m and 70m, made up of a succession of sand and clayey formations arranged as follows, from top to bottom (Figure 2):

(1) A layer of alluvium sands and silt;

(2) Clayey Siltstone;

(3) Clay; and

(4) Sands.

In addition to the main stratification above, various intercalations and horizontal heterogeneities exist within the layers. The ore body is hosted in the crystalline rock formation, beneath the overburden series.

As indicated above, the overburden material contains two sand aquifers separated by impervious clayey material. The thickness and bottom elevation of the aquifers vary across the site. The presence of two aquifers with high storage capacity and hydraulic conductivity required the use of dewatering wells to reduce groundwater inflows into the pit. The total observed inflow of groundwater (pit and dewatering wells) is about 60,000m^3/day. Because of the presence of clayey material between the two aquifers there was need to install two sets of dewatering wells, each targeting a specific aquifer (**Fehler! Verweisquelle konnte nicht gefunden werden.**). Accordingly, a total of 85 wells were installed in the top aquifer to an average depth of around 25m, whilst 77 wells were installed in the deep aquifer to an average depth of about 75m.

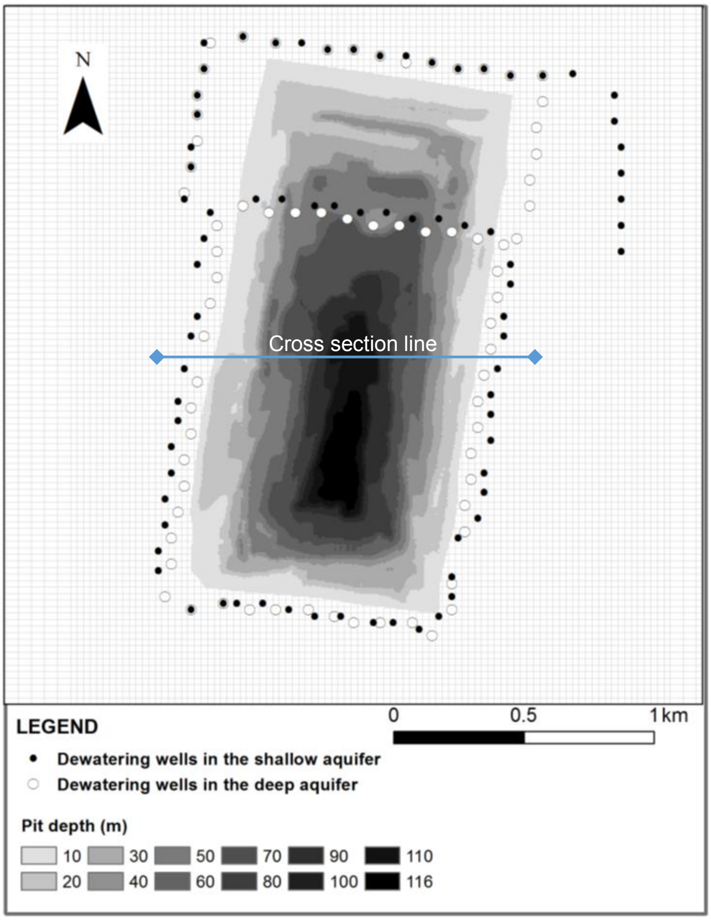

Figure 1 *Configuration of the pit and the dewatering wells in the shallow and deep aquifers.*

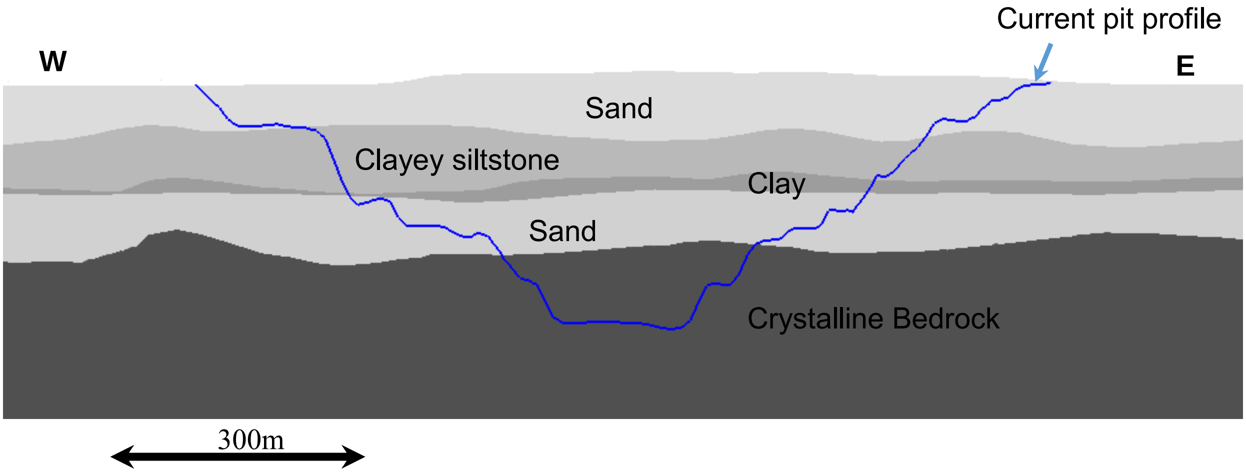

Figure 2: *East-West geological section across the pit (vertical exaggeration: 3x)*

The pumping wells were not properly tested initially (upon completion of the installation) to determine the initial well efficiency and monitoring of the pumping rate has not been carried out in the wells since the dewatering operation began. The dewatering wells system is divided into 7 fields, each consisting of a cluster of variable number of wells. Accordingly, the pumping discharge from each field is combined in a single pipeline that conveys water into the discharge locations along surface water streams. Monitoring of the pumping flow rates was not carried out at each pumping well, but rather at the discharge points of wellfield pipelines only, using flow meters.

Over time some of the dewatering wells started failing and the system was unable to reduce the inflows of groundwater into the pit to the desired level. Therefore, borehole rehabilitation and replacement have been carried out on a number of wells. However, due to the scale of the operation, the heterogeneity of the aquifers and the lack of accurate monitoring of the pumping rates from the dewatering wells over time, it was difficult for the mine to know which wells were not performing well and plan the rehabilitation programme properly. Therefore, it was envisaged to use groundwater modeling tools to simulate the pumping system and assess the performance of each well and prioritize accordingly the well replacement and rehabilitation work depending on the magnitude of the failure of each well and the contribution of this to the observed inflows of groundwater into the pit.

The diagnosis technique presented in this paper can be applied to other mines with complex borehole dewatering systems. It can help the mine to save cost and time by targeting the testing and rehabilitation work of dewatering wells with a particular focus on the ones that are more relevant to reducing groundwater inflows into the mine.

Groundwater Model Setup

Groundwater modeling was carried out to assess the efficiency of the dewatering wells and effectively plan the rehabilitation or replacement of the deficient wells. Modflow [7, 8] was used to simulate the groundwater flow in the project area. A regional groundwater flow model was initially calibrated for the site, and this consists of a finite-difference model with a grid consisting of 274 rows and 193 columns, and 15 layers. For the evaluation of groundwater inflows into the mine, the model grid was refined to 499 rows and 331 columns, and 15 layers. The model grid cells within the open-pit and surrounding area were initially discretized to 50m x 50 m cell size in the calibration model and then refined to 12.5 m in the predictive model. The horizontal dimensions of the outer cells of the groundwater model grid range from 200 to 50 m.

The hydrogeological input parameters (horizontal (K_h) and vertical conductivity (K_v), specific storage (Ss) and specific yield (Sy)) were assigned to model cells or zones depending on the geology of the area. The parameters were estimated based on field data from borehole tests, and model calibration. Due to the lateral variation of hydraulic conductivity of the two aquifers, spatially distributed maps were generated from the pumping test results and used in the model (Figure 1).

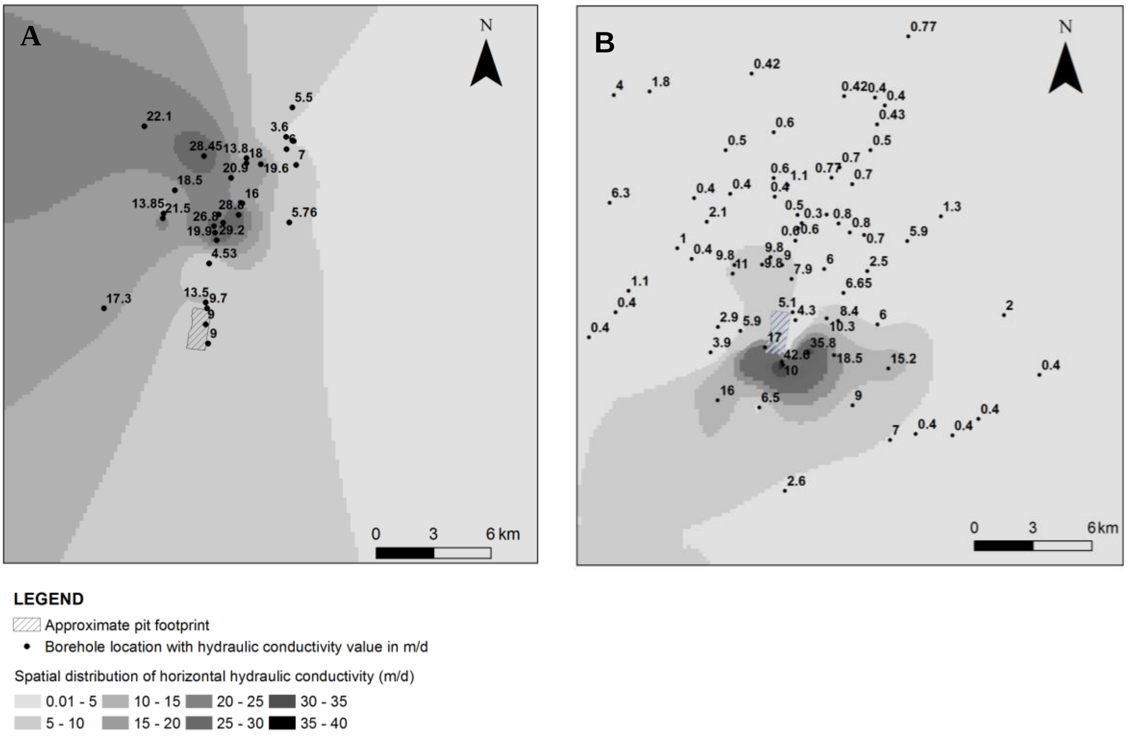

Figure 1: *Spatial distribution of hydraulic conductivity of shallow aquifer (A) and deep aquifer (B)*

The hydraulic conductivity of the top aquifer varies between 1 and 26 m/d across the model area, whilst the deep aquifer shows greater variation with values ranging between 1 and 40 m/d. The hydraulic conductivities of the shallow and deep sand aquifers vary between 3.6 and 29.2 m/d; and 0.3 to 42.6 m/d, respectively. The layer thickness (calculated from elevations of the top and bottom interfaces) of each geological formation was obtained from several boreholes across the site, and spatially distributed thickness grids prepared by interpolation of the points data and used in the model. The geological model was verified at various new borehole locations and compared to observations from the pit excavation to confirm the accuracy of the layers configuration.

The spatial variation of the above hydraulic parameters and aquifer thicknesses have significant impact on the dewatering wells yields and therefore the groundwater model is an effective tool to combine these parameters and simulate inflows into the dewatering wells and the pit.

Simulation of the dewatering system

Because the initial groundwater level at the pit location was only less than 5m below the ground surface, active dewatering, using vertical wells, has been carried out since the start of the mine excavation. Locations of the dewatering wells targeting both aquifers are shown in **Fehler! Verweisquelle konnte nicht gefunden werden.**. For the calibration of the model, simulation of the borehole dewatering system was carried out using Modflow "Well" package. The wells were started and shut-off in the model according to the actual operation schedule provided by the mine, as shown for the shallow wells in **Fehler! Verweisquelle konnte nicht gefunden werden.**. The pumping rates assigned to the dewatering wells were either provided by the mine for the periods where such data are available, or assigned according to the capacity of the corresponding pump where no data are available.

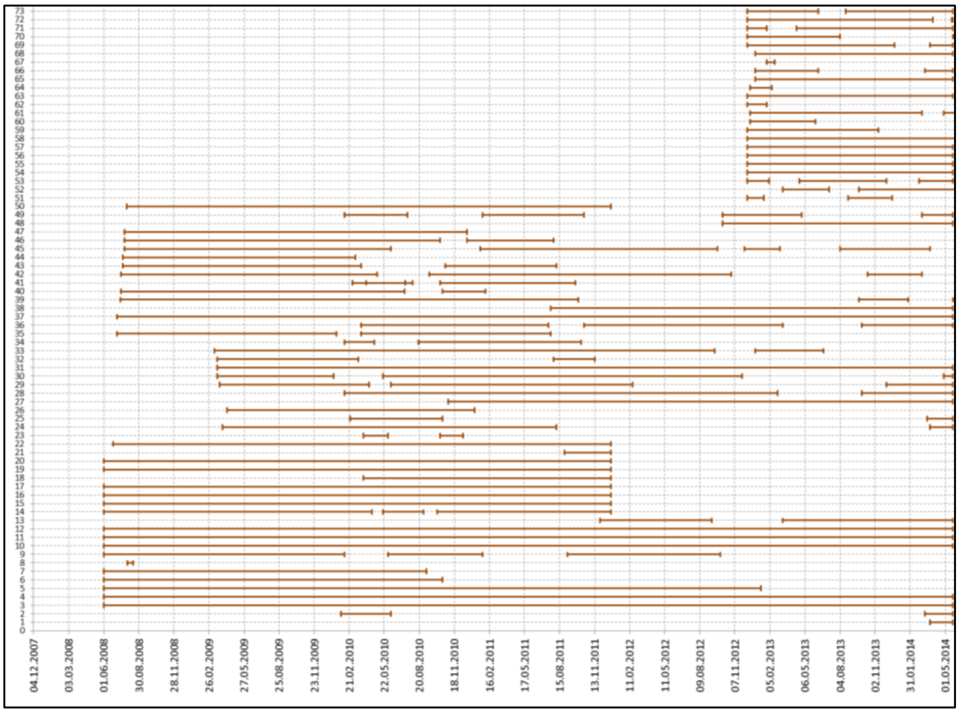

Figure 4: *Pumping schedule of the shallow dewatering wells.*

Once the model was calibrated, the dewatering wells were replaced by drain cells in the model to assess the efficiency of the wells. To ensure no restriction of flow into the well-drains, high conductance was applied to the drain cells. Several dewatering wells around the pit have been inactive and others reported to be operating at low debits. Simulation of the dewatering wells as drains for the period 2008-2014 provides an estimate of flow rate that is likely to be achieved in each well location assuming all wells are 100% efficient. The comparison between the predicted inflows into the ideal well-drains and the current/observed pumping rates in the dewatering wells provides an insight into the wells that are not functioning properly, those where the inflows are too low to run a pump, and those that are operating properly (at full capacity).

Groundwater model results and discussion

The main results of the model for estimating the well efficiency are the predicted achievable rates (inflows into the well drains) that are compared to field dewatering well records. The following criteria are applied to assess if the existing dewatering wells are efficient or not:

- The minimum threshold of 10m^3/h has been applied, which means a well is put in operation only if the flow rate is 10m^3/h or more. If the actual pumping rate from a dewatering well in 2014 is equal or more than what is predicted by the model, or it is lower but by less than 5m^3/h, the well is considered efficient and acceptable.
- If the achievable pumping rate predicted by the model in an operating well is more than 10m^3/h AND at least 5m^3/h higher than the operating rate of 2014, this indicates that the well needs either rehabilitation or replacement.
- If the achievable pumping rate predicted by the model in a well that is indicated as inactive from the database, is more than 10m^3/h, this indicates that such dewatering well needs replacement if it is inactive because of being dry.
- If the predicted flow rate is less than 10m^3/h the well is considered as not needing replacement because the low flow rate doesnt justify active pumping.

The comparison between the predicted inflows into the ideal well-drains and the current/observed pumping rates in the dewatering wells in both aquifers allowed the identification of wells that can be considered acceptable, the wells that are actually dry and may not need replacement because the predicted inflows are too low, and the wells that possibly need rehabilitation or replacement. Based on such diagnosis, specific action (or no action) was recommended for each dewatering well. Recommendations were made to the mine to guide the rehabilitation programme, with the aim to prioritize the wells that were identified as failing and can contribute to reducing significantly the inflows into the mine if rehabilitated or replaced. Table 3 shows a summary statistics of the diagnosis of the dewatering wells in both the deep and shallow aquifers.

As shown in Table 3, based on the efficiency criteria defined above, the following conclusions are made concerning the deep dewatering wells:

- 35.4% of the existing 65 deep dewatering wells are acceptable (this means 23 wells are operating at the expected rate). The total number of wells is 65 because some of the wells were decommissioned during the pit extension;
- 12.3% of the deep wells (8 wells) are actually dry or low yielding wells, and this is in accordance with the model prediction that these wells are expected to be dry or low yielding. Therefore these 8 wells do not need replacement or rehabilitation;
- 52.3% of the deep wells are operating at a flow rate lower than 10m^3/h or higher than 10m^3/h but 5m^3 less than expected. This means these 34 wells need either rehabilitation or replacement.

The following conclusions are made concerning the shallow dewatering wells (Table 3):

- 18% of the 61 existing shallow wells are acceptable (this means 11 wells are operating at the expected rate);
- 36% of the shallow wells (22 wells) are actually dry or low yielding wells, and this is in accordance with the model prediction that these wells are expected to be dry or low yielding. Therefore these 22 wells do not need replacement or rehabilitation;
- 46% of the shallow wells are operating at a flow rate lower than 10m^3/h or higher than 10m^3/h but 5m^3 less than expected. This means these 28 wells need either rehabilitation or replacement.

Table 3 *Summary statistics of well efficiencies based on the groundwater model results.*

Well categories according to model results	Shallow wells		Deep wells	
	Number of wells	Percentage	Number of wells	Percentage
Acceptable wells	11	18%	23	35.5%
Dry or low yielding Wells that do not need replacement	22	36%	8	12%
Wells that may need rehabilitation or replacement	28	46%	34	52.5%

It is worth noting that in some circumstances, the well flow rate predicted by the model is lower than that reported in the 2014 monitoring data. This is likely to be due to the fact that in the model the entire network of dewatering wells are assumed active (withdrawing water), contrary to reality where gaps of inactive wells exist, and therefore the wells at the edges of each gap may be withdrawing more water from the aquifer than the model shows. Part of the discrepancy would also be due to inaccurate measurements of flow rate in the well, because of lack of flowmeters, and the numerical model error but the contribution of these to the overall rate difference would be limited.

The amount of $5m^3/h$ difference between observed flow and predicted flow that was applied in the criteria above was selected to allow for the errors of both the model and the flow measurements, which are expected to be generally lower than $5m^3/h$.

Conclusions

The efficiency of dewatering wells is a very important factor in mine dewatering to keep groundwater inflow into the mine at manageable level. Usually pumping well efficiency is estimated from pumping tests. In the present paper, groundwater modeling was used instead of pumping tests to assess the efficiency of operating dewatering wells around an operating pit. Because the hydraulic parameters and the thickness and bottom elevation of the productive aquifers vary across the site, pumping rate can decline despite the efficiency of the pumping well itself. Therefore instead of pump testing all the dewatering wells, some which may be dry or low yielding due to the natural conditions cited above, groundwater modeling is a suitable tool to assess the efficiency of the wells before any field test is carried out.

The groundwater flow model was first calibrated using existing field data, and the dewatering wells were simulated using observed flow rates and according to the actual pumping schedule. To assess the efficiency of the dewatering wells, the latter were subsequently simulated as drains to estimate the achievable flow rate into the well.

The calibrated model simulation, in which drains were used instead of wells, enabled the comparison between the observed flow rate in the dewatering wells and the achievable rate predicted by the model. Such comparison allowed identification of wells that need rehabilitation or replacement, and those that are acceptable or dry because of depletion of groundwater storage and do not need replacement.

According to the pumping threshold/criteria used in this paper, the model results suggest that 52% of the existing 65 deep wells (34 wells) need either rehabilitation or replacement. For the shallow wells, 46% of the 61 wells (meaning 28 wells) need either rehabilitation or replacement.

Based on the results of the assessment of the existing dewatering wells efficiency using the groundwater model, a monitoring programme and down-hole survey were recommended for the dewatering wells that have been identified by the model as potentially deficient wells.

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Adit Dewatering at a Proposed Gold Mine: Numerical Analysis of a Large-Scale Long-Term Pumping Test

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Abstract

The high-grade gold Brucejack Project, an underground mine located in northwestern British Columbia, Canada, is in the process of being developed. Surface topography has a dominant influence on the groundwater flow system at the mountainous, remote site, which is bounded by temperate glaciers. The complex hydrostratigraphy comprises thin, discontinuous unconsolidated deposits underlain by fractured and faulted sedimentary, metamorphic and volcanic bedrock; coupled with the subarctic climate and abundant precipitation, this geologic setting leads to considerable seasonal variation in groundwater elevations.

As part of site exploration and evaluation, five kilometres of historical underground workings were dewatered and expanded over a three year period. The resulting field observations provided a dataset not typically available at such an early stage of project development – essentially a large-scale, long-term, variable-rate pumping test.

Groundwater monitoring and numerical flow modeling were completed in support of regulatory approvals and engineering design. The numerical model was developed using MODFLOW-Surfact and was calibrated in stages to available data, including seasonal hydraulic heads, vertical hydraulic head gradients, streamflow and winter low-flow estimates, and volumetric dewatering flowrates. Two distinct approaches were used to represent the underground workings in the model; a passive approach using drain boundaries, which helped to constrain estimates of hydraulic properties, and an active approach using a fracture well. Detailed calibration to observed dewatering flowrate data and benchmarking against hydraulic head response data suggested that the bulk hydrogeological properties of this complex system were well characterized and suitable for further analyses.

The calibrated groundwater flow model was subsequently used to: 1) estimate groundwater inflow rates to the proposed underground mine throughout mining operations for the calibrated, base case scenario as well as a range of sensitivity scenarios; 2) simulate groundwater discharge rates and flow paths to possible surface water receptors under pre-disturbance conditions, throughout mining operations, at closure, and in the post-closure period; and, 3) predict drawdown throughout mining operations, recovery of the groundwater system in the closure period, and steady-state water table configuration post-closure.

Key words: Mine water hydrogeology, hydrogeological modeling, water-related mine design

Introduction

Pretium Resources Inc. is in the process of developing the Brucejack Gold Project (the “Project”) at their Brucejack property located in northwestern British Columbia, Canada (Fig. 1). The Project focuses on the Valley of Kings and West Zones, which contain vein-hosted gold mineralization. Advanced exploration activities in the 1980’s saw the development of approximately 5 km of underground workings. These workings were dewatered and expanded starting in 2011.

The Project will occur over an approximately 40-year period in four phases: a 2 year pre-production (construction) phase, an 18 year operations mining phase, and a 20 year closure and a post-closure phase. Mine infrastructure will include the underground mine with associated waste rock dumps, subaqueous tailings disposal, and a plant site (Fig. 2). Water-related infrastructure will include a mine water treatment plant, surface water diversion channels, and a contact water pond.

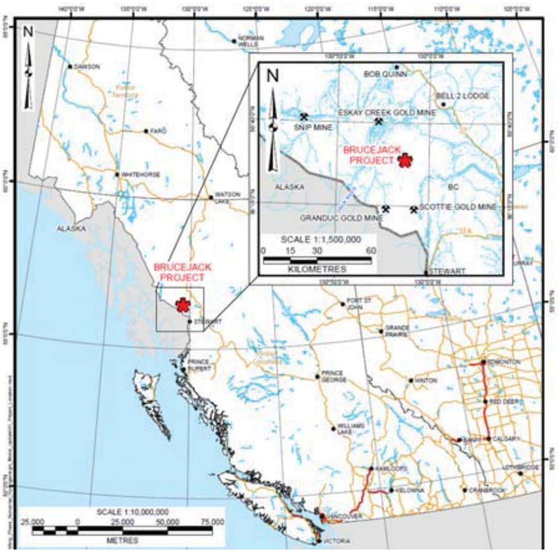

Figure 1 Brucejack Project location map

A three dimensional (3-D) MODFLOW-Surfact numerical groundwater flow model was developed for the Project, covering an area of approximately 12 km^2, to meet current industry standards and regulatory requirements.

This paper outlines the conceptual understanding of the hydrogeologic system, and describes the development of the groundwater flow model, with emphasis on the use of the unique dewatering dataset in model calibration and benchmarking.

The paper also describes the application of the groundwater model to support project feasibility assessment, and to predict the potential hydrogeologic impact of mining and groundwater extraction on surface water flows both during the operations period, and in the closure and post-closure periods.

Conceptual Hydrogeologic Model

Surface topography has a dominant influence on the groundwater flow system at the site. The elevation in the vicinity of the Project ranges from approximately 1,300 m to over 2,000 m at the highest peaks, while elevations in the modeled area descend as low as 500 m in the adjacent Sulphurets Creek Valley. Measured groundwater elevations suggest that the water table is a subdued replica of topography, with depths to groundwater typically greater in the uplands relative to the valley bottoms.

The climate in the immediate vicinity of the Brucejack Project is considered subarctic, with variable temperature and precipitation generally exceeding 1,900 mm/yr. Groundwater enters the flow system from infiltration of precipitation, snowmelt, and glacier melt, with a lesser component supplied by surface water infiltration in lakes. Groundwater discharge zones are pervasive in this high-topography environment, and include lakes, creeks, gullies, seeps and breaks in slope. In addition, the Brucejack Lake catchment is approximately 5.6% glaciated, and the Project is bounded by temperate glaciers.

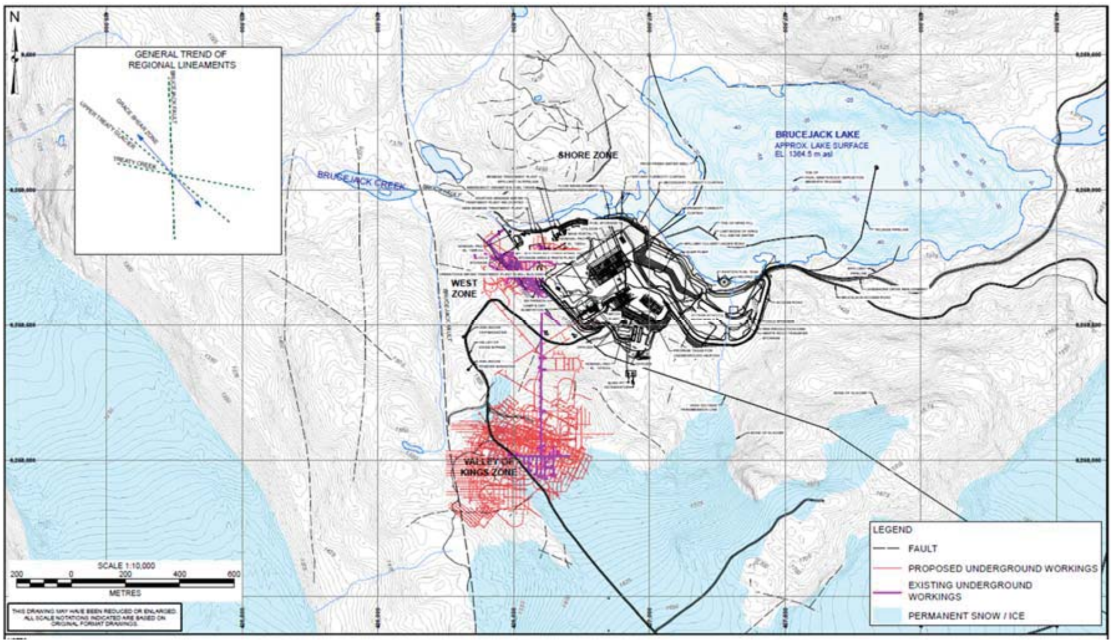

Figure 2 Brucejack Project area site plan.

The hydrostratigraphy at the site comprises a thin, discontinuous layer of glacial till or colluvium underlain by bedrock. Thicker unconsolidated deposits are confined to local sections of the valley bottom and are not present in the vicinity of the proposed underground mine. Regional bedrock can be broadly divided as follows:

- Triassic marine sedimentary and volcanic rocks of the Stuhini Group
- Jurassic sediments and volcanic rocks of the Hazelton Group
- Early Jurassic dikes, sills, and plugs of diorite, monzonite, syenite and granite, the most common of which are grouped as the “Sulphurets Intrusions”

Baseline characterization of the hydrogeologic system included completion of 67 point-scale hydraulic response tests in bedrock (i.e., slug tests and packer tests), and installation of a network of approximately 30 monitoring wells and vibrating wire piezometers. Site-wide, a general trend of decreasing bedrock hydraulic conductivity with depth is observed, although the point-scale hydraulic conductivity may vary by 2 to 3 orders of magnitude at any given depth. Based on available data there is no apparent relationship between hydraulic conductivity and the major structure in the immediate vicinity of the Project, the Brucejack Fault (Fig. 2). However, groundwater flow does appear to be influenced by the Bruce Fault, a westward trending feature that underlies Brucejack Creek at the outlet of Brucejack Lake (Fig. 2).

Numerical Groundwater Model Development

The conceptual hydrogeologic model was used as the basis for the development of a numerical model, built using the graphical user interface Groundwater Vistas (Environmental Simulations Inc. 2011) and the MODFLOW-Surfact code (Harbaugh et al. 2000, HydroGeoLogic 2012).

The elevation of the top grid layer was set at ground surface or glacier surface, where applicable. The model domain was divided into ten layers, ranging in thickness from 5 m in layer 1 to over 1,000 m below ridge tops in layer 10. The base of the model domain was set at sea level, which is approximately 1,000 m below the deepest extent of the proposed underground mine workings. Surface water features, including Brucejack Lake and local streams were represented by general head, drain or river boundary conditions, depending upon the conceptualization of the hydraulic connection of the feature to the groundwater system.

The numerical model was calibrated in stages to available hydrogeologic data collected within the study area, including: steady-state and transient hydraulic head targets; vertical hydraulic head gradients; streamflow data and winter low-flow estimates for the period 2008 to 2014; and, volumetric discharge data available from mine dewatering activities for the period 2011 to late-2014.

An iterative approach was adopted to adjust parameter values and compare results for the average annual, or steady-state simulations, and transient simulations for both seasonal and dewatering conditions, until a suitable calibration was achieved. The groundwater model was considered calibrated when good matches to hydraulic head targets and winter low-flow streamflows were achieved for steady-state simulations of average pre-disturbance conditions, while maintaining good matches to seasonal head variations, dewatering drawdowns and observed mine inflows for transient simulations representing seasonal water inputs and mine dewatering activities. This paper does not present the full numerical model calibration, but rather focuses on the calibration and benchmarking completed using the 2011 to 2014 mine dewatering dataset.

Numerical Analysis of Large-Scale Long-Term Pumping Test: Model Calibration & Benchmarking

Two distinct approaches were used to represent the underground workings in the model and gain insight from the available mine dewatering data: 1) a passive approach using drain boundaries, which helped to constrain estimates of hydraulic properties; and, 2) an active approach using a fracture well to simulate observed dewatering and benchmark against observed hydraulic head data.

Numerical Model Calibration

The fall 2013 to fall 2014 time period was selected for the transient calibration to observed mine inflows because it represented relatively controlled conditions with no injection of drilling water and static geometry of the underground workings. Drain boundary conditions (i.e., head-dependent boundaries) were used to represent the underground workings; the conductance of the drains was calculated using the Thiem solution and the Peaceman (1983) formula for calculating conductance for a borehole or underground opening. Elevations for water levels within the drain cells were specified according to the existing adit dimensions down to 1,300 m asl, the maximum depth at which dewatering occurred. The calibration simulation was run using 1-month stress periods, and a sufficient spin-up period to establish dynamic equilibrium.

While the calibration simulation did consider hydraulic head, vertical gradient, and streamflow targets, the primary objective was calibration to mine inflow data – observations that represented a large-scale test of the hydraulic response of the rockmass to pumping stresses. These calibration data reflected an integration of the influence of all hydraulic parameters impacting flow to the subsurface workings over an extended period of time. Furthermore, because the existing exploration workings were coincident with sections of the proposed mine workings, the observed responses and inflows are considered to be the most representative available data for predicting future conditions and behaviour.

Close agreement between simulated and observed mine inflows was achieved (Fig. 3).

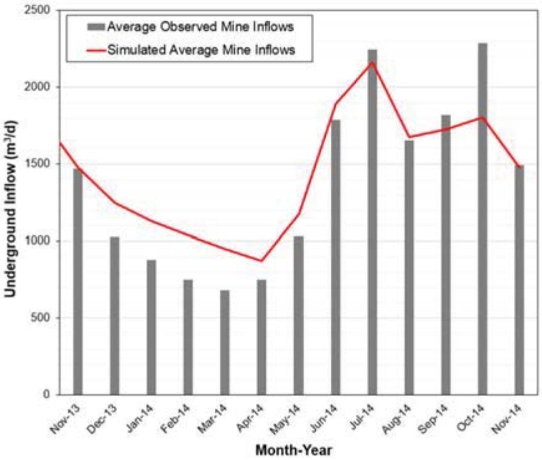

Figure 3 *Model-predicted mine inflows vs. monthly average observed mine inflows for the period November 2013 to November 2014.*

Simulated flow to the underground workings (i.e., flow to drain boundaries representing the workings) varied from approximately 900 m^3/d to 2,200 m^3/d over the fall 2013 to fall 2014 period. The lowest observed and simulated inflows occur in late-winter, before seasonal recharge associated with snowmelt commences, and the highest inflows occur during summer and early-fall. The bi-modal distribution of predicted summer and fall inflows is driven by the temporal distribution of recharge.

Numerical Model Benchmarking

Transient model benchmarking was completed for the period fall 2008 to fall 2014 to further evaluate the transient response of the model to underground dewatering. The benchmarking simulation comprised 57 individual stress periods; seasonal 6-month stress periods were used to represent the period from November 2008 to May 2010, and 1-month stress periods were used thereafter.

The Fracture Well (FWL) package available in MODFLOW-Surfact was used to simulate pumping from the underground workings. A vertical FWL was assigned within the centre of the existing underground workings, with an average radius of 2 m and a well screen from 1,390 m asl to 1,200 m asl. Due to the large radius of the adit, wellbore storage effects were incorporated. Model cells in layers 2 to 7, within which the existing workings fell, were assigned enhanced hydraulic conductivity to allow water to freely drain into the simulated well.

Average monthly pumping rates were specified using the FWL package for the period November 2011 to January 2012 and August 2012 to November 2014 (i.e., specified rates corresponded to observed pumping from the underground). An exploration drift was advanced at the site over the spring 2013 to fall 2013 period to extract a bulk sample for resources estimation purposes; the associated evolution of the underground workings was simulated in the numerical model using the MODFLOW-Surfact time-varying properties (TMP) package, which allows for the transient modification of hydraulic parameters.

A summary of the simulated and observed transient response to dewatering is provided in Table 1, and selected time series plots of simulated and observed hydraulic head responses are provided as Fig. 4. Head offsets are generally present at each calibration target location, but the groundwater time series plots illustrate that the numerical model successfully captured observed seasonal fluctuations in hydraulic head in addition to overall decline in hydraulic head in response to dewatering. This good representation was achieved despite temporal and spatial complexity introduced by irregular drilling activities, variable dewatering rates, seasonal recharge and geological uncertainty.

***Table 1** Summary of model-simulated and observed transient head response to mine dewatering.*

Well ID	Observed Responses			Simulated Responses		
	Maximum (m asl)	Minimum (m asl)	Range (m)	Maximum (m asl)	Minimum (m asl)	Range (m)
1A	1367.6	1314.7	52.9	1381.2	1328.0	53.2
1B	1369.1	1346.5	22.6	1379.2	1336.5	42.6
2A	1374.0	1361.8	12.2	1388.5	1365.3	23.1
3A	1369.4	1345.7	23.7	1368.1	1340.3	27.8
3B	1369.8	1358.4	11.4	1364.6	1347.3	17.3
4A	1383.6	1372.5	11.1	1382.4	1372.6	9.8
4B	1382.6	1364.7	17.8	1384.3	1373.2	11.1
5A	1527.0	1457.5	69.5	1517.3	1454.4	62.9
5B	1530.8	1475.7	55.1	1519.4	1454.3	65.2
6A	1378.5	1364.6	13.9	1371.2	1365.9	5.4
6B	1368.8	1363.4	5.4	1372.7	1367.4	5.3
8A	1392.2	1370.2	22.0	1387.4	1352.6	34.8
8B	1394.3	1365.4	28.9	1387.3	1352.3	35.0
9B	1487.1	1469.1	18.0	1488.2	1404.9	83.3
12A	1538.4	1485.0	53.4	1545.9	1489.9	56.0
DH19	1300.9	1358.7	57.9	1384.8	1257.6	127.2
SU77	1352.6	1464.1	111.5	1502.4	1447.1	55.3
SU82D	1475.7	1514.8	*	1525.2	1458.2	67.0
SU82S	1516.8	1534.6	*	1490.3	1442.7	47.6
SU88D	1326.6	1364.8	38.2	1363.7	1348.8	14.9

* Insufficient data (i.e., less than one year of observed heads) were available and therefore no observed range is presented.

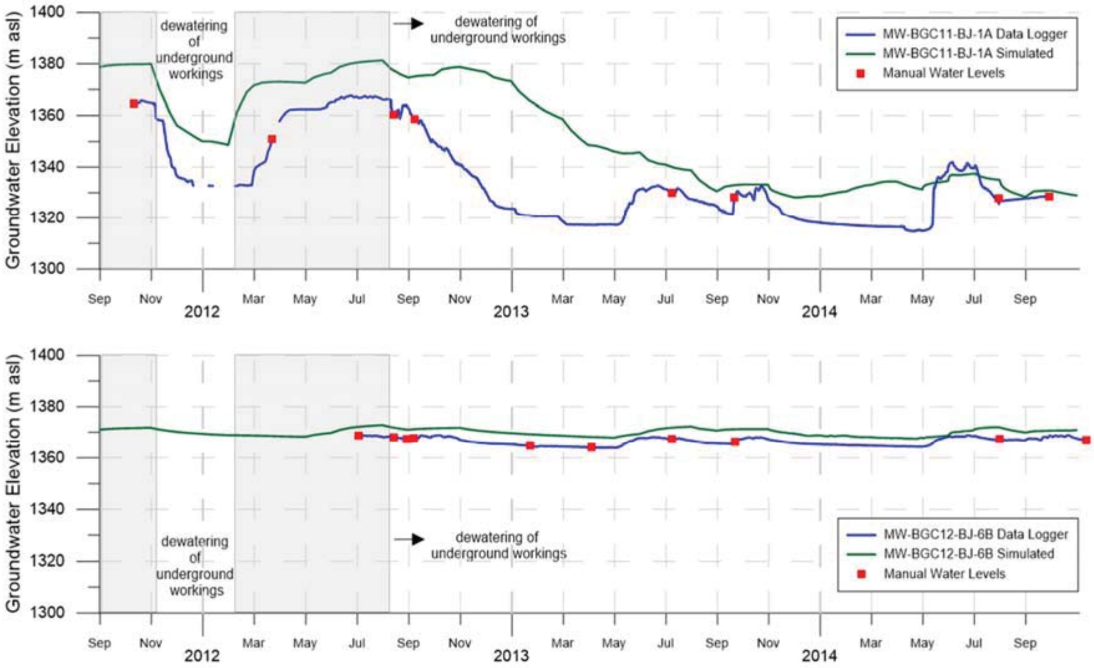

***Figure 4** Groundwater elevation time series plots showing observed and model-simulated response to underground dewatering at wells 6B and 1A.*

Numerical Groundwater Model Application

Evaluation of the results of model calibration to both pre-disturbance and post-disturbance conditions, and benchmarking to adit dewatering and transient head response suggested that the numerical representation of the hydrogeologic system was suitable for further predictive analyses.

The calibrated groundwater flow model was subsequently used to: 1) estimate groundwater inflow rates to the proposed underground mine throughout mining operations for the calibrated, base case scenario as well as a range of sensitivity scenarios; 2) simulate groundwater discharge rates and flow paths to potential surface water receptors under pre-disturbance conditions, throughout mining operations, at closure, and in the post-closure period; and, 3) predict drawdown throughout mining operations, recovery of the groundwater system in the closure period, and steady-state water table configuration post-closure.

Numerical Model Predictive Simulation Results

With the advent of mining operations, groundwater flow in the immediate vicinity of the Brucejack Project is predicted to become largely directed towards the dewatered mine workings. The average annual rate of groundwater inflow to the underground workings is predicted to remain relatively stable throughout operations, ranging between 2,500 m^3/d and 3,500 m^3/d. The overall average flow for the entire simulated mining period is 2,900 m^3/d, and model-simulated groundwater inflow to the underground workings is predicted to vary seasonally by about 2,000 m^3/d.

The elevation of the water table is predicted to be drawn down substantially throughout operations – up to approximately 400 m within the footprint of the underground workings (Fig. 5). By the end of mine life, drawdown contours are predicted to propagate over an area 2 to 3 times the size of the mine footprint, and the cone of depression associated with 10 m or more of drawdown due to mine dewatering has an areal extent of approximately 2 km by 3 km (Fig. 5).

In general, the surface water features closest to the proposed underground mine are expected to be most impacted by mine dewatering. Changes in groundwater discharge to surface water receptors was measured as a function of predicted baseflow to select monitoring points and/or gauging stations in the proximity of the Project (as groundwater baseflow was interpreted to be the sum of net groundwater flow to boundary conditions upstream of these points). A 20% reduction in average baseflow reporting to the adjacent gauging station on Brucejack Creek throughout mining operations was predicted, with some streams or reaches of streams receiving no groundwater discharge during operations.

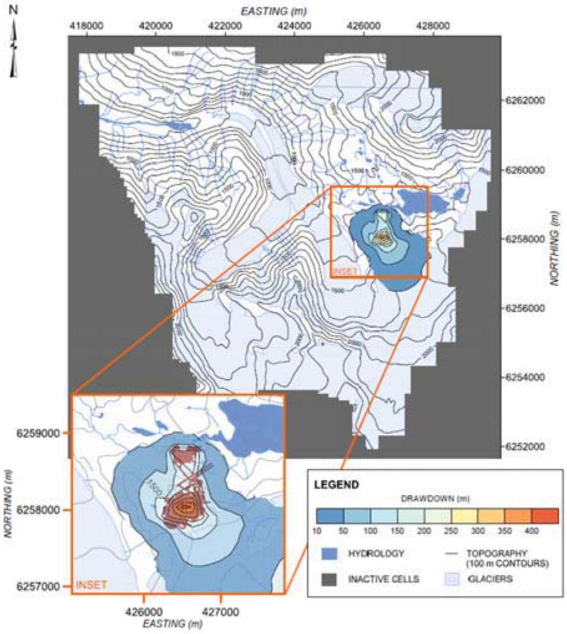

Figure 5 *Simulated drawdown at end of mine life (operations year 18).*

The transient closure and post-closure simulations indicate that most recovery happens within one year of the end of active mining operations (i.e., after dewatering ceases), with the groundwater flow system approaching a new equilibrium within 2 to 3 years after the end of active mining. Post-closure, the configuration of groundwater elevation contours is consistent with pre-disturbance conditions: the water table is predicted to be a subdued replica of the surface topography, with local groundwater flow occurring from areas of higher topographic elevation towards Brucejack Lake and Brucejack Creek. Within the footprint of the mine workings, the post-closure water table is predicted to be locally depressed compared to pre-disturbance conditions; this arises because the specified hydraulic conductivities of the mine backfill materials are higher than the surrounding bedrock. In the post-closure period, the areal extent with drawdowns of 10 m to 25 m relative to pre-disturbance conditions is approximately 0.5 km by 1 km.

Groundwater discharge to surface water receptors is predicted to return to rates approaching pre-disturbance conditions within approximately 2-3 years following the end of active mining. This finding suggests that mining operations associated with the Brucejack Project will not result in any significant long-term impact to baseflow in the Brucejack Creek watershed.

Application of Predictive Simulation Results

Results of the predictive groundwater flow model simulations were integrated with the Project site-wide water balance model (WBM), and dependent water quality prediction model used to evaluate project effects for the environmental assessment. The WBM and water quality models were also used to support water management design and evaluation, and development of triggers for monitoring and adaptive management requirements as part of project permitting.

Conclusions

A MODFLOW-Surfact groundwater flow model was developed to evaluate impacts of mine development on the groundwater flow system at the Brucejack Project, located in northwestern British Columbia, Canada. Dewatering of existing underground workings at the site afforded a unique dataset for model calibration and benchmarking – essentially a large-scale, long-term, variable rate pumping test. The numerical model was calibrated to volumetric mine inflow data and was subsequently benchmarked against the response of hydraulic heads to mine dewatering. The availability of mine dewatering data at this early stage of project development was fortuitous, as the dewatering data represent a large-scale stress to the hydrogeologic system, allowing for increased confidence in definition of hydraulic parameters and boundary conditions. Model benchmarking suggested that the bulk properties of this complex hydrogeologic system were well represented, and that the model was suitable for further analyses.

The calibrated groundwater flow model was subsequently used for a suite of predictive simulations to estimate groundwater inflow rates to the underground workings, simulate groundwater discharge rates to surface water features, and predict drawdown and recovery of the groundwater system throughout Operations and into the Post-Closure period. All results of predictive simulations were presented in support of the Project feasibility studies, environmental approvals, and regulatory permitting. The Brucejack Project received a British Columbia Environmental Assessment Certificate in March 2015, Federal Environmental Decision Statement in July 2015, and Mines Act and Environmental Management Act Permits in September 2015. The Project is currently undergoing construction.

Acknowledgements

The authors thank Pretium Resources Inc. for involving them in the Brucejack Project.

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Open Pit Mine Flooding Prognosis making use of Analytical Element Modelling in Fractured Hard Rock

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Abstract

A large number of South Africa's open pit mines are located in fractured rock. Analytical solutions to pit flooding mainly make use of the Dupuit-Forchheimer approximation. A typical example of such a solution is the solution proposed by Marinelli and Niccoli (2000). The challenge with most of these solutions is that the pit geometry is generally chosen as symmetrical and that the solution cannot accommodate geological structures. Numerical solutions to partial differential equations are available in the form of finite-difference, finite-volume and finite-element schemes. These solutions are able to solve for complex geometries and can accommodate geological structures, but require appropriate grid refinement to represent geological structures.

The analytical element method (AEM) is a numerical method used to solve partial differential equations. It was initially developed by Strack (1989). The method does not rely upon discretization of volumes or areas in the modelled system; only internal and external boundaries are discretized. The AEM allows the open pit to be modelled as an asymmetrical element with thin and irregular inhomogeneities, which can be used to represent geological features.

The AEM solution to pit flooding is more realistic than the typical analytical solution due to the relaxation of the pure analytical solution restrictions. This is especially true for scenarios where strip mining is simulated with continuous backfill taking place.

Applying the AEM solution to open pit flooding scenarios is a quick and effective way to obtain first order flooding results. The advantage is that elements e.g. inhomogeneities that constitute the model, can be switched on or off since they are not dependent on a specific grid. This allows for quick changes to the model, by introducing new elements or removing elements to determine their influence on the result obtained.

Key words: Open pit mines, geological lineaments, hard rock, analytical element method

Introduction

Mining in South Africa started in the mid 1800s and has been a key driver of the economy. There are two main mining approaches namely extraction by means of open pits or extraction by means underground workings. The approach chosen to mine a deposit is based on the maximization of profits given the unique characteristics of the deposit and its location, limits imposed by safety and environmental impacts. Both approaches present their own set of challenges but the focus of this paper will be on open pits.

An open pit mine can broadly be defined as a mine in which the deposit can be extracted by removing the covering layers of rock and soil and requires no roof support. Although the basic concept of an open pit is quite simple, the planning required to mine a large deposit is a very complex and costly undertaking. One of the key challenges is the management of water seeping into/flooding the open pit mine. The quantification of these volumes are dependent on a number of factors including:

- Size and the shape of the deposit
- Geology in which the deposit is located
- Conduits (e.g. fractures and faults) intercepting the open pit mine
- Barriers (e.g. dykes) intercepting the open pit mine

- Mining plan and method (e.g. strip mining)
- Mine closure options (e.g. backfilling and pit lakes)

While detailed three dimensional numerical modelling may be required in some studies, simpler methods for estimating open pit inflows can be informative and not so time consuming. The aim of this paper is therefore to motivate the use of the Analytical Element Method (AEM) as a tool calculate seepage/flooding volumes without having to to develop detailed finite-difference, finite-volume and finite-element numerical models which take time to setup, calibrate and can be computationally expensive.

Modelling Methods

The first method was developed by Marinelli and Nicoli (2000) and is based on the Dupuit-Forchheimer approximation. The flow into the pit is divided into 2 zones as shown in Figure 1. Zone 1 represents flow through the pit walls. Zone 2 represents the inflows from the base of the pit.

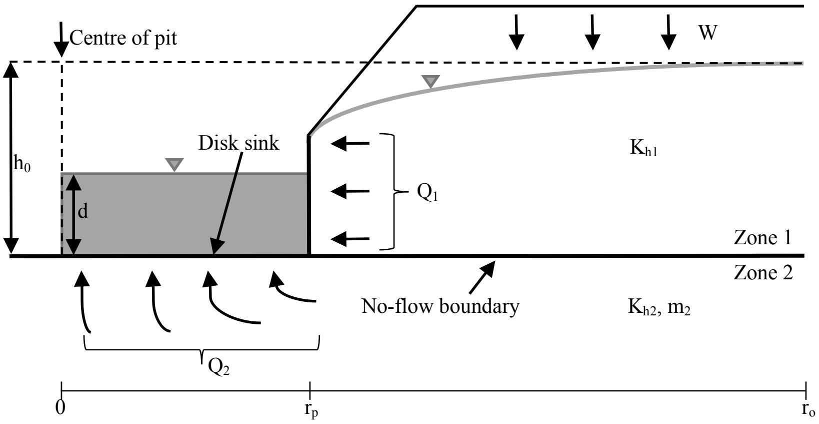

Figure 1 *Pit inflow model adapted from Marinelli and Nicoli (2000).*

The analytical equation for the inflow into the pit from Zone 1 can be expressed as:

$$Q_1 = W\pi\left(r_o^2\text{-}r_p^2\right)$$

where

Q_1 = volumetric flow rate from Zone 1
W = recharge flux
r_o = radius of influence
r_p = effective pit radius

The analytical equation for the inflow into the pit from Zone 1 can be expressed as:

$$Q_2 = 4r_p\left(\frac{K_{h2}}{m_2}\right)(h_0\text{-}d) \text{ with } m_2 = \sqrt{\frac{K_{h2}}{K_{v2}}}$$

where

Q_2 = volumetric flow rate from Zone 2
K_{h2} = horizontal hydraulic conductivity
K_{v2} = vertical hydraulic conductivity
m_2 = anisotropy parameter
h_0 = pre-mining saturated thickness above base of Zone 1
d = depth of lake

The assumptions on which the analytical solutions for Zone 1 and Zone 2 are based are summarised in Table 1.

Table 1 *Assumptions (Marinelli and Nicoli 2000).*

Zone 1 Analytical solution	Zone 2 Analytical solution
Pit walls are approximated as circular a cylinder Groundwater flow is horizontal The pre-mining water level is horizontal Uniformly distributed recharge occurs Groundwater flow towards the pit is axially symmetrical	The hydraulic head is initially uniform The disk sink has a constant hydraulic head equivalent to the elevation the water level in the pit Flow to the disk sink is three-dimensional and axially symmetrical Materials are anisotropic and the principal directions are horizontal and vertical for hydraulic conductivity

The AEM is a numerical method used for the solution of partial differential equations. It does not rely on discretization of volumes or areas in the modelled system. Only internal and external boundaries are discretized. The basis of the AEM is that, elementary solutions may be superimposed to obtain more complex solutions. A number analytic solutions known as elements are available. These elements typically correspond to a dependent variable or its gradient along a boundary.

Each analytic solution is infinite in space and/or time. In addition, each analytic solution can be calculated to meet specified boundary conditions. To obtain a solution, a system of equations is solved such that the boundary conditions are satisfied along all of the elements. The governing equation is satisfied exactly except along the border of the element, where there is a discontinuity.

The ability to superpose numerous elements in a single solution means that analytical solutions allows for complex boundary conditions. Therefore, models that have complex geometries, multiple boundaries, transient boundary conditions etc. can be solved.

The AEM has been applied in modeling open pit mines and shows reasonable results compared to that of finite-element and finite-difference models for the same study area. Monthly simulated pit inflow values making use of AEM for the groundwater component and accounting for direct rainfall into pit and evaporation is shown in Figure 2.

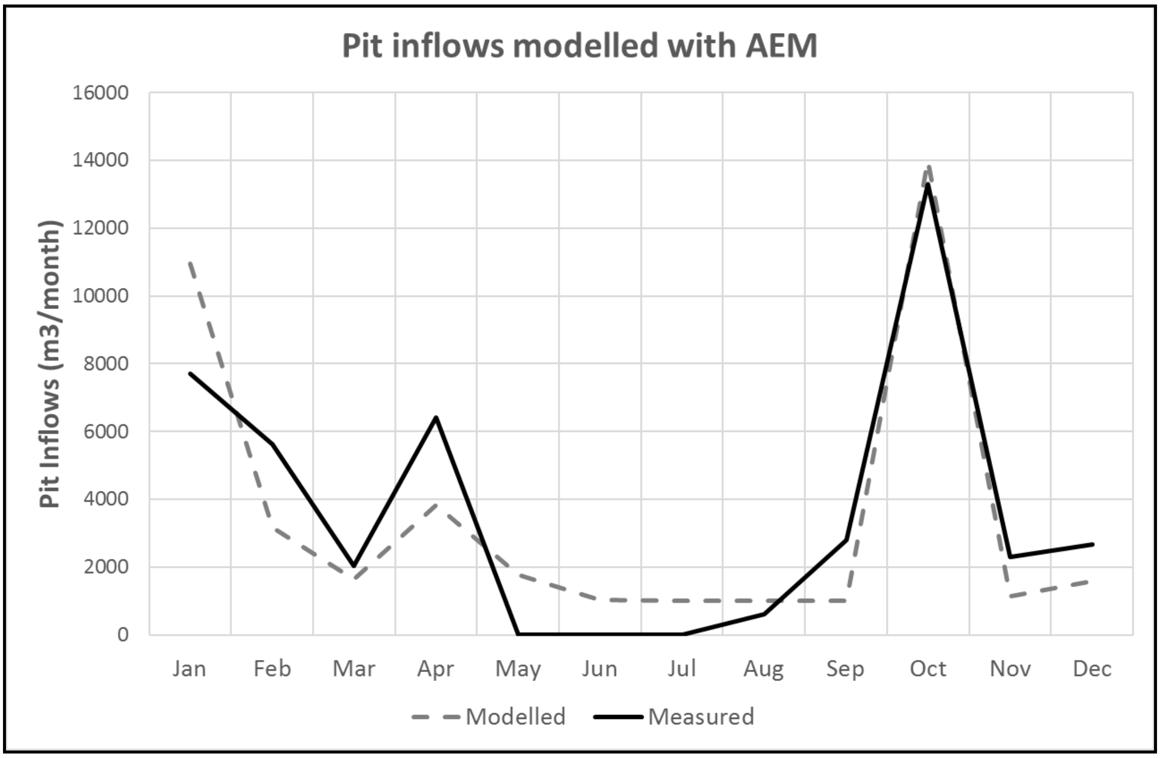

Figure 2 *Example of modelling results.*

Limitations include that the Dupuit-Forchheimer conditions are valid which include Craig (2007):

- Hydraulic heads may be represented by its average value in the vertical direction
- Resistance to flow is negligible in the vertical direction
- The vertical flux is calculated by means of a mass balance and not Darcy's Law.

The AEM has limitations, but provides a flexible modelling tool when considering it is not dependent on a predefined grid with the ability to switch hydrogeological features in and off in a simulation with the click of a button. The method is capable of handling a range of applications, from simple screening models, to regional models multilayer models (Hunt, 2006).

Study Area

The layout of the study area is shown in Figure 3 and comprises two open pits, Pit A and Pit B. To the south of the study area is a river and to the north is a geological fault considered to be a high transmissive zone which intersects Pit A. The geology is characterized by predominantly norite and for the purpose of this paper only a single layer model is considered for comparison purposes. The light grey contour lines in Figure 3 represent the surface topography.

There are eight boreholes located within the study area. The comparison of average water level with surface elevation is presented in Figure 4 which shows a strong correlation between surface topography and water levels. Note that BH2 is close to Pit A and has a relatively deeper water level compared with other observation boreholes and therefore was not used in the linear regression calculation.

A summary of the study area parameters used for modelling is listed in Table 2.

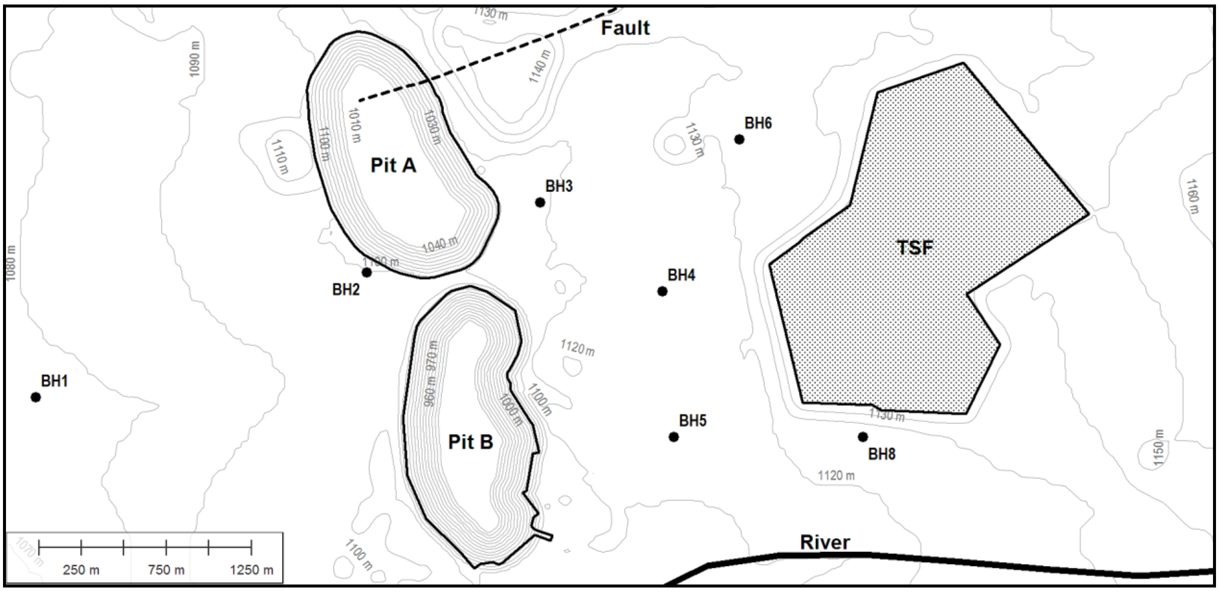

Figure 3 *Layout of study area.*

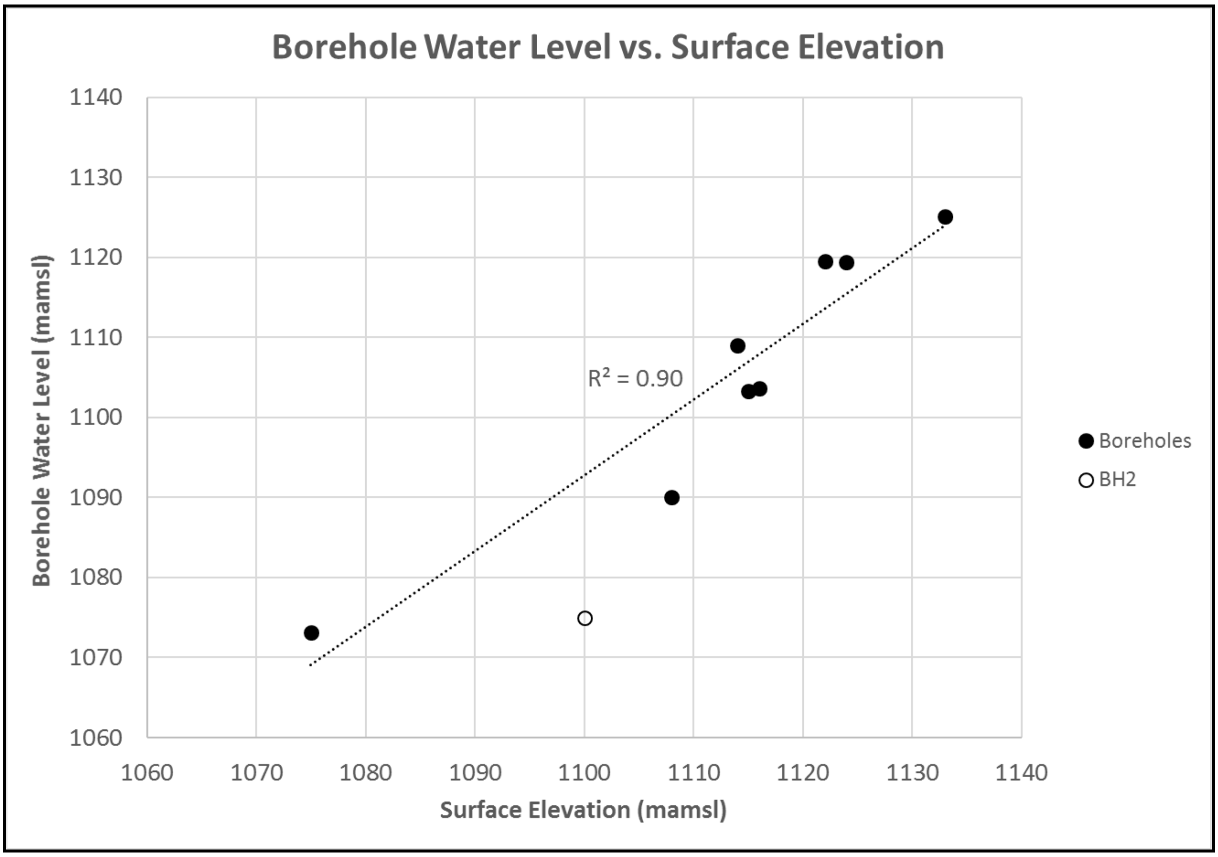

Figure 4 *Correlation between groundwater levels and elevation.*

Table 2 *Parameters.*

Parameter	Value
Mean Annual Precipitation (mm/a)	52
Recharge as % of MAP	3.0
Average Water Level (mbgl)	6.8
Norite Hydraulic Conductivity (m/d)	0.02
Fault Hydraulic Conductivity (m/d)	2.0
Aquifer Thickness (m)	200
Geological Fault Width (m)	2
Pit A - Surface Elevation (mamsl)	1100
Pit A – Depth (m)	100
Pit B – Surface Elevation (mamsl)	1070
Pit B – Depth (m)	110

Modelling Methodology

Both pits in the study area are modelled with the analytical solution proposed by Marinelli and Niccoli (2000). The same system is then modelled by making use of the AEM which can account for both the pit interference and the high transmissive geological fault feature.

Using Marinelli and Niccoli (2000), the first step is to transform the pit geometry to an equivalent cylinder represented by a pit radius. The pit floor geometry is used as the representative pit geometry for the purpose of this paper. The geometrical pit transformation can be done either by using the physical pit area or the physical pit perimeter. Two very different radii can be the result, as illustrated in Figure 5. This figure shows some typical examples together with the 1:1 line which will represent a perfect circle.

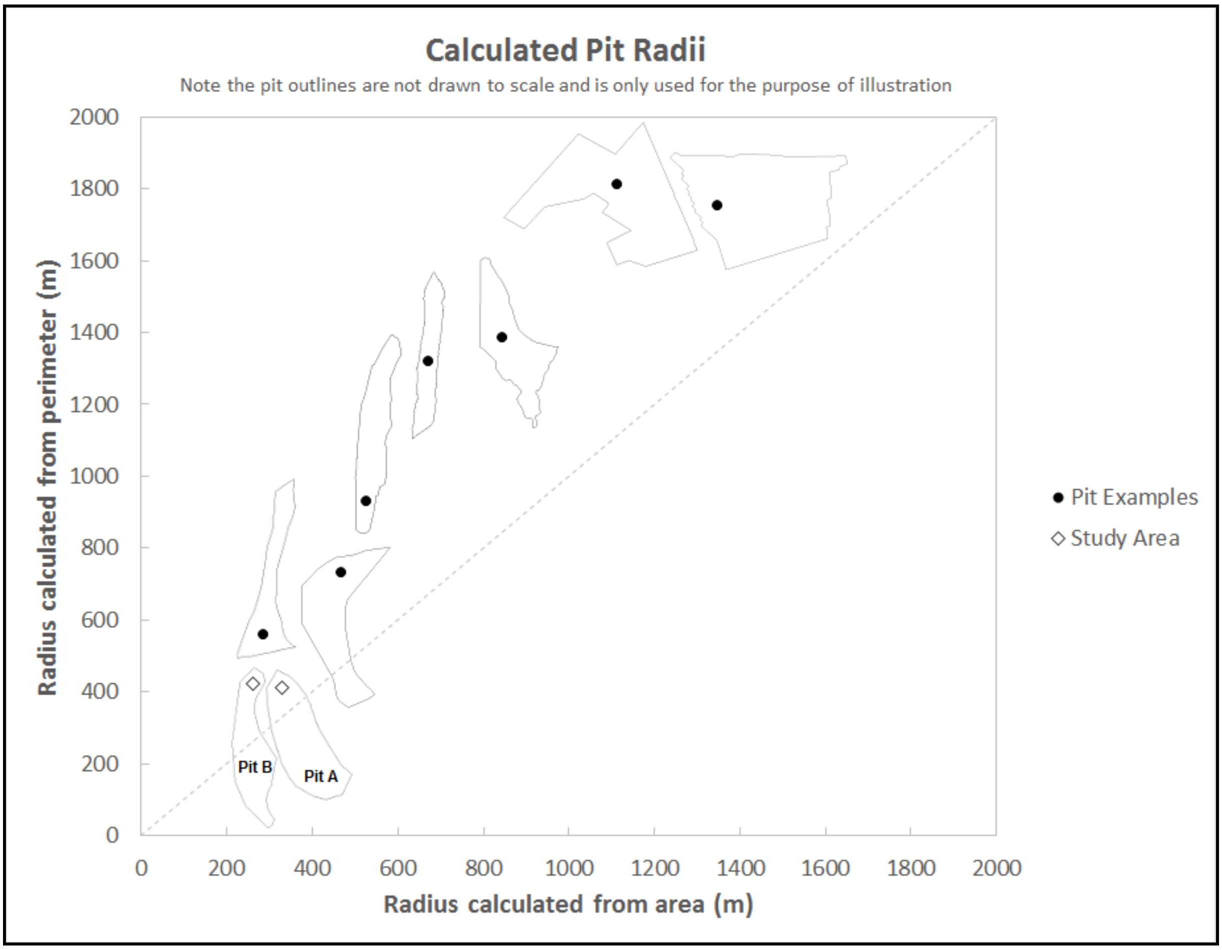

Figure 5 *Calculated pit radii.*

The calculated radii for Pit A and Pit B are presented in Table 3. The AEM results showed a better correlation with the pit radii calculated from the physical pit perimeter and was therefore used in the modelling. It is clear from Table B that the radii calculated through the pit perimeter represents a larger area than the physical pit area, therefore it is important to use the physical pit area if water balance calculations are performed and not the area represented by the newly calculated pit radius.

Table 3 *Pit radii.*

Pit Name	Area (m^2)	Perimeter (m)	Radius from Area (m)	Radius from Perimeter (m)
A	339627	2583	329	411
B	216644	2655	263	423

Only a single layer model is considered for the study area and therefore the horizontal hydraulic conductivity for both Zone 1 and Zone 2 (see Figure 1) are set to 0.02 m/d. The vertical hydraulic conductivity for Zone 2 is used to calibrate the analytical model results of Pit A to that of the analytical element model of Pit A for comparison purposes. Pit A is selected for the calibration procedure as its geometry is closer to that of a circle than that of Pit B (see Figure 3).

Due to the fact that the analytical solution does not make provision for modelling a fault, which is a high transmissive zone in this case, an effective hydraulic conductivity is calculated for Pit A. The effective hydraulic conductivity (K_{eff}) for the cylindrical pit is calculated by assuming a skin around the cylinder consisting of the matrix hydraulic conductivity (K_m) and the geological fault hydraulic conductivity (K_f) as shown in Figure 6. Equation 1 is used to calculate K_{eff}, where L is the length of the associated hydraulic conductivity along the circumference of the pit.

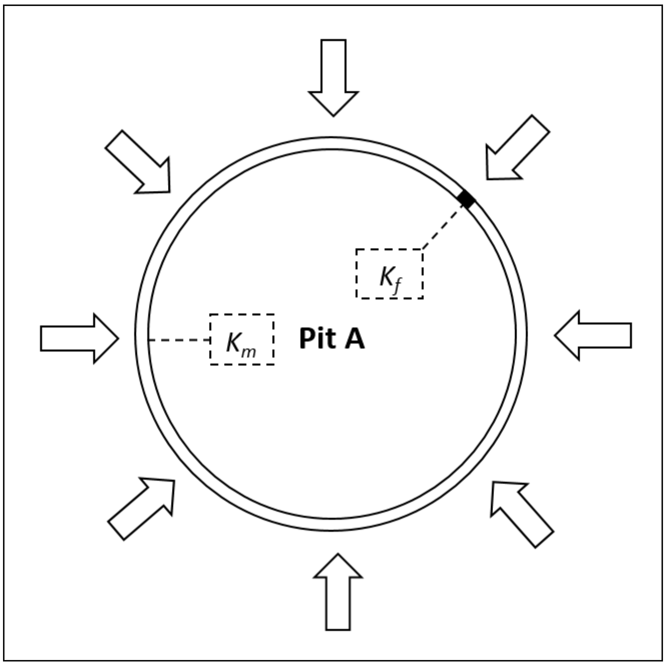

***Figure 6** Various hydraulic conductivity values.*

$$K_{eff} = \frac{(L_m K_m) + (L_f K_f)}{L_m + L_f} \quad (1)$$

A Visual AEM model is setup. In addition to the standard aquifer parameters the digital elevation model and a river are introduced in the model and calibrated making use of the observed water levels. Note the parameters presented in Table 2 are already the calibrated parameters.

Model Results

The comparison of the two models and their results are presented in Table 4.

***Table 4** Model results.*

Scenario Description	AEM Pit Inflow (m^3/d)		Analytical Solution (AS) Pit Inflow (m^3/d)		AS/AEM (%)	
	Pit A	Pit B	Pit A	Pit B	Pit A	Pit B
Single pits considered in isolation from each other	1675	1914	1675	1857	100%	97%
Only Pit A with geological fault	1746	*	1720	N/A	103%	*
Pit A and Pit B simultaneously, without the geological fault	1142	1369	*	*	*	*
Pit A and Pit B simultaneously, with the geological fault	1211	1364	*	*	*	*

** Scenario not applicable*

Conclusions

It is well known that the open pit analytical solution proposed by Marinelli and Niccoli (2000) provide a convenient means for estimating groundwater inflows to open pits. The primary value of such analytical solutions is providing preliminary estimates to be used in the initial phases of mine planning. It has further been shown that for a single pit, an effective hydraulic conductivity can be calculated to account for a high transmissive geological fault and applied to the analytical solution proposed by Marinelli and Niccoli (2000).

A good correlation exits between the AEM and the open pit analytical solution of Marinelli and Niccoli (2000) when only single pits are considered. This is even the case for a high transmissvive geological fault is included by means effective hydraulic conductivity.

When considering more than just a single pit, a model is required that adequately describes the system in question. The AEM model allows the modelling of multiple open pits together with inhomogeneities and other hydrogeological features. The model does require calibration, but is grid independent, allowing the addition of various hydrogeological features which can be switch on or off with the click of a button to interrogate various scenarios. The model further makes use of the physical pit geometry and no translation to an equivalent feature is required.

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From Catchment Hydrology to Dewatering at Mine Sites

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Extended Abstract

Large volumes of water are used in mineral processing, for dust suppression, and for normal municipal uses. However, maintaining the optimal supply and storage is tricky. Groundwater pumping may exacerbate already low groundwater tables. Sporadic and highly seasonal rainfall and snowmelt may require the mine to use complex water management rules. If dewatering rates are high, or storage options limited, then discharge to local surface water systems is usually necessary.

The catchment is the spatial context in which a mine is located. All mines impact the groundwater and surface water in their catchment. These impacts are highly spatial and complex, and may be cumulative across multiple mines and mine sites. Yet, traditional water balance modelling simplifies the feedbacks and interactions between groundwater, surface water and catchment hydrology. Failure to get this right can lead to poor operational decisions and increased costs.

For a copper mine in Africa, we have developed novel methodologies to integrate complex groundwater models for dewatering, with regional physics based catchment models. The two models are linked via the dynamic, spatially distributed groundwater recharge, as well as through the dynamic lateral groundwater boundary flow. The overwhelming advantage of this approach is the ability to look at detailed dewatering scenarios, while taking into account the feedbacks and exchanges in the regional hydrology.

The physics based catchment model surrounding the mine is being used to simulate catchment related water issues, such as the siting of tailings disposal facilities, planning for stream diversions, and screening for flood impacts.

In general, such hydrology models can be used to answer both operational and social questions, such as:

- How will surface water disposal of dewatering water impact river flow and downstream users?
- Are water management plans and operational rules robust enough to accommodate both very wet and very dry years?
- What are the implications of irrigation, drainage, and storm water management on social, mining and environmental users?
- Is the mine closure plan sustainable with respect to long term hydrology – especially in the context of climate change?

Whereas, the detailed groundwater model takes into account the complex geology around the mine (imported from MineSight), as well as the mine development over time to address operational issues, such as:

- What are the optimal locations and depths for dewatering wells?
- What are the expected changes in dewatering rates as mining progresses?
- Can the mine plan be optimized to minimized dewatering costs and maximize effectiveness?

Key words: Mine water management, groundwater-surface water interaction, groundwater modelling, catchment hydrology, physics-based modelling

Modeling groundwater and heat flow subject to freezing and thawing

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Abstract

A newly developed FEFLOW plug-in module, piFreeze, provides simulation capabilities to cover freezing and thawing of subsurface water. The governing balance equations account for the respective volume fractions of frozen and liquid water and for the density difference between both phases. Extensions have been developed for both unsaturated and saturated conditions. Constitutive relations describe the temperature dependency of the heat capacity including the latent heat associated with the phase change, of permeability and fluid viscosity, and of the thermal conductivity. A flexible empirical expression describes the local freezing progress im tems of liquid/ice mass fractioning over a finite temperature range around the freezing point.

Application potential for FEFLOW with piFreeze is seen wherever natural or artificially induced freezing and thawing processes significantly affect the groundwater flow, for example in mining, construction, permafrost conditions, and geothermal energy.

Key words: Numerical modeling, FEFLOW, piFreeze, groundwater, freezing, thawing, permafrost, artificial ground freezing

Notation

Subscripts *a*, *l*, *s*, *i* identify air, liquid, solid (other than ice), and ice phases, respectively.

ε_x	Volume fraction of phase x
ε	Flow-accessible volume fraction (‘porosity’), $\varepsilon = \varepsilon_a + \varepsilon_l$
ρ_x	Density of phase x
φ	Mass fraction of liquid water to total (liquid + frozen) water, $\varphi = \dfrac{\varepsilon_l\,\rho_l}{\varepsilon_l\,\rho_l + \varepsilon_i\,\rho_i}$
T	Temperature
L_f	Latent heat of freezing/melting
λ	Effective thermal conductivity
λ_x	Thermal conductivity of phase x
C	Effective volumetric heat capacity
C_x	Volumetric heat capacity of phase x
s	Liquid-phase saturation, $s = \varepsilon_l / \varepsilon$
h	Liquid-phase pressure head
Q	Liquid-phase volumetric source
Q_f	Liquid-phase volumetric source from freezing/melting
S_o	Liquid-phase specific storage coefficient
K_s	Saturated hydraulic conductivity
$K_{r,s}(s)$	Hydraulic-conductivity reduction factor due to saturation (empirical relation)
$K_{r,f}(\varphi)$	Hydraulic-conductivity reduction factor due to melting/freezing (empirical relation)
K	Effective unsaturated hydraulic conductivity, $K = K_s\,K_{r,s}(s)\,K_{r,f}(\varphi)$
$\boldsymbol{q}$	Liquid-phase (Darcy) flux, $\boldsymbol{q} = -K\,\nabla(h + z)$

Theory

We assume that the respective volume fractions of air, liquid, solid, and ice add up to unity everywhere and at all times,

$$1 = \varepsilon_a + \varepsilon_l + \varepsilon_s + \varepsilon_i$$

The local transition from ice to liquid and vice versa is described by the ‘freezing function’ $\varphi(T)$, shown in Fig. 1 as both an empirical linear and a smooth higher-order relation.

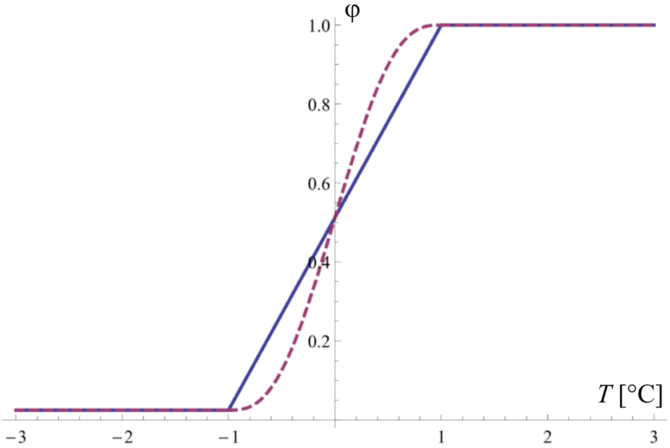

Figure 1 *Alternative empirical shapes expressing the local mass fraction of liquid water to total (liquid + frozen) water as a function of temperature.*

Under partially saturated conditions ($\varepsilon_a > 0$, $s < 1$), it is assumed that water as it transitions from liquid to ice phase expands into space occupied by the air phase. As no water is transferred across the boundary of a representative elementary volume (REV) due to freezing/melting, the local water mass remains constant (i.e., $\varepsilon_l\,\rho_l + \varepsilon_i\,\rho_i =$ const. with respect to φ) so that

$$\varepsilon_l = \varphi\left(\varepsilon_l + \varepsilon_i \frac{\rho_i}{\rho_l}\right) \quad \text{and} \quad \varepsilon_i = (1-\varphi)\left(\varepsilon_l \frac{\rho_l}{\rho_i} + \varepsilon_i\right)$$

In contrast, under fully saturated conditions ($\varepsilon_a = 0$, $s = 1$), there is no air present and water must transfer across the REV boundary due to the change in density as it transitions from liquid to ice phase or vice versa. In this case there is a fixed total local volume fraction available to water, (i.e., $\varepsilon_l + \varepsilon_i = 1 - \varepsilon_s =$ const. with respect to φ), and it follows that

$$\varepsilon_l = \frac{\varphi\,(\varepsilon_l + \varepsilon_i)\,\dfrac{\rho_i}{\rho_l}}{1 - \varphi\left(1 - \dfrac{\rho_i}{\rho_l}\right)} \quad \text{and} \quad \varepsilon_i = \frac{(1-\varphi)\,(\varepsilon_l + \varepsilon_i)}{1 - \varphi\left(1 - \dfrac{\rho_i}{\rho_l}\right)}$$

Mass-conservation considerations give rise to an additional source term Q_f appearing in the Richards equation

$$S_o\, s \frac{\partial h}{\partial t} + \varepsilon \frac{\partial h}{\partial t}\frac{\partial h}{\partial t} + \nabla \cdot \mathbf{q} = Q + Q_f$$

with

$$Q_f = 0 \quad \text{for} \quad s < 1$$

and

$$Q_f = -\frac{\partial\varphi}{\partial T}\frac{\partial T}{\partial t}\left(\frac{\rho_i}{\rho_l}\frac{\partial\varepsilon_i}{\partial\varphi} + \frac{\partial\varepsilon_l}{\partial\varphi}\right) \quad \text{for} \quad s = 1$$

An effective thermal conductivity is presumed to follow from the local phase composition, considering the contribution from the air phase as negligible,

$$\lambda = \varepsilon_l\,\lambda_l + \varepsilon_s\,\lambda_s + \varepsilon_i\,\lambda_i$$

A similar assumption is made for the heat capacity which must further account for the latent heat of freezing/melting associated with any change in the local ice fraction,

$$C = \varepsilon_l\,C_l + \varepsilon_s\,C_s + \varepsilon_i\,C_i - L_f\,\rho_i\,\frac{\partial\varepsilon_i}{\partial\varphi}\frac{\partial\varphi}{\partial T}$$

As shown in Figure 2, general agreement was observed between predictions for the "Frozen Wall" Benchmark (McKenzie et al. 2007) by FEFLOW (Diersch 2014) with piFreeze and by SUTRA-ICE, which handles fully saturated conditions (McKenzie et al. 2007).

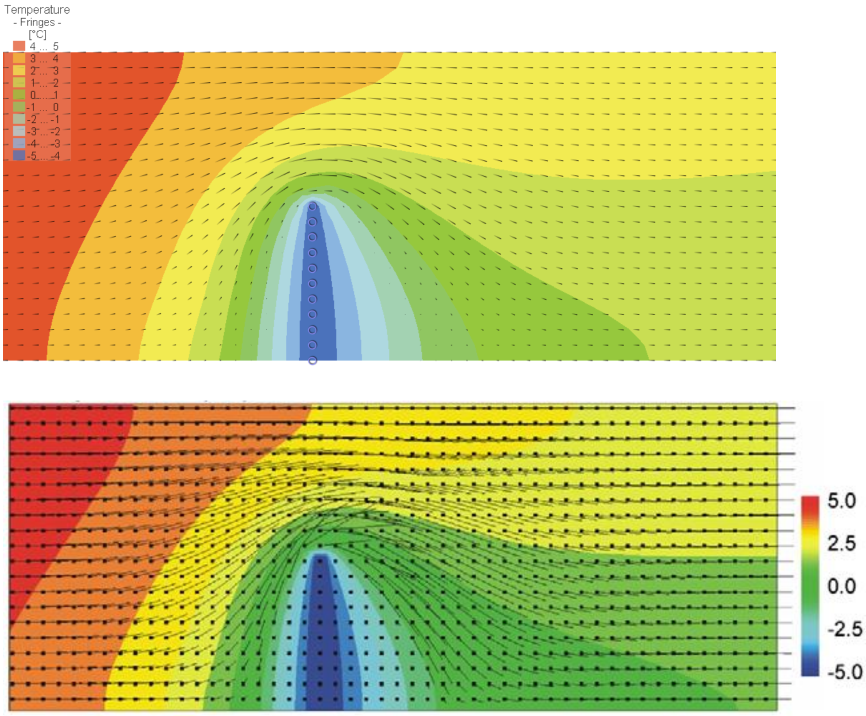

Figure 2 *"Frozen Wall" Benchmark, Temperature distribution and flow field after 800 d computed by FEFLOW with piFreeze (top) and SUTRA-ICE (bottom).*

Application

A hypothetical three-dimensional freeze-wall investigation is illustrated in Figure 3. Below, Figure 4 clearly shows the effect of the prevailing hydraulic-head gradient on the freeze-wall closure dynamics, the flow field, and the temperature distribution.

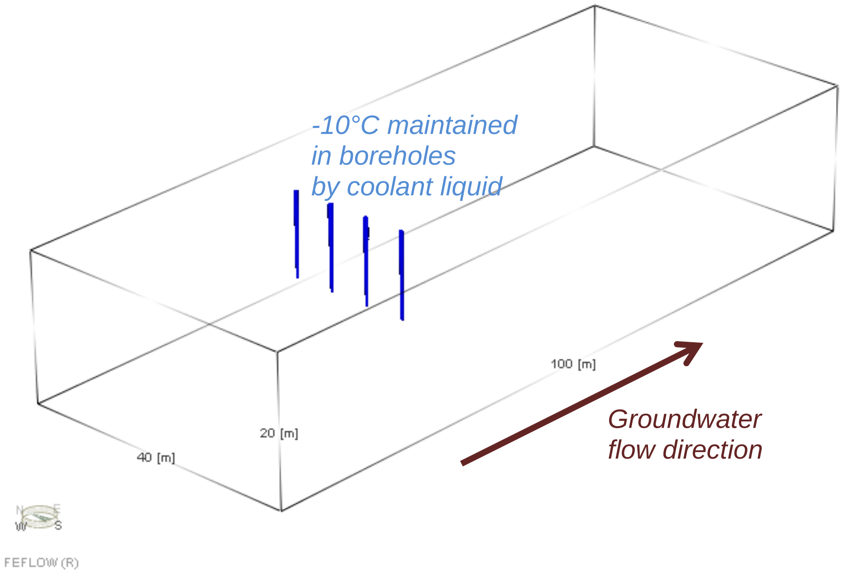

***Figure 3** 3D Freeze-wall study.*

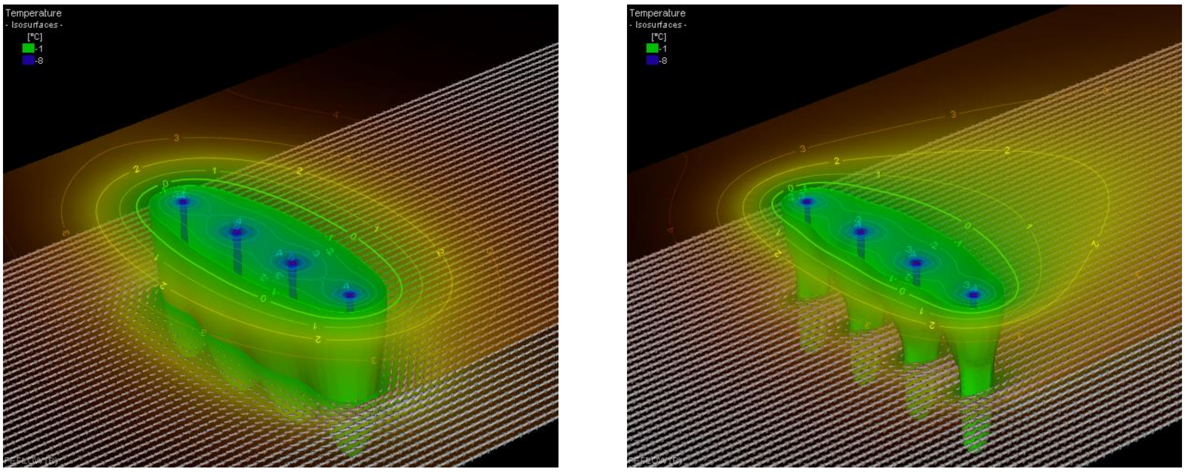

***Figure 4** Temperature distribution two years after initiation of freezing compared for a groundwater hydraulic-head gradient of 10^{-4} (left) and 10^{-3} (right).*

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Field Tests and Ecological Assessment of an Opencast Mine-Dewatering using a Horizontal Directional Drilled Well

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Abstract

Nowadays vertical filter wells are the main element of dewatering in opencast mines in Germany. An alternative – e.g. suitable in cases of limited water levels, reduced thickness of aquifers, or basin structures – are horizontal directional drilled wells (HDD wells). By the use of HDD wells with considerably longer filter screens in combination with free discharge of the drained water out of the pit slope, economies in costs, materials, and land use are anticipated.

With respect to the dewatering effects using HDD wells, some questions remained unanswered so far. Therefore, field tests with a 200 m long HDD well combined with a vertical well interconnecting two hydraulically separated aquifers were realized within the central German lignite district in the south of Leipzig. Based on a structural model, details of the horizontal directional drilling as well as an appropriate position of the HDD well were investigated. For this purpose the information of 250 available exploratory drillings was evaluated. A numerical groundwater flow model was used to simulate the drainage using the software PCGEOFIM.

Besides technical and economic issues an environmental assessment was made. On the basis of the information gathered in the field test, HDD wells and vertical wells were compared theoretically. Therefore a calculation model was set up to investigate the conventional dewatering method using vertical wells in comparison with HDD wells under environmental issues.

Key words: horizontal directional drilled Wells (HDD wells), groundwater modeling, ecological assessment

Introduction

Dewatering of near-surface unconsolidated rock is an important prerequisite for the technical implementation and safety of mining projects. The removal of water from the overlying rock is also a basic necessity concerning stable pit walls and working planes (Mansel et al. (2015)). Higher residual water levels in overburden operations and out-of-control rising ground water levels could cause pit slope failures.

Nowadays vertical filter wells are commonly used on a large scale in lignite-mine dewatering and depressurization in Germany. Vertical filter wells have a short screened section, particularly in thin aquifers, which is continuously being reduced during the dewatering process (Struzina et al. (2011)). The negative impact of dewatering on resources and the environment must, however, be minimized in time and space.

The research and development project, the results of which are the subject of this paper, focuses on two parts:

- field tests with a 200 m long horizontal directional drilling (HDD) well combined with an infiltration well (fig. 1),
- ecological assessment comparing vertical and horizontal dewatering in open cast mines

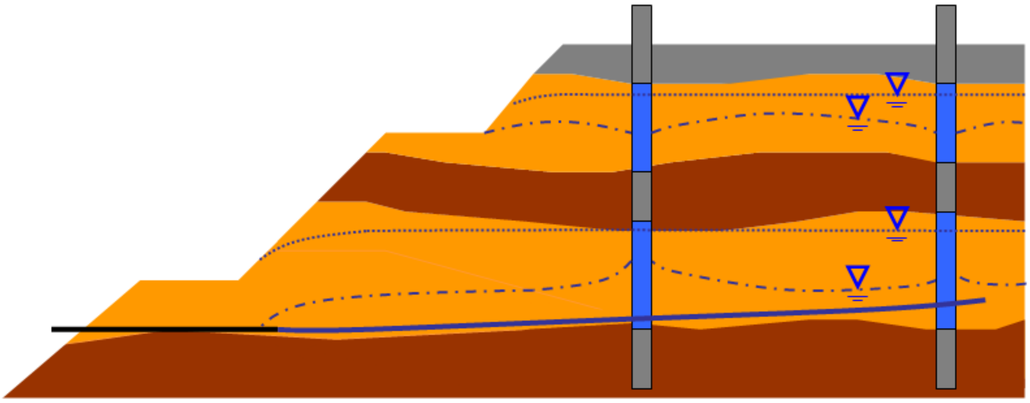

Figure 1 *HDD well and two vertical wells draining hydraulically separated aquifers (Struzina 2012).*

The aim of the field test was the combined dewatering of two aquifers using a vertical well for the hydraulic connection and a horizontal well, installed at the bottom of the underlying aquifer, for the dewatering. The application was simulated using numerical groundwater modelling software PCGEOFIM.

The objective of the ecological assessment was to accomplish scientific and practical basic for the application of HDD wells as an environmentally sound method of dewatering in opencast mining.

Methods

Based on the results of successfully completed project phases (Müller et al. (2009)) the aim of the research project was to develop the scientific and practical basis for the application of an alternative dewatering method. Furthermore, the application of HDD wells has a potential to overcome the environmental drawbacks of the use of vertical filter wells.

Study area

The study area is located in the Central German Lignite District in the south of Leipzig. By gaining a local industrial partner, it was possible to run the field tests in a practical relevant way. Due to the presence of an intermediate 3-10 m thick clayey intercalation within the unconsolidated rock material of aquifer 3, this aquifer is hydraulically divided into an overlying section (aquifer 3.1) and an underlying section (aquifer 3.2). By means of particle size analyses, the sediments of the overlying section are considerably finer and show a better sorting.

Structural Model and Numeric Groundwater Flow Model

In order to identify an appropriate position for the horizontal and the vertical well a structural model was developed using Groundwater Modeling System (GMS) by Aquaveo. It is based on information of more than 250 drillings to investigate the geological characteristics like storing conditions, thickness of aquifers and aquicludes and grain size, etc.

Besides, the structural model provides the basis for the hydraulic modelling. The groundwater flow model – modeling software PCGEOFIM (Blankenburg et al. (2013)) was used – is characterized by a dimension of 2.5 x 2.5 km with a basic raster of 50 m cell size. In between this basic raster there are two nested grid refinements of 25 x 25 m and 5 x 5 m, respectively. (fig. 2)

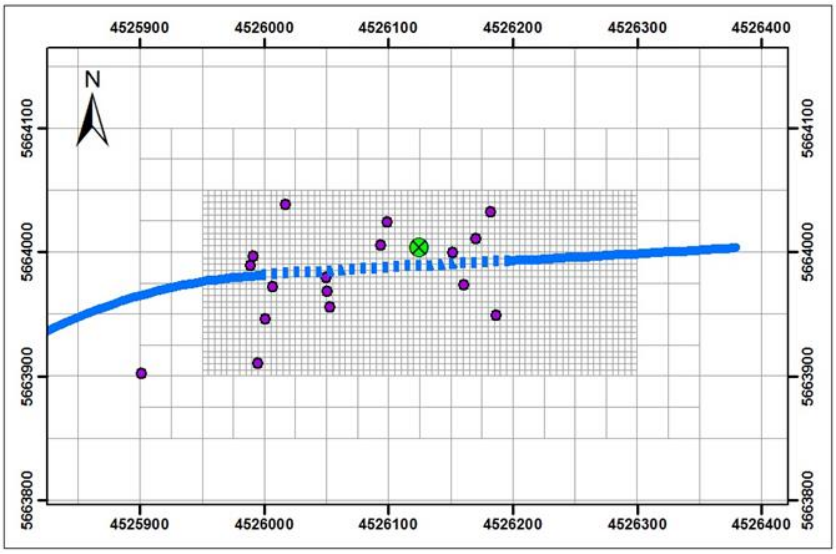

Figure 2 *Model resolution, position of HDD well (blue), vertical well (green), monitoring wells (purple).*

The model was calibrates using the measurements from 62 monitoring wells - 36 monitoring wells in direct periphery of the horizontal well, 18 in each aquifer – as well as flow volumes from both wells. Therefore, adjustments of the hydraulic conductivity in between several raster cells were made. In addition, the progress of the extraction process was taken into account. Achieving a standard deviation of 0.35 m of the value pairs (measured - calculated) the calibration was completed successfully.

Horizontal well

Differing from the usual design of horizontal directional drillings where the exit point of the drilling is situated on the terrain surface, it was necessary to place it below (fig. 3) to allow dewatering by gravity flow. This lead to adverse circumstances for using drilling mud, which was flowing out of the exit point and had to be pumped to the starting point. Due to the length of the borehole, a protective pipe was used to install the filter well and prevent partial damage (Mücke (2014)). Shortly after the filter screen was positioned in place, the protective tube was pulled out. Finally, a magnetic-inductive flow meter was installed to measure the amounts of drained water.

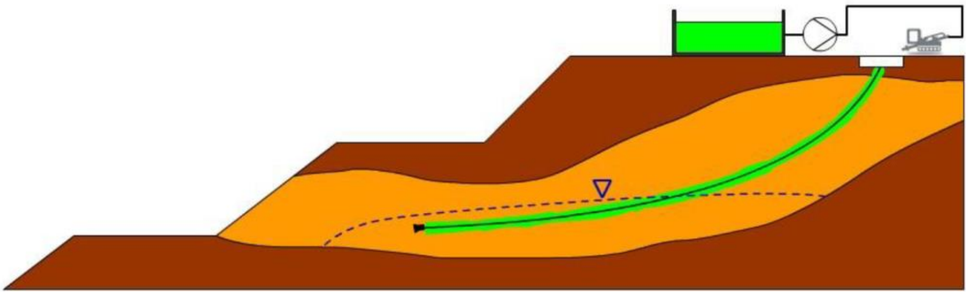

Figure 3 *Scheme Horizontal Directional Drilling (Harzer (2012))*

Vertical well

Shortly after the installations of the horizontal well, the vertical well was installed to connect the separated aquifers hydraulically. Concerning the interconnection of both dewatering elements an indirect connection was used to avoid damaging of the horizontal well (fig 4). To measure the amount of water that infiltrated from the upper into the lower aquifer a magnetic-inductive flow meter (MID) was installed. The MID was part of a hydraulic shutoff device to measure the entire amount of infiltrated water (fig 5).

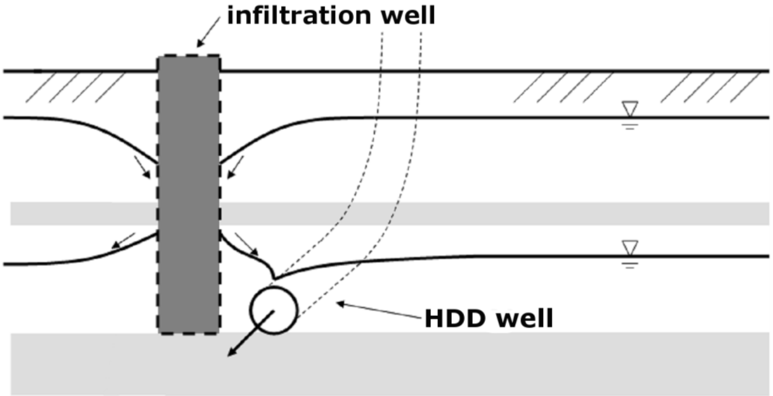

Figure 4 *Indirect connection of the vertical and the horizontal well (Struzina, Drebenstedt (2011)).*

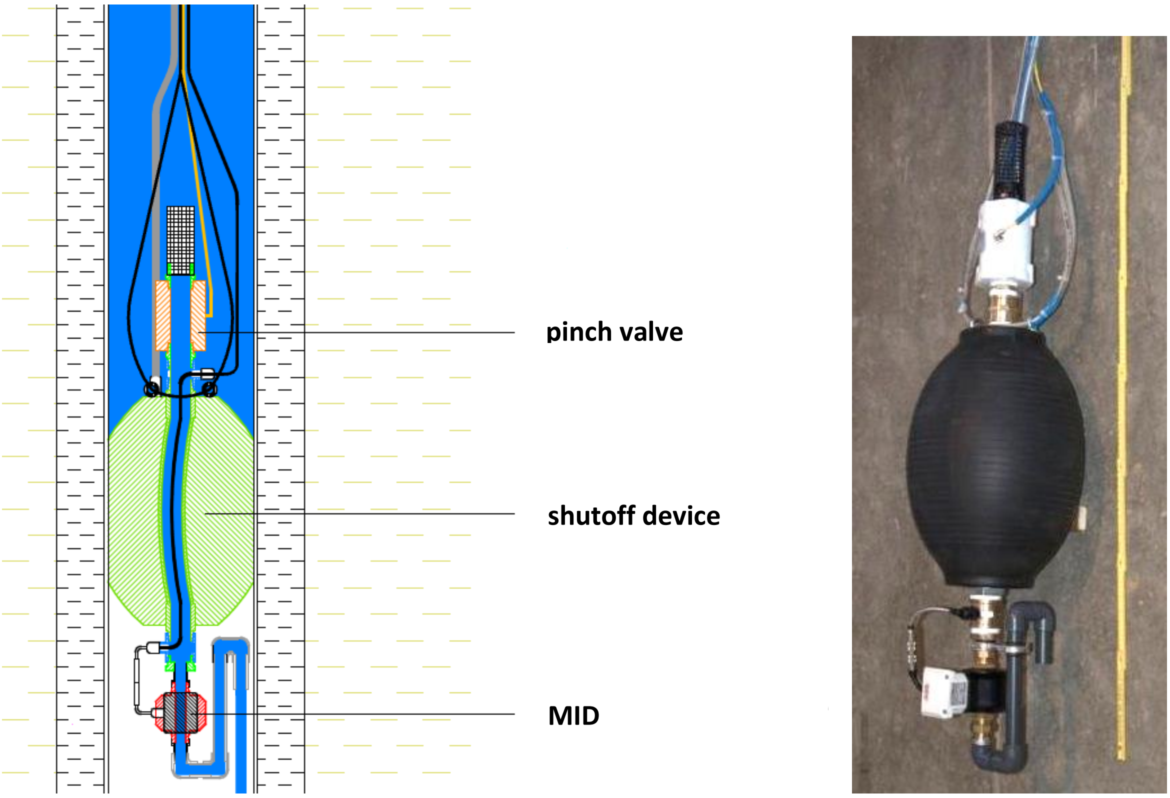

Figure 5 *Concept (left) technical implementation (reght) of the measuring device*

Ecological assessment

Besides technical and economic issues especially environmentally relevant benefits were motivation for the study. Based on the field test, horizontal and vertical wells were compared theoretically. For this purpose, an ecological assessment was made according to Schmieder, Drebenstedt (2007).

Regarding the dynamic operation mode of an opencast mine different parameters were taken into account.

Input parameters:

- materials (e.g. pipes, cables, pumps, etc.)
- technique (e.g. drill rig, crane, caterpillar, etc.)
- energy consumption for installation and operation

Ecological parameters:

- cumulative expenditure of energy
- cumulative material expenditure
- CO2-equivalent
- SO2-equivalent
- land use

A calculation model was set up as a tool for comparison considering expenses and environmental impacts of opencast mine dewatering (Mansel et al (2015)). Since partially not enough operational data was collected, it was necessary to revert to values of the GEMIS-Database. The result is an assessment of environmental impacts concerning several periods as well as the whole term of the mine operation.

Results and Discussion

Vertical well

For the installation of the vertical well a flush drill was used which lead to unfavourable conditions regarding well capacity because of decreased hydraulic conductivity. In addition, the dewatering of the lower aquifer was slower than expected which resulted in low infiltration rates. However, during 280 days of operating time 642 m³ of water were drained out of the higher and infiltrated into the lower aquifer.

HDD well

Due to the usage of drilling fluid and borehole silting several well developments were necessary to increase the well capacity. The average flow rate of the horizontal well was approximately 80 l/day. During the operating time of 313 days ca. 26.000 m³ of water were drained out of a nearby slope using the horizontal well. The flow volume was measured using a MID (fig 6).

Figure 6 *Measuring device of the HDD well.*

Ecological assessment

After evaluating retrieved data it became clear that the advantageousness of HDD wells is associated with a close distance to the pit slopes because of shorter pipe sections and the usage of existing pumping stations and their configuration. With long screened sections combined with high lead-time in terms of time and space of the dewatering process, the advantages of horizontal wells are predominant.

Apart from the examined parameters, some influencing factors were not taken into consideration. These are for example:

- amount of residual water
- geometry of the water table drawdown
- geotechnical stability of the excavation slope
- horizontal well with annular backfilling
- horizontal well built with blind hole technique

Conclusions

Concerning dewatering of opencast mines in Germany, the usage of horizontal dewatering wells is currently limited to a few special cases. Advantages of horizontal wells arise from long screened sections and reduced consumptions of energy, material and land use, whereby environmental relief can be expected.

By means of a field test where the interconnection of two aquifers allowed a combined dewatering with free water runoff using a horizontal well with a 200 m long screened section, information concerning technical, economic and environmental issues was gathered. During the project the modeling software PCGEOFIM was developed further to take channel and pressure pipe flow into account. A numerical flow model was built up to simulate the field tests.

Regarding relevant input parameters, an ecological assessment was made comparing vertical and horizontal wells as main dewatering element. As a result, the length of the screened section as well as the distance to the pit slope and the pumping system turned out to be the main influencing factors for the advantages of horizontal wells.

Acknowledgements

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Best Practices Checklist for Modelling Mine Waters

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Abstract

Modelling the flow, concentrations and load of mine waters often entails the use of different tools and software to represent different aspects of the mine and the receiving environment. However, there are steps common to all modelling applications that can improve accuracy, transparency and interpretation by the modeller. These steps will also help the client who may need to make management decisions based on the model results, or regulators or stakeholders who will ultimately rely on the model results to make permitting or policy decisions.

This paper provides a 15-point modelling checklist, along with examples of what to do and what to avoid, drawn from case studies. The case studies include modelling completed for oil sands, diamond and copper mining projects in Western and Northern Canada. The models used in the case studies include mass balance, hydrogeological and geochemical modelling of mine waters; dispersion modelling of effluent; hydrodynamic modelling of pit lakes; and watershed modelling in the receiving environment.

The best practice modelling checklist is as follows: 1. Define objectives for the model; 2. Develop a conceptual model; 3. Establish output metrics; 4. Establish screening criteria; 5. Select the model framework; 6. Gather input data; 7. Implement quality assurance procedures; 8. Set up model physical domain, boundary conditions, and parameterization; 9. Calibrate stepwise: physical, chemical and biological; 10. Simulate scenarios; 11. Compare output to criteria; 12. Iteratively modify mitigation, models and screening criteria, as appropriate; 13. Conduct an uncertainty and/or sensitivity analysis; 14. Identify and simulate "black swan" events; and 15. Conduct a post-audit.

Key words: Modeling, calibration, validation, hydrodynamic, dispersion, mine waters

Introduction

Many types of models are applied to mine waters. The basic mine water model is a water balance, which is often constructed as a "spreadsheet-like" accounting system. Components of the water balance may be modelled in more detail using numerical models, such as a hydrogeological model or a hydrodynamic model. A model's utility and range of application can be improved by coupling it with a larger water quality model. Generally this requires a geochemical model to derive the composition of contact waters from waste rock, tailings, ore, and roadways; waters originating from the mill; and other site-specific inputs. For complex moving and dynamic flows, a hydraulic, hydrodynamic, or watershed model may be required. Most mines require a hydrogeological model to understand pit dewatering, refilling and exfiltration. A whole-system model that represents the mine throughout the life of mine and post closure will actually require most of the aforementioned models in a system of linked or coupled models. All of these types of models share a common set of fundamental steps, along with their unique set of requirements, limitations, uncertainties, data needs and quality assurance practices. It is the aim of this paper to present a basic set of "Best Practices" that are applicable to mine water models, based on a number of case studies drawn from projects that included multiple sets of coupled models.

Recognizing that there is no "recipe book" approach to modelling that will fit all applications, the list of steps presented in this paper is put forward for consideration when developing a model and serves as a checklist for reviewing models by others.

1. Define objectives for the model

Definition of the model objective(s) is the most important step in mine water model development, as it determines many aspects of subsequent steps. The objective should be clearly defined and agreed to by the entire modelling team and the client. There may be multiple objectives for different scientific disciplines within a project, but there must be one defined objective for a given model. A few examples of a mine water model objective are to: test a hypothesis; support a permit application; evaluate mitigation; conduct an environmental assessment; forecast future conditions; guide research by identifying knowledge gaps.

The objective should be clear, actionable and achievable. All subsequent modelling tasks should be aimed at meeting this objective. For example, the choice of inputs to a model will change depending on the objectives. For permitting, the emphasis will be on constructing a defensible model, and inputs which are known to be biased to produce conservative results are common and acceptable. Conversely, for hypothesis testing or design work, accurate or likely inputs are usually preferred over conservatively high inputs.

In systems of linked or coupled models (e.g., Vandenberg et al. 2015), there may be multiple modellers simulating different aspects within the overall model domain, each with individual objectives. While it is important for the entire team to be working toward a shared overarching objective, it is also important that modellers understand each other's individual objectives as those may affect the data required, as well as how the data being transferred from one model to another are generated.

2. Develop a conceptual model

A conceptual model is a description of the system of study, preferably accompanied by a schematic or diagram. Conceptual models can be the traditional source-pathway-receptor diagram as used in risk assessment, or more commonly in mine water applications, they are schematics of mine facilities with simplified water balances that illustrate storage, inflows and outflows. More complex, mechanistic models may warrant detailed conceptual models. Generally the complexity of the conceptual model informs the complexity of the numerical model; it follows that if a process is important enough to illustrate in the conceptual model, it is likely relevant to include it in the numerical model.

The conceptual model serves two main purposes. First, it helps the modelling team brainstorm and agree on which processes are most important to the system of study. Equally important, it communicates these important processes to clients, reviewers, regulators and stakeholders who will have a more limited view of the modelling process that was used to generate the results they will rely on to make decisions.

3. Establish output metrics

Before commencing the processes of numerical model development, it is important to consider the type of output that is required to achieve the model's objectives. The most basic information will be flow and concentration; virtually all models will be capable of producing this information. However, the granularity of output required can vary greatly depending on the system to be modelled. For example, knowledge of high-flow and low-flow events are often the most critical to results even though they occur infrequently. Similarly, high concentrations may occur with limited spatial and temporal extents, but may be critical to the overall system (e.g., a seepage to spawning habitat during low flow). Knowing which types of model output will be required and the temporal periods of interest will help select the right model platform, and/or help plan for level of effort in developing post-processors that convert or format the model output.

4. Establish screening criteria

In most mine water applications, model results will need to be compared to some threshold or criteria. Establishing the screening criteria in advance will help interpret results as they are being generated. It is not unusual to generate several iterations of results; a pre-defined set of criteria make it easier to judge whether mitigation or model refinements are necessary.

Ideally, the frequency of model output should be aligned with the given screening criteria. For example, many water quality guidelines are derived from (and are therefore applicable to) a given exposure duration. If the model cannot meaningfully output as frequently as the specified criteria due to an inherent limitation such as model time step, the model or criteria will need to be adjusted. Conversely, if the model outputs too frequently, the results can be post-processed for comparison to screening criteria.

Will you be concerned with relative changes or absolute values? When dealing with low water concentrations, the relative change can be very large but not ecologically significant. In contrast, a relative change may be required to determine significance when the results are near the margins of a threshold. In some models, a relative change may be all that can be confidently relied upon, because there is a high uncertainty in the absolute values. Provided a transparent reason is stated, either of these types of output may be justified.

It is sometimes useful to have two or more levels of criteria, based on return period of flows, biological response, generic guideline, or regulatory limit. The frequency of compliance for the different levels of criteria may differ, which is another capability to consider when selecting a model.

Most chemical models can output all water quality parameters that are simulated, but the units can vary. If this is going to be the case, plan for pre-processing and additional quality control of results. Where models are linked or coupled, the output of one model becomes the input to another model. In this case, it is critical to have matching input/output frequencies, spatial nodes, and units.

Regardless of the model output and screening criteria, it is up to the modeller to provide conclusions regarding the model results. For the model to have maximum credibility and persuasiveness, the justification for the screening criteria should be clearly laid out.

5. Select the model framework

There are many software packages available to develop a mine water model, and even multiple choices available for a given sub-discipline within the broader category of mine waters. A num-ber of criteria should be considered when selecting a framework, including: built-in functionality, dimensionality, availability of input data, ability to simulate sensitivity analysis or Monte Carlo simulations, scalability, linkages to other models, and computational efficiency.

Of these criteria, built-in functionality and dimensionality will normally be the first differentiators. If hydraulic, hydrologic, hydrogeolologic, hydrodynamic or geochemical functionality is required, the choice of model for those processes is limited. For analytical (or semi-analytical) water and mass balance models, generic software such as Excel, GoldSim or Matlab are commonly applied. These programs may also be used to integrate the results from several more complex models within the overall system. A good rule of thumb for selecting a model is that it must be capable of simulating the processes illustrated in the conceptual model.

Computational efficiency can be a major factor when simulating mine closure, because the time frames of interest extend for decades to centuries. A long-term simulation to understand the vertical mixing regime of a pit lake, for example, can take days to run, even if care is taken to make the grid efficient. Likewise, transient simulations of groundwater flows to a refilling pit can take substantial amounts of time. If this is the case, consider standalone simulations using the minimum required dimensions (which are site-specific) to reduce total run times. Similarly, if the input data required for a complex 3-D model are not available, consider using a more simple system until additional data can be acquired.

The choice of open-source versus proprietary software is sometimes made on the basis of license fees, but there are additional considerations. The fees associated with proprietary soft-ware often include technical support, which is important for new modellers who do not have a large support network within their institution. The drawback of proprietary models is that reviewers and stakeholders may not have access to the software, in which case they sometimes view it as “black box” software, which, rightly or not, can diminish the credibility of the overall project.

Lastly on this topic, modellers should be wary of becoming too invested in a given software package and automatically applying that tool to every mine water application. The applicability of a given software package to one mine site does not necessarily confer applicability to any other site.

6. Gather input data

The task of gathering input data can be one of the most time consuming and challenging; the effort required is often under-estimated. In mine water model applications, it is not unusual to have sub-sets of the input data maintained by the mining company, previous consultants, various government agencies, and combinations thereof. For example, the mining company may have a site-specific weather station that has detailed meteorological information – but from a limited time period that needs to be integrated into a long-term dataset from a nearby government station. Similarly, baseline water levels, flows and hydrogeological information may be available from neighbouring developments or with another consulting firm, and these may need to be adjusted based on long-term datasets from a regional monitoring station that is maintained by government. Geochemical data used for input to water quality models requires both computational organization, and an evaluation of the results of geochemical testing in the context of the conceptual model (e.g., the estimated metal leaching and acid generation potential of materials in laboratory conditions versus field conditions, the effect of project specific mitigation on the acid generation potential of a material, etc.). Each of the organizations supplying data will inevitably use different formats and conventions for storing data, which means the modeller may need considerable time to re-format and assemble datasets once compiled.

Once all data are obtained and compiled, there will often be gaps in time or space that need to be filled. For geochemical data, if site-specific information is not available for all water quality parameters, proxy data from a mine with similar geological characteristics may be applicable, such as that presented in Plumlee et al (1999).

Be aware that using proxy data of any type (i.e., geochemical, hydrologic, meteorologic, etc.) will increase the uncertainty of results. Recommendations for monitoring to reduce data gaps should accompany any model results that were derived using incomplete data sets, if the gaps could affect the conclusions drawn from the model.

Ideally, an independent dataset should be used for calibration and validation; that is to say, calibration and validation data should not be used as inputs to the model.

7. Implement quality assurance procedures

Quality assurance (QA) is an overarching process that begins before modelling and includes quality control (QC) of field and laboratory data. Ideally, the quality control applied to model inputs and outputs will be integrated into an overall QA program and the modeller will have input into the data collection process.

In practice, most mine water models are developed by modellers after the data have been collected by other groups and provided to the modeller. In this case, the modeller should examine the QC steps and results that have already been applied, such as screening of analytical data for outliers, ion balances, checking total versus dissolved metals, measured versus calculated TDS, etc. If these types of checks have not been documented, they should be completed prior to accepting data as valid.

After data have been validated, compiled and assembled into input files, all input data should be graphed in a time series. This applies to flow, chemistry, meteorology or any other time-varying input. If ranges of dates have been interpolated or substituted to fill gaps, the raw data should be graphed along with the synthetic timeseries to check for differences. This QC step has proven to be a reliable method for exposing anamalous data in model inputs. At a glance, one can usually spot the following types of errors in an input dataset: outliers; zeros or nulls in a dataset; negative values; changing detection limits; and nonsensical values, which are those that do not fit the data type, season, or variable.

While the visual method can usually identify extreme outliers, batch statistical tests can be used to identify statistical outliers. “Outlier” is a collective term that refers to either a contaminant or discordant observation (Beckman and Cook 1983). A discordant observation appears surprising or discrepant, but the origin of the result is unknown. A contaminant is an observation that may induce bias to a fitted probability distribution, and the reason for its characteristics can be explained. If a measurement is identified as a statistical outlier, the origin of the result can be investigated to validate the results of outlier detection tests performed on the dataset. Outliers of explainable origins (i.e., there was a reason for the anomalous result) are considered contaminants and are generally justified to be removed from the dataset without further consideration. Outliers of unknown origin are considered discordant observations and may be retained in the dataset for further investigation.

Given that statistical tests can identify, but usually not explain outliers, a conservative approach to removing outliers based on statistical tests is to apply multiple tests, and only remove those that are flagged by all tests. Three commonly used tests are: the three times standard deviation (3σ) rule; the Hampel identifier; and the combined Rosner – Dixon test, descriptions of which are presented elsewhere (Lauzon et al. 2011).

As a final step in validating input files, compare the ranges of values and units to the original dataset to confirm that any unit conversions along the way have been done correctly.

During the modelling process, a helpful QC check is to compare preliminary results against simple hand calculations or spreadsheets to confirm that output falls within the right range. This step will identify gross errors, which are common during initial runs. A peer or senior review of inputs and coefficients provides additional QC during the model simulation step.

Final model output can also be checked against simple calcuations as a QC step. This can be done by the modeller or the peer reviewer. If the output from one model becomes an input to another model (e.g., flows from a hydrologic model being input to a water quality model), those outputs should be critically reviewed by the receiving modeller.

8. Set up model: physical domain, boundary conditions, parameterization

The model setup process will vary greatly depending on the type of model and complexity of the system. Generally applicable steps and lessons learned related to model parameterization are provided below.

Whether using a single model or a series of linked or coupled models, the first step is usually to set up a physical domain, which may include a grid or series of compartments in one or more dimensions. At discrete points or along planes of the domain, boundary conditions such as flows, heads, solar radiation and winds are applied. When linking multiple models, it is important for both teams to agree on the dimensions and fluxes that will be output and input at these locations. In models that have coupled hydrogeology-solute transport or hydrodynamics-water quality, the physical model should generally be set up, run and verified before proceeding to chemical inputs. Even in simpler systems such as a water and load balance, the water balance should be fully operable before simulating any chemical loads. Likewise, chemical parameters that involve fate processes, and biological parameters, should be included after all conservative chemical species have been set up. In models with complex feedback interactions, such as an eutrophication model, the set up and calibration will be an iterative process, because the simulation of one species can influence another species that was previously thought to be fully set up.

When generating model input files, be aware that many variables in mine waters will covary seasonally and may also exhibit autocorrelation. Knowing the degree of autocorrelation to include in a given input can be challenging. If the variable has been measured frequently, the historical values will demonstrate this pattern; however, sufficient datasets are usually only available for existing mines with stringent monitoring conditions, such as those with active discharges to the receiving environment. If a comprehensive dataset is unavailable, proxy datasets can be examined; the dataset with the most similar hydraulic residence time and seasonality will give a good indication of autocorrelation (and perhaps, by extension, a template to follow for the sparser but site-specific dataset).

Depending on the amount of calibration data available, parameterization may be a simple step of inputting values from previous applications, literature, or professional judgement. If calibration data are not available, a sensitivity analysis can be completed on key inputs to evaluate the potential effect on results if another value were chosen for a given coefficient.

Lack of calibration data is generally a knowledge gap that the modeller can identify and help rectify by recommending monitoring that could be undertaken in the existing or future mine water system that is being modelled. Collection of monitoring data is a key component of the post-audit, discussion in Step 15.

9. Calibrate stepwise: physical, chemical, biological

The process of calibration will also vary depending on the specific model applied, the complexity of the system and the amount of data available. The term 'calibration' itself is not consistently applied, but in this context, it is considered to be

> *the process of adjusting model rates, coefficients and unknown or unmeasured variables such that the numerical model produces a reasonable hindcasted match compared to past observations.*

'Validation' is a related step, usually undertaken after calibration, and is defined here as

> *comparing model predictions to measurements that are collected after the model predictions have been made; or, extending a calibrated model with recent boundary condition data, and comparing predictions to field data, without adjusting the calibration.*

Similar to the model set up, calibration should proceed stepwise from the physical domain to the chemical and then to biological, which reflects the order of key drivers acting upon the system as well as an increasing level of complexity.

When applying any fate process to a mine water model, which will commonly be a loss of some mass with time, consider the actual mechanism that is being simulated. Often in calibrating a model, some rate that is observed in an existing facility will be applied to a future facility. If that is the case, critically examine the following: Is the mechanism known to the degree of confidence that justifies applying the calibration to future settings? Are conditions in the observed system the same as those in the future system? Are byproducts or feedback loops being generated that should be accounted for elsewhere in the model?

10. Simulate scenarios

Model simulation is generally straightforward. The main things to consider are that the simulation period, output nodes of interest and output format should all fit the model objectives. It is a given that models are imperfect representations of reality, and the degree of imperfection within a model will vary with time and space. What is important is that the model reflects a level of realism at the time and location of interest to the predictions, in a way that achieves the overall model objectives.

11. Compare output to criteria

After generating model results, the metrics and criteria derived or set in Step 3 can be applied to the results. Again, it is important to consider the model's objectives when comparing results to criteria. For a detailed design project, a high level of accuracy may be required, whereas for a regulatory application or risk assessment, a lower level of accuracy may be acceptable, provided conservatism is applied to uncertain inputs.

While models may produce vast arrays of results, not all results may be applicable to the selected criteria. For example, water quality guidelines are often derived using some averaging period, which can differ from an instantaneous result, or a model result that is averaged over a different time step. In some cases, it may be possible to line up the applicable time periods; if not, a description of the difference should be noted to those who rely on tables of data that compare model results against criteria.

Likewise, when comparing a statistical result to criteria, the probability chosen to represent model results should align with the derivation of the criteria or the design objectives. Using probabilistic or Monte Carlo simulations, described more under Step 13, is a common approach to assigning a probability to a model result.

If a deterministic simulation is completed using a single statistic to represent inputs (e.g., 95th percentiles), the probability of the output from that simulation is not possible to estimate (except to say that it will be much less likely). Therefore, the results should not be labelled with the same statistic (i.e., the likelihood of an outcome that assumes multiple, independent events, each with a likelihood of one in twenty, will be far lower than one in twenty).

12. Iteratively modify: mitigation, models & screening criteria, as appropriate

It is usual in mine water modelling to require several iterations with refinements to any of the previous steps. Often, conservatively high inputs in the first round of modelling will lead to results that exceed screening criteria, and the modeller may adjust the inputs to be more accurate and less conservative. Similarly, the screening criteria themselves may be too stringent and may need to be discarded in favour of site-specific thresholds.

One of the main reasons to employ mine water models is to identify and select mitigation measures. If an initial simulation identifies the need to add mitigation, and that measure is adopted, it will need to be incorporated into the model to assess potential efficacy. The mitigation may take many forms, such as a water treatment plant, barrier wall, soil or water cover, water diversion, or changes to the mine plan. Accordingly, all parts of the model process, including the conceptual model, are subject to modifications and may require iterations. In some modelling projects of dynamic mine environments, a model scenario may be deemed 'frozen', so that the entire team has a fixed basis that can no longer iterate. This can be an essential step in preparing large regulatory approvals where the preparation of a linked set of models takes extended time periods. The modeller needs to be aware that assumed changes in one part of the model may lead to discrepancies in a regulatory application with another part of the model that has not been frozen.

Ideally, a mine water model will be constructed with the intention of keeping the model as a living tool that will updated throughout the life of mine and into post-closure. Updates can entail frequently appending input data that are continually being collected, and occasional updates to the domain as the mine plan progresses, as outlined in Step 15.

13. Conduct an uncertainty and/or sensitivity analysis

There are many sources of uncertainty to a mine water model. Some can be understood and quantified using standard methods, while others cannot. The former type of uncertainty (known unknowns) is discussed in this section, and the latter (unknown unknowns) in the next section.

Some types of uncertainty can be identified, understood and quantified (at least approximately). For example, analytical variability, seasonality, anisotropy and heterogeneity in a given system can be quantified or estimated through intensive monitoring. If you are fortunate enough to know the approximate range of values for a given variable based on a thorough dataset (i.e., adequate length, spatial coverage and frequency of measurement over a range of seasonal and climactic conditions), along with the probability of each value, then the uncertainty due to this single variable may be estimated. If the uncertainty profile of multiple variables are known, they can be combined in a stochastic simulation. If all dominant variables are well characterized, they can be combined in a Monte Carlo simulation to quantify known unknowns.

In order for the resulting output profiles to provide realistic likelihoods associated with each result, the variables that co-vary must be identified, and the covarying nature of each input must be aligned. The alignment need not be perfect, but any discrepancies will add uncertainty to the results, and that uncertainty can be hard to quantify. Correlation plots provide a quick way to establish temporal patterns among inputs, such as flow and TSS concentrations, and if these are not already linked mechanistically in the model, they can be linked statistically when deriving inputs and generating model input files.

The results of a Monte Carlo simulation can be evaluated over time or in aggregate – again, whichever fits the model objectives. In either approach, there is a likelihood associated with any concentration, which provides a basis for estimating and communicating the overall model uncertainty. But the key limitation to consider when applying these methods is that they only account for uncertainty that has been identified and incorporated into model inputs.

A more straightforward and less computationally and data-demanding exercise that can be used to quantify uncertainty is a sensitivity analysis. This is done by changing one variable, which could be a coefficient or time series of input data, keeping all other model inputs fixed, and re-running a scenario. The difference in results indicate the effect or ‘sensitivity’ to that single input. This can provide valuable information when the modeller cannot obtain specific input data, has uncertainty about aspects of the calibration, or cannot defensibly choose one input over another to apply to future conditions. The sensitivity analysis can answer the question of *what if some other input turns out to be real?* The limitation of this approach is that it may oversimplify the problem because few, if any, variables are truly independent of all other variables.

14. Identify and simulate "black swan" events

To discuss the unknown unknowns, we borrow and adapt two metaphors of the black swan to modelling:

The first black swan metaphor by Sir Karl Popper deals with falsifiability. Prior to 1697, every swan that had ever been observed by Europeans was white, which inductively led to reasoning that "all swans are white". Were a biologist to go searching for more swans to prove this theory, they would indeed find that all empirical evidence supported that theory and they might be tempted to accept this as "proof". However, with the discovery of a black swan in Australia in 1697, a single observation falsified that theory. In this context, a black swan is a single observation that falsifies a previously held theory.

The second metaphor by Nassim Nicholas Taleb deals with predictability. In his book *The Black Swan* (Taleb 2007), he describes events that come as a surprise, have a major effect, and are often inappropriately rationalized after the fact with the benefit of hindsight. His metaphor is primarily concerned with events that have a major impact on civilization.

Extending these metaphors to a mine water model, a black swan can be thought of simply as a process, event, or input to the actual mine water system that, if encountered in the future, will invalidate the model results because it was not considered by the model. A black swan event is not reasonably foreseeable and its probability cannot be quantified with any accuracy. Therefore, the approach to deal with black swans is to attempt to identify possibilities and to have contingencies available where they are identified. The challenge is to distinguish between black swans from implausible or impossible scenarios.

An example of a black swan event in a mine water context is a landslide into a meromictic pit lake with submerged mine waste. The likelihood and consequence of lake overturn and release of contaminants to surface water and introduction of oxygen to the submerged waste are possible to estimate considering a plausible range of limnologic and climactic conditions. But if an earthquake or other geological event intervenes, all bets are off. The earthquake is a black swan that would invalidate all model results. In this case, the event needs to be evaluated and planned for using means besides the model. If the model can be modified appropriately, it may be able to be used to understand the consequence of such an event by assuming it happened.

The modeller need not arrive at contingencies for all such events (though that would be a value added service). The modeller's challenge, and their responsibility, is to identify and communicate to managers or stakeholders the types of events and processes that may render the model results invalid – the black swans.

15. Conduct a post-audit

While there is some debate over the definition and utility of model validation and verification (Konikow and Bredehoeft 1992; Nordstrom 2012), it is in the interest of all to understand whether model predictions turn out to be accurate. In the broader context of managing mine waters, regulators need to know whether to place confidence in models; stakeholders need to know whether the clean water, mitigation, or other resulting prediction came true; mine managers need to be able to adaptively manage based on differences in reality versus what was predicted; and the modeller needs to know which predictions were accurate and which were not in order to improve their approach with subsequent models.

A post-audit is a series of measurements, collected after the model predictions have been posted, and during or after the mine development proceeds, which are compared to the previously made model predictions. A post-audit provides a means of testing the model predictions against reality and verifying whether (a) the model was accurate;(b) the assumed mitigation was effective; and (c) that the correct decision was made (i.e., that the model objectives were ultimately met).

Conclusions

A checklist of best practices is provided above for developing and applying mine water models. The most important steps are to set clear objectives and to develop a conceptual model, as these steps will affect nearly all subsequent steps. The final steps of identifying uncertainty and comparing predictions to post-development observations are the most critical in terms of understanding the limitations and performance of the model and for communicating those to stakeholders.

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Prediction of Source Term Leachate Quality from Waste Rock Dumps: A Case Study from an Iron Ore Deposit in Northern Sweden

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Abstract

The prediction of source term water quality from mine waste disposal facilities is an important aspect of the design and management of mining operations. Predictive numerical calculations have been completed for the assessment of long-term leachate chemistry emanating from a proposed Waste Rock Dump (WRD) at an iron ore deposit in Northern Sweden. The prediction required the generation of source term water quality for the WRD in terms of solute concentrations and loading, in addition to assessing the effects on water quality in the receiving watercourse adjacent to the facility. A source term was developed from the results of laboratory static and kinetic testwork carried out on drillcore samples of representative waste rock lithologies. Based on static testwork results, the WRD material consists of two broad material types: (i) Potentially Acid Forming (PAF) skarn with a sulfur content >1%, which makes up 34.3Mt of the 124Mt estimated waste, and (ii) Non-Acid Forming (NAF) material types with a sulfur content <1%, making up the remaining waste. Mass balanced Humidity Cell Test (HCT) and Net Acid Generation (NAG) test results were used to develop source terms for WRD scenarios during Life of Mine (LOM) and post-closure. Model scenarios included: (i) segregated and unsegregated waste; (ii) spring and average snow melt conditions; and (iii) the application of standard soil and qualified covers post-closure. Modelling results demonstrated that loading of metals from the WRD was greatest during spring for the LOM scenarios; when seepage through the WRD is greatest and the material is uncovered. However, due to river flow being highest during the spring months, a dilution factor is experienced and predicted metal concentrations in the adjacent watercourse are generally lower than for average flow conditions. In all cases, segregation of high sulfur material was shown to give the best results in terms of elemental load release and predicted elemental concentrations in the adjacent river.

Key words: Water Quality, Waste Rock Dump, Source Term Predictions

Introduction

Acid Rock Drainage and Metal Leaching (ARDML) from waste rock at mine sites can be a major environmental liability that greatly complicates and adds to the expense of site closure. There are strong economic and environmental arguments for improving the accuracy of predicting if and when a Waste Rock Dump (WRD) will turn acid. Quantitative model parameters need to be obtained from a systematic laboratory study of the waste material in question. To allow a meaningful prediction of long-term leachate quality to be made, a detailed knowledge and understanding of site specific hydrologic, climatic and geological conditions is required.

Numerical modelling and assessment of long-term leachate chemistry was carried out for a proposed WRD at an iron ore deposit in Northern Sweden. The main objective of the modelling exercise was to predict source term water quality in terms of solute concentrations and loading emanating from the WRD into the adjacent watercourse during Life of Mine (LOM) and following closure.

Methodology

Sampling

Leapfrog 3D visualisation software package (Version 2.2.1.44) was used to identify spatially and lithologically representative samples of waste rock for geochemical characterisation testing. A total of thirty three waste rock samples from drill core were collected and sent for analysis at a commercial accredited laboratory. Details of the sampled lithologies are shown in Table 1.

Table 1 *Breakdown of sampled lithologies*

Rock Type	Lithology	Number of samples
Skarn	Actinolite skarn	2
Skarn	Clinopyroxene actinolite	3
Skarn	Clinopyroxene skarn	6
Skarn	Clinopyroxene-Actinolite	1
Skarn	Serpentine skarn	2
Skarn	Skarn (Tactite)	2
Skarn	Tremolite skarn	1
Granite	Granite	3
Volcanic	Intermediate Volcanic Rock	1
Volcanic	Mafic Volcanic Rock	3
Marble	Marble	3
Other Meta/Intrusives	Amphibolite	1
Other Meta/Intrusives	Greenstone	1
Other Meta/Intrusives	Monzodiorite	2
Other Meta/Intrusives	Quartz Phyllite	2

Laboratory Testwork

Static and kinetic laboratory tests were undertaken, in addition to a mineralogical study, on the samples in order to determine the elemental and mineralogical composition of the waste rock, and to understand the leaching behaviour of each rock type. The static tests completed were: multi-element analysis using aqua regia digest following by ICP analysis; Acid Base Accounting (ABA); Net Acid Generation (NAG) testing with leachate analysis; short term leach test (in accordance with BS EN 12457-3 [BSI 2002] at a 2:1 and 8:1 liquid to solid ratio) and mineralogical analysis.

The results of the static test showed that the majority of samples fall into Non-Acid Forming (NAF) category; having a sulfide sulfur content less than 0.5% or a Neutralising Potential Ratio (NPR) greater than three and a NAG pH less than 4.5. Based on the ABA results, five skarn samples are classified as Potentially Acid Forming (PAF) and the remaining samples were classified as NAF or uncertain.

Based on the static results, the WRD material is defined as consisting of two main material types:

(i) PAF skarn with a sulfur content >1%, which makes up 34.3Mt of the 124Mt estimated waste (i.e., 28%); and

(ii) NAF material types (granite, marble, volcanics) with a sulfur content <1%, make up the remaining 72% of waste (approximately 89.7Mt).

Subsequently kinetic Humidity Cell Tests (HCT) in accordance with ASTM D5744-96, were run on two NAF skarn samples, a NAF marble sample and three PAF skarn samples for a period of between 40 – 60 weeks. Weekly leachate analysis was carried out by ICP-OES and ion chromatography.

Conceptual Model

Conceptual geochemical models were developed from a review of background and site-specific data. Conceptual models were developed for both a LOM scenario and a post-closure scenario and are illustrated in *Figure 1*. Mass balanced HCT and NAG test results were used to develop source terms for the following model scenarios:

(i) Segregated (PAF and NAF cells) and unsegregated (blended PAF and NAF) waste;

(ii) Spring and average snow melt conditions; and

(iii) The application of standard soil and qualified covers post-closure (reducing infiltration).

Source term results for LOM average, LOM spring and closure options using different qualified covers have been combined with average (0.7m^3/s) and high spring (7.29m^3/s) river flow conditions in the adjacent watercourse to determine the impact of seepage on receiving surface water.

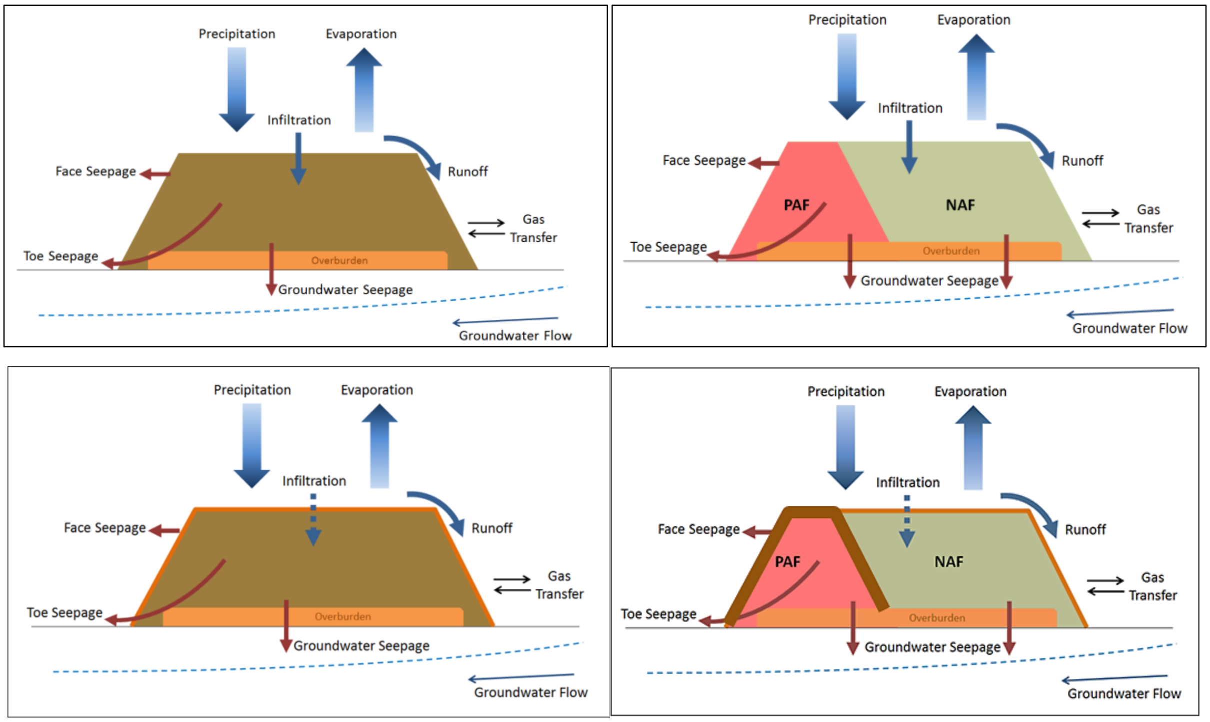

***Figure 1** Conceptual models for blended (left) and segregated (right) WRD during LOM (top) and post-closure (bottom)*

A scaling factor was applied to the laboratory data in order to account for the differences in reaction rates and liquid to solid ratios between the laboratory test and field conditions. The chemical and physical scaling factors applied in this paper are based on methods presented by Kempton (2012), whereby up-scaling factors are applied to the prediction of field scale seepage from laboratory tests. A summary of the scaling factors applied are presented in Table 1 below. Climate monitoring data for the site was utilised to provide estimates of evaporation and precipitation rates. Surface water quality for source term mixing was obtained from river water sampling previously completed by SRK. The rainwater used in the models is generic Northern Europe rainwater (USGS 1997). Water chemistry predictions were made using the geochemical modelling code PHREEQC, version 3.3.5-10806 (Parkhurst & Appelo 1999) together with an in house modified version of the MINTEQ.v4 database.

***Table 2** Modelling parameters summary*

Parameter		**Value Applied**		
		LOM Average	**LOM Spring**	**Closure**
	Infiltration (mm/yr)	265	1694	98
	Seepage (m^3/day)	1278	5951	471
	Oxygen ingression	Based on ANSTO model[*1]		
Scaling factors	NAG	0.001% for all scenarios		
	HCT	No distinct factor used		
Chemical scaling	Temperature	26% for all scenarios		
	O_2[*2]	50% of atmospheric for all scenarios		
Physical scaling	Proporation fines	20% for all scenarios		
	Proporation fines flushed	50% for all scenarios		

[*1] *Convective airflow minimised and O_2 mass transport by diffusion*

[*2] *Average concentration over penetration depth*

Results and Discussion

The predicted source term water quality output results from each iteration of the model scenarios (using NAG and HCT data) are shown in Table 3. Source term results for the LOM average, LOM spring and the closure scenarios have been assessed against average (0.7 m^3/s) and high spring flow (7.29m^3/s) conditions in the river adjacent to the WRD in order to predict river water quality as shown in Table 4.

Generally the predicted concentrations of metals in the source term waters are found to be greater when using the NAG tests results. Modelling results indicates that loading of metals from the WRD is the greatest during spring for the LOM scenarios; when seepage through the WRD is greatest (at 5951m^3/day) and it is uncovered (Table 3). However, due to river-flow being higher during the spring months a dilution factor is experienced and predicted metal concentrations in the adjacent watercourse are therefore lower than for average flow conditions (Table 4).

Post closure loading of metals from the WRD is significantly lower than during the LOM, this is due to the lowering of seepage from the dump (to 471m^3/day) through the application of a qualified cover. By reducing the global oxidation rate (GOR) into the dump through the application of a cover the loadings subsequently decrease due to infiltration and oxidation being limited. By decreasing the oxidation rate within the dump the mobilisation of elements is also decreased resulting in an improvement in the river water quality. Scenarios in which NAG data was run generally produced higher concentrations/poorer water quality.

In all cases, segregation of high sulfur (PAF) material is shown to give the best results in terms of elemental load release and predicted elemental concentrations in the adjacent river. None of the scenarios predicted the generation of acidic conditions due to a combination of segregation and buffering from silicate phases. The seepage pH was near neutral, ranging from 7.45 - 7.64 in all model scenarios.

***Table 3** Predicted chemical loadings from the WRD based on NAG/HCT test results.*

		Predicted chemistry based on NAG test results						**Predicted chemistry based on HCT test results**					
		Segregated WRD			**Blended WRD**			**Segregated WRD**			**Blended WRD**		
		LOM Average	**LOM Spring**	**Closure Average**	**LOM Average**	**LOM Spring**	**Closure Average**	**LOM Average**	**LOM Spring**	**Closure Average**	**LOM Average**	**LOM Spring**	**Closure Average**
Seepage m^3/day		***1278.4***	***5950.9***	***470.7***	***1278.4***	***5950.9***	***470.7***	***1278.4***	***5950.9***	***470.7***	***1278.4***	***5950.9***	***470.7***
Cl	g/day	1250	5730	461	1260	5840	460	264000	1310000	263000	397000	294000	350000
F	g/day							2300	3750	2130	1990	1450	1810
SO4	g/day	1040000	3750000	989000	1030000	1040000	1010000	669000	2030000	666000	759000	552000	603000
N as NO_3	g/day	85.9	395	31.3	86.5	404	31.3	255	669	197	230	511	153
Ca	g/day	114000	738000	67800	174000	345000	137000	122000	531000	109000	141000	291000	115000
K	g/day	64000	64600	80800	34900	35600	34600	101000	256000	101000	105000	76800	98500
Mg	g/day	155000	538000	101000	137000	279000	121000	363000	1210000	325000	422000	423000	344000
Na	g/day	279000	401000	344000	171000	175000	170000	98500	106000	97700	77000	58700	71900
Al	g/day	0.03	0.128	0.0106	0.0281	0.137	0.0102	0.0298	0.135	0.0118	0.0294	0.134	0.0113
Fe	g/day	0.503	3.19	0.221	0.655	2.32	0.309	0.568	2.7	0.294	0.615	2.51	0.312
Ag	g/day	1.95	10.5	0.919	2.57	6.29	1.28	6.75	15.9	8.15	9.42	6.2	7.26
As	g/day	0.00148	3.95	5.98	0.00168	0.00148	0.00113	0.0129	0.724	0.00544	0.0116	0.005	0.000109
Cd	g/day	1.51	3.28	6.33	1.87	0.177	1.58	21.5	133	18.4	43.6	4.31	0.598
Co	g/day	543	237	560	584	152	508	21.3	34.3	18.4	18.9	4.9	0.753
Cr	g/day	0.000662	1.67	0.101	0.000912	0.0000585	0.000493	0.0000874	1.41	0.0000399	0.000252	0.0000255	0.00000123
Cu	g/day	23	78	9.37	19	6.82	7.19	0.54	40.7	0.168	1.22	0.244	0.00762
Hg	g/day	0.903	2.67	4.29	0.707	0.407	0.281	1.47	2.44	1.5	1.5	0.619	1.09
Mn	g/day	1140	912	1030	1680	397	1480	650	1560	579	682	165	24.8
Mo	g/day	1380	1270	2180	731	718	599	875	729	770	614	427	67.5
Ni	g/day	28.9	25.7	54.2	32.1	4.77	23.3	16.3	51	10.8	16.1	2.25	0.184
Pb	g/day	0.035	11.8	2.64	0.0304	0.00248	0.0151	0.00374	3.27	0.00118	0.00298	0.00034	0.0000117
Sb	g/day	18.5	16.7	23.4	9.97	10.1	9.9	27.9	38.2	27.8	23	16.8	20.4
Se	g/day	0.974	11.8	19.9	1.55	1.22	0.787	1.89	10.5	0.655	1.35	0.605	0.0137
U	g/day	8.05	13.3	9.87	5.33	5.37	5.28	42.1	78.8	41.6	38.5	28	28.2
Zn	g/day	113	69.1	165	109	12	81.1	6.03	48.8	3.82	6.38	0.673	0.0547

***Table 3** Predicted water quality in river adjacent to WRD for average and spring flow conditions*

			Predicted chemistry based on NAG test results						**Predicted chemistry based on HCT test results**					
			Segregated WRD			**Blended WRD**			**Segregated WRD**			**Blended WRD**		
		SS30-Median	**LOM Average**	**LOM Spring**	**Closure Average**	**LOM Average**	**LOM Spring**	**Closure Average**	**LOM Average**	**LOM Spring**	**Closure Average**	**LOM Average**	**LOM Spring**	**Closure Average**
	Flow m^3/s	***0.7***	***0.7***	***7.29***	***0.7***	***0.7***	***7.29***	***0.7***	***0.7***	***7.29***	***0.7***	***0.7***	***7.29***	***0.7***
Cl	mg/L	0.623	0.644	0.632	0.631	0.644	0.633	0.631	5	2.71	4.97	7.18	1.09	6.42
F	mg/L								0.038	0.00595	0.0353	0.0329	0.0023	0.0299
SO4	mg/L	1.4	18.6000	7.35	17.8	18.4	3.04	18.2	12.5	4.62	12.4	13.9	2.28	11.4
N as NO_3	mg/L	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51
Ca	mg/L	4.24	6.13	5.41	5.36	7.12	4.79	6.51	6.25	5.08	6.05	6.57	4.7	6.15
K	mg/L	0.587	1.65	0.69	1.92	1.16	0.644	1.16	2.26	0.993	2.25	2.32	0.709	2.22
Mg	mg/L	1.15	3.71	2	2.81	3.42	1.59	3.15	7.16	3.06	6.52	8.12	1.82	6.83
Na	mg/L	1.42	6.03	2.05	7.1	4.24	1.69	4.22	3.04	1.58	3.03	2.69	1.51	2.6
Al	mg/L	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4	26.4
Fe	mg/L	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78
Ag	µg/L		0.0323	0.0167	0.0152	0.0424	0.00998	0.0212	0.112	0.0252	0.135	0.156	0.00985	0.12
As	µg/L	0.097	0.097	0.103	0.196	0.097	0.097	0.097	0.0972	0.0981	0.097	0.0971	0.097	0.097
Cd	µg/L	0.00435	0.0293	0.00955	0.109	0.0352	0.00463	0.0305	0.36	0.216	0.308	0.725	0.0112	0.0142
Co	µg/L	0.11	9.08	0.486	9.37	9.77	0.351	8.52	0.462	0.164	0.415	0.423	0.118	0.122
Cr	µg/L	0.228	0.228	0.231	0.23	0.228	0.228	0.228	0.228	0.23	0.228	0.228	0.228	0.228
Cu	µg/L	0.346	0.727	0.47	0.501	0.66	0.357	0.465	0.355	0.411	0.349	0.366	0.346	0.346
Hg	µg/L	0.0036	0.0185	0.00784	0.0745	0.0153	0.00425	0.00824	0.0279	0.00747	0.0284	0.0284	0.00458	0.0217
Mn	µg/L	21.4	40.3	22.8	38.4	49.2	22	45.9	32.1	23.9	31	32.7	21.7	21.8
Mo	µg/L	0.262	23	2.28	36.3	12.3	1.4	10.2	14.7	1.42	13	10.4	0.94	1.38
Ni	µg/L	0.157	0.634	0.197	1.05	0.687	0.164	0.542	0.426	0.237	0.334	0.423	0.16	0.16
Pb	µg/L	0.0342	0.0348	0.0529	0.0778	0.0347	0.0342	0.0344	0.0343	0.0394	0.0342	0.0342	0.0342	0.0342
Sb	µg/L	0.0116	0.317	0.0382	0.399	0.176	0.0276	0.175	0.472	0.0722	0.47	0.392	0.0382	0.349
Se	µg/L		0.0161	0.0187	0.33	0.0257	0.00194	0.013	0.0313	0.0167	0.0108	0.0223	0.00096	0.000226
U	µg/L	0.023	0.156	0.044	0.186	0.111	0.0315	0.11	0.719	0.148	0.711	0.66	0.0674	0.488
Zn	µg/L	1.26	3.13	1.37	3.98	3.06	1.28	2.6	1.36	1.34	1.32	1.37	1.26	1.26

Conclusions

A numerical predictive exercise has been reported for the assessment of long-term leachate chemistry on a proposed WRD at an iron ore deposit in Northern Sweden. The prediction required the generation of source term water quality in terms of solute concentrations and loading emanating from the WRD (for segregated and unsegregated waste rock cases) and the mixing of this in the adjacent receiving watercourse both for LOM and closure scenarios at average and high spring flow conditions.

Predicted metal concentrations in the source term waters were higher when NAG test results were used to generate source term chemistry. Predictive calculations indicate that loading of metals from the WRD is the greatest during spring LOM scenarios; when seepage through the dump is greatest and the dump is uncovered. However, predicted metal concentrations in the adjacent watercourse are lower for spring high flow than average flow conditions due to dilution caused by significantly higher river flow volumes. Post closure loading of metals from the WRD is significantly lower than during the LOM, due to the application of a qualified cover reducing infiltration and seepage.

In all cases, segregation of PAF material is shown to give the best results in terms of elemental load release and predicted elemental concentrations in the adjacent river. The application of a qualified cover over the PAF material post-closure saw a reduction in oxidation rates and a further decrease in source term metal concentrations.

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Coupled reactive mass transport for the East Rand Basin (RSA)

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Abstract

Gold mining in South Africa began in the late 1800s in the Witwatersrand area. The East Rand Basin (ERB), some 50 km east of Johannesburg is such an area of approximately 800 km^2. With gold mines in ERB having closed down over time, mine operators switched off their pumps. This has left the largely interconnected underground mines within the region to flood. In addition to mines being interconnected, there are also links to overlying aquifers and associated river systems. Therefore separate models for surface water, mine water and groundwater would not be appropriate. Another reason is seepage from tailings dams does not drain directly to the river systems and mine voids, but percolates through groundwater before reaching surface water bodies or mine voids. Furthermore a portion of polluted river water is also seeping into the groundwater system at some locations and then into the underlying mine voids.

In order to simulate the system, DMT's integrated Box Model was used. This is a reactive mass transport model which allows irregular polygons for individual mine fields, relatively regular raster elements for the groundwater layers and linear elements for the depiction of rivers. The model is then used to assist in addressing the following questions:

- Which horizons are mainly responsible for inflow into the mine voids?
- What are the dynamics of groundwater rebound?
- When is the Eastern Basin going to decant?
- How can the head differences in the interconnected mines system be interpreted during flooding?
- What contaminant loads are expected in the river systems?
- What influences does decanting mine water have on local river systems?
- What is the contribution of other surface pollution sources (e.g. tailings dams) have on mine water quality?

Key words: Reactive transport modelling; couples models; East Rand Basin

Introduction

In the Witwatersrand area, mining has taken place in the three underground mining basins of the East, Central and West Rand since the discovery of gold in 1886. During this time the more than 120 mines would have been required to pump out the water that had entered the mines in order to allow for safe mining conditions. As the mines were worked out and were abandoned, dewatering of the mine voids became the responsibility of fewer and fewer mines, and the voids (tunnels, drives and shafts) started filling with water as seen in Figure 1. Pollution generated through the ingress of water into the mine voids, is generally characterised by one or more of the following: low pH, high salt content (mostly made up of sulphates), and high levels of metals – particularly iron. In cases where uranium is present, radiological risks may also be present. There are numerous high ingress areas within the study area for example sinkholes, subsidence due to shallow mining activities, opencast mining pits etc.

As the water levels in the mine voids rise, pollution can pollute shallow aquifers. Once the polluted water reaches the surface and starts to decant, it flows down to wetlands, streams and rivers, and mortality of aquatic biota may occur. Since the rivers are inter alia used as a water source for the supply of water for agriculture, recreation and drinking purposes, polluted water potentially affects the fitness for use of such water. Polluted water can also have a cost implication further downstream due to elevated constituents that may be caused. Hence the apportionment study, to quantify the impacts and who is responsible for these impacts.

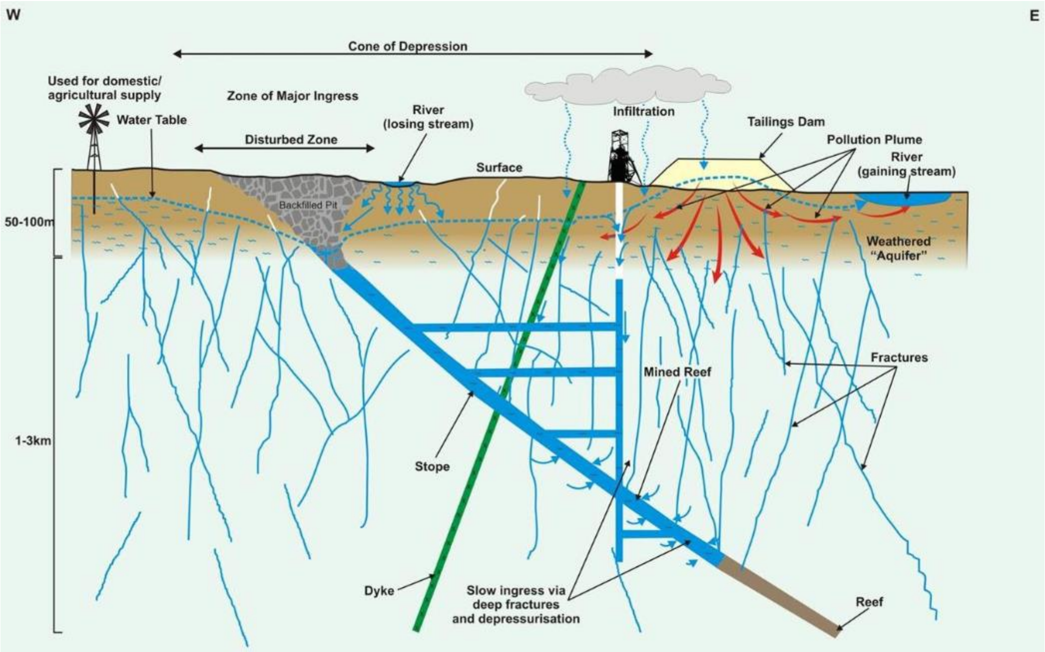

Figure 1 *Hydrogeological model showing flooding mechanisms (taken from: DWA, 2013).*

Background

The study area is located in the Gauteng Province and covers the East Rand area, including the towns of Boksburg, Germiston, Brakpan, Benoni, Heidelberg, Springs and Nigel. In mining terms the area is referred to as the ERB. The mine lease areas in the basin are shown in Figure 2. It is important to note that the ERB is geographically, hydrologically and hydrogeologically different from the other Witwatersrand mined basins (Scott, 1995).

The climate in the study area is temperate Highveld, with short cold winters and hot summers. Most of the rainfall occurs in summer in the form of thunderstorms. The average annual rainfall is between 650 mm and 700 mm.

Gold bearing conglomerates, which were extensively mined from surface down to depths in excess of 2500 m, outcrop at two localities near Benoni and again near Nigel. For the rest of the area, the reefs sub-crop against the Transvaal or Karoo Sequences. The Main Reef was mined extensively and the Kimberly Reefs to a lesser extent. For the majority of the area, the Witwatersrand Formation is overlain by the Transvaal Sequence, which in this area comprises the Black Reef Quartzite Formation and the overlaying Malmani Dolomite Formation. The Black Reef, which was also locally mined for gold, occurs at the base of the Black Reef Quartzite Formation. Sedimentary rocks of the Karoo Sequence overlie the Transvaal Sequence. It consists mainly of shale, sandstone and mudstones of the Ecca formation. Economic coal layers, which were mined at a number of localities, occur within some of the strata. Structurally, the basin is marked by prominent folding, resulting in a number of sub-basins. These faults tend to strike east-west, while another major fault-set strikes north-west south-east. A number of diabase and syenite dykes and sills occur in the area.

Groundwater occurrences is predominantly restricted to the following types of terrains: (a) perched aquifers, (b) weathered rock aquifer in the Witwatersrand, (c) Ventersdorp and Transvaal Formations,

(d) Fractured rock aquifer in the Witwatersrand, Ventersdorp and Transvaal Formations, (e) Dolomitic and karst aquifers; and (f) Artificial aquifer created by mining.

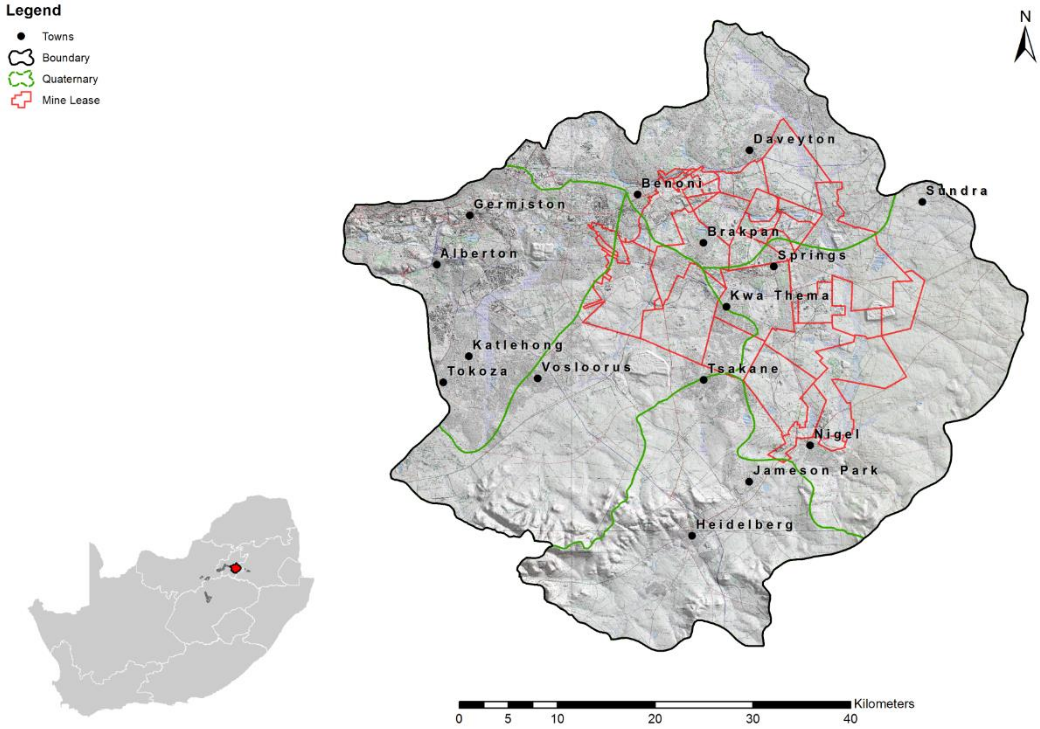

***Figure 2** Location of study area*

The watercourses within the study area predominantly north to south. In the east there is the Blesbokspruit. The Blesbokspruit flows over alluvium covered dolomite for much of its course. There are also numerous dams on the Spruit, originally constructed mainly to supply water to the mines. The water supply of the Blesbokspruit comes from a variety of sources, some of which include industrial, residential and mine discharge, several non-perennial streams and tributaries as well as urban runoff and shallow groundwater flow.

The Rietspruit drains the central and western parts of the study area, covering an area of 820 km^2. Within this area the stream is made up of numerous, small ephemeral tributaries.

Three main wetland systems are found in the study area, namely the Rietspruit, Withkspruit and Blesbokspruit wetlands. The Blesbokspruit wetlands system is a Ramsar Site.

In 2012, the then Department of Water Affairs (DWA) determined the eco-classification for the Blesbokspruit as a Class III[1] and the proposed management class was also set as a Class III.

The water levels in the ERB are rising and decant is expected within the next year or two.

Methods

This large-scale system of interconnected mines is linked with overlying aquifers and associated river systems. It is necessary to understand the systems within the area in order to answer the following questions:

- Which horizons are mainly responsible for inflow into the mine voids?
- What are the dynamics of groundwater rebound?

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[1] Class III - Heavily used (configuration of ecological categories significantly altered from its pre-development condition).

- When is the ERB going to decant?
- How can the head differences in the interconnected mines system be interpreted during flooding?
- What contaminant loads are expected in the river systems?
- What influences does decanting mine water have on local river systems?
- What is the contribution of other surface pollution sources (e.g. tailings dams) have on mine water quality?

In order to understand these hydrological/hydrogeological issues/relationships and to provide answers to the questions listed above, a coupled mine water-groundwater-river-model has been developed. Due to the complexity of the system and associated interactions separate models for surface water, mine water and groundwater would not be appropriate. Another reason is seepage from tailings dams does not drain directly to the river systems and mine voids, but percolates through groundwater before reaching surface water bodies or mine voids. Furthermore a portion of polluted river water is also seeping into the groundwater system at some locations and then into mine voids.

Because of the very different geometries of the groundwater/mine voids/rivers, a flexible discretisation method is required to solve the problem of coupling the systems. Therefore DMT's Box Model (Eckart *et al.*, 2004 & 2005) was used. The Box Model is a reactive mass transport model which allows the consideration of individual mining areas in the form of irregular polygons, the groundwater layers by means of relatively regular raster elements and the rivers as linear elements. Figure 3 provides a conceptual overview of this coupled system.

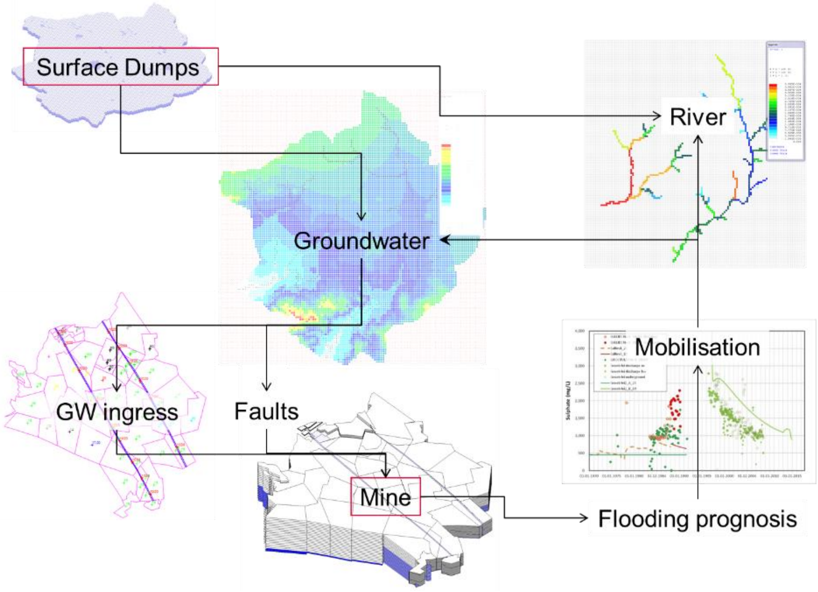

Figure 3 *Scheme of an interconnected model concept*

Once all data needed for the modelling was collected, individual models for groundwater, rivers and mine voids were developed and calibrated. Thereafter the three models were coupled and re-calibrated. The groundwater seepage rate into deeper horizons is then equal to the inflow into the mines from above.

The next step was then to set up and calibrate the multicomponent reactive mass transport model. Historic flooding data (measured rising water levels, abstraction rates and sampled chemical parameters) were used during this calibration process and the results thereof are shown in Figure 4.

Once the flow models are calibrated, the reactive mass transport model is calibrated, using water quality data collected at Grootvlei while pumping was taking place (June 1996 – January 2011). The reactive mass transport model integrates 15 main transport units with nearly 140 species. The calibration results for pH and sulphate are shown in Figure 5 and Figure 6.

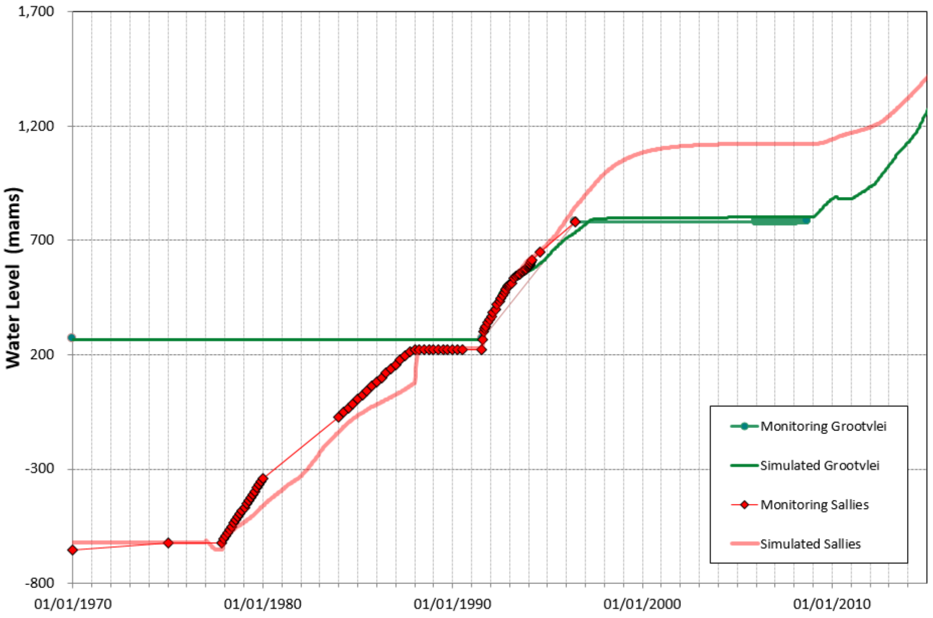

***Figure 4** Calibration results – flooding*

The ERB is expected to start decanting within the next two years. The average predicted ingress is 80 ML/d (Scott, 1995). However from the integrated model results it is clear that this ingress volume is dependent on a specific scenario. DWA (2013) estimated that the ingress would be 70 – 80 ML/d and recommended that 80 ML/d is pumped at Grootvlei #3 Shaft at a depth of 100 m (1470 metres above mean sea level). This level is referred to as the Environmental Critical Level (ECL). The coupled model indicated that the average ingress is 72 ML/d if the mine is not going to flood. It also calculated that it would be necessary to pump 19 ML/d to maintain the ECL. The model calculated the decant rate as 7 ML/d.

The calculated resulting development of sulphate after flooding for the scenarios discussed above is shown in Figure 7. The 50th, 75th and 95th percentile of the sulphate values predicted by DWA (2013) are included in Figure 7. The South African National Standard (SANS) 241:2011 drinking water guidelines are also included for comparison purposes. It is clear that these sulphate drinking water guidelines are exceeded in all scenarios. All scenarios are completed with uncertainty analysis using a monte-carlo method. The model varies the kinetic coefficient and the available mass in the source term for a range of comparable examples and experiences. The range of uncertainty for the 3 scenarios is shown in Figure 8.

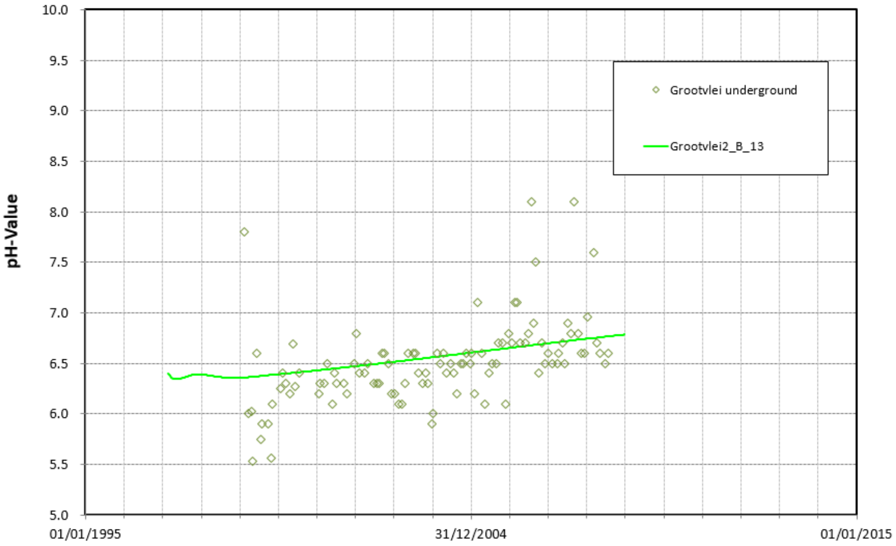

***Figure 5** Calibration results – pH*

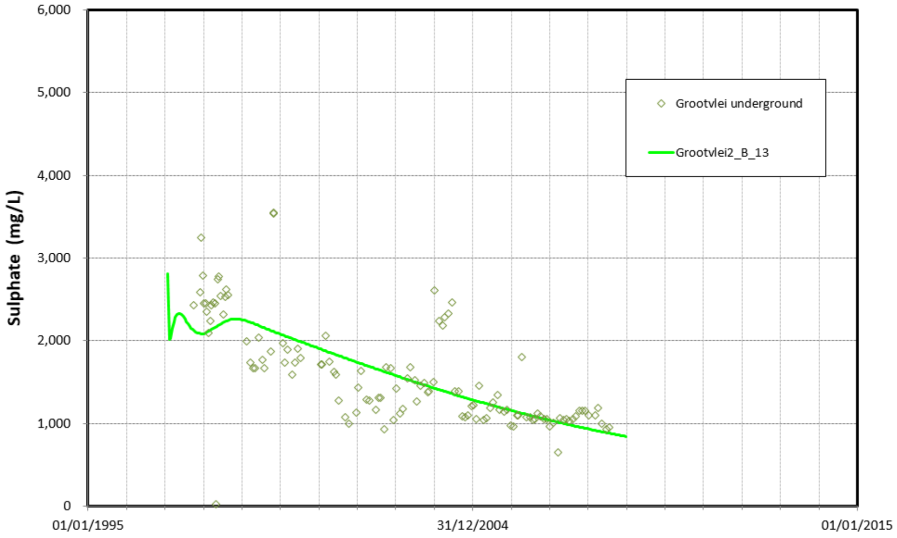

Figure 6 *Calibration results – sulphate*

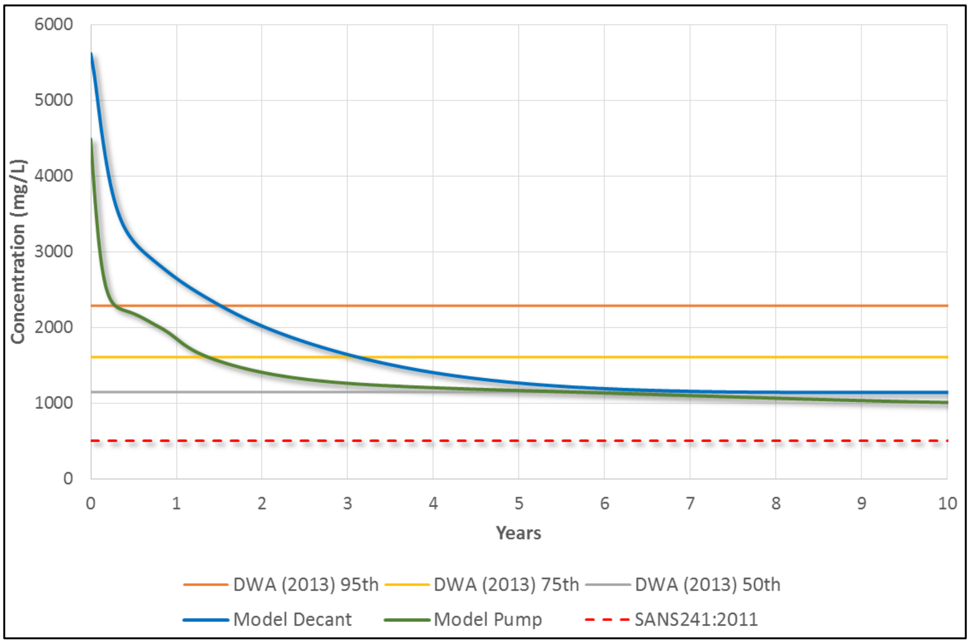

Figure 7 *Calculated sulphate development for various scenarios*

The final scenario was to determine the cumulative impacts on the Blesbokspruit if the ERB decants. This scenario takes into account the decanting mine water discharge to the river and groundwater – river water interaction. Figure 9 shows the pre-decant observed sulphate concentrations for the months April, July and November along a north - south 70 km stretch of the river. Also included in the diagram are the simulated sulphate concentrations due to decant and the average cumulative flow in the river. Included on the horizontal axis of Figure 9 are the landuse activities that can influence the sulphate load in the river. All these landuse activities are included in the coupled model.

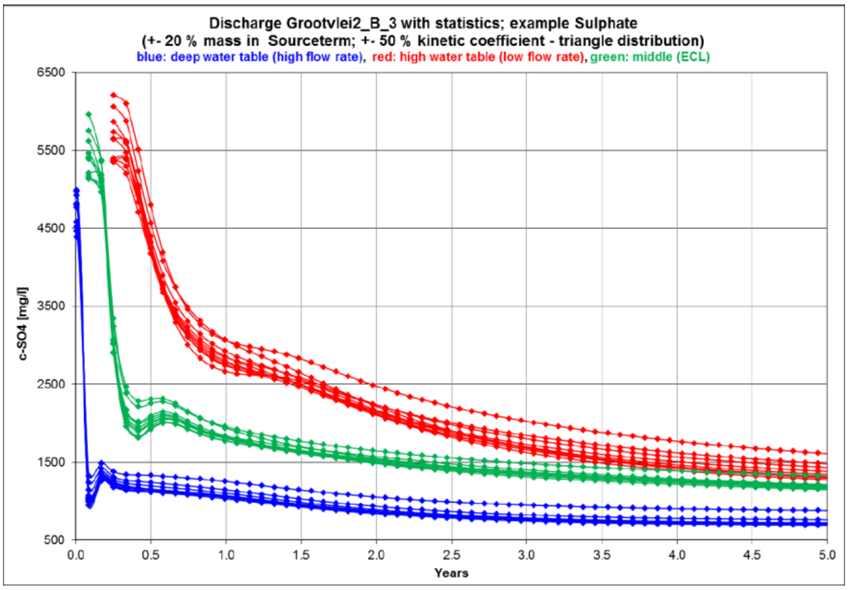

Figure 8 *Uncertainty analysis - calculated sulphate development*

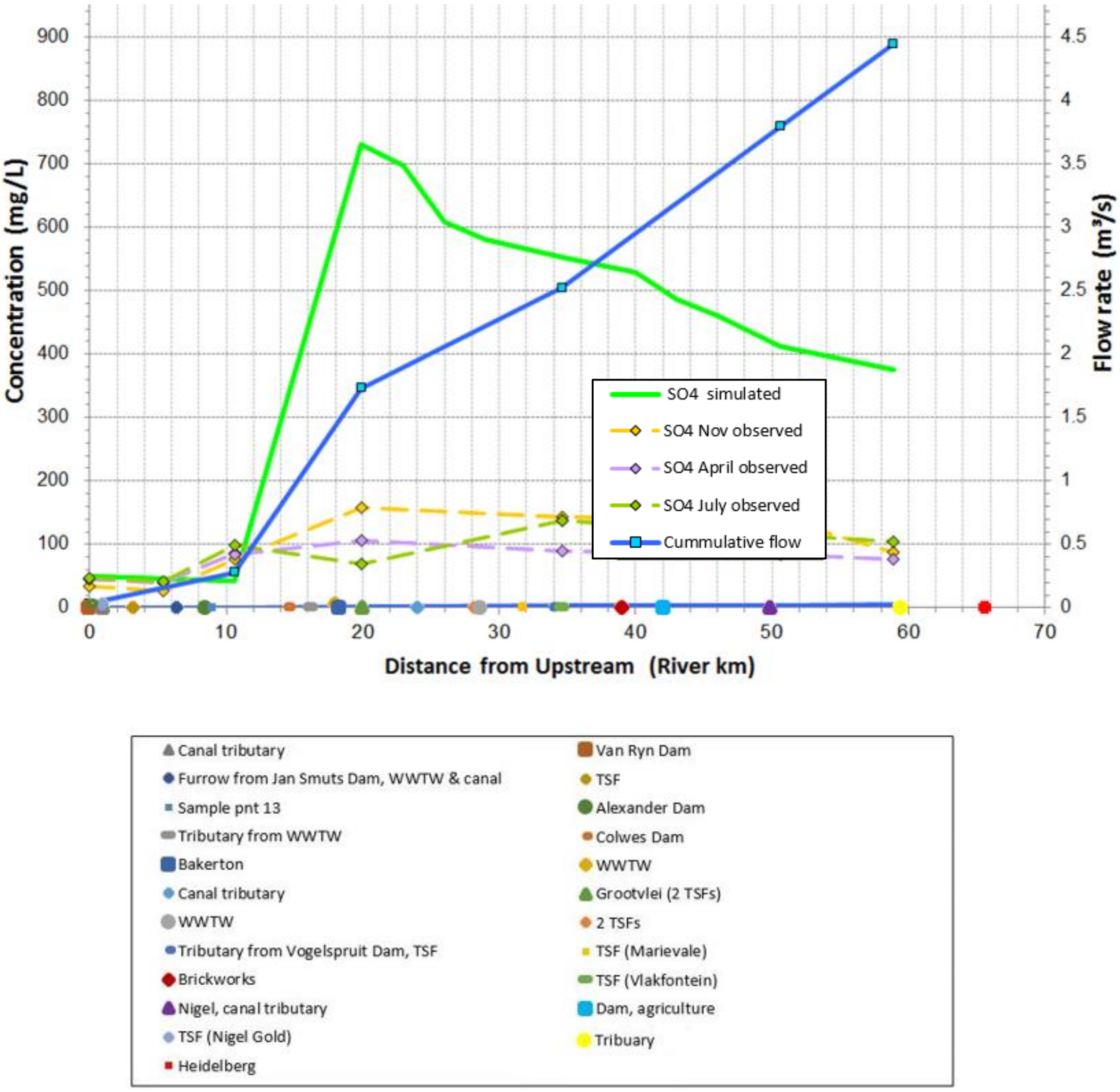

Figure 9 *Sulphate development along river course*

Conclusions

This paper summarizes some of the findings of a four year study conducted in the ERB. As the mine voids are currently flooding concerns are raised regarding the impacts the mines in the area have and are going to have (e.g. seepage from tailings dams, decant volumes and qualities) on surface water and groundwater bodies. To determine these impacts a coupled flow and reactive transport model was developed for the area.

The results of different scenarios are presented in this paper. The scenarios include: (1) Ingress if mine voids are not flooded, (2) Pumping to maintain ECL and (3) Allow total flooding and associated decanting.

The resultant sulphate values in all these scenarios are above the drinking water guidelines specified for South Africa. In the long term the sulphate values for pumping (scenario 2) is slightly better than the decanting (scenario 3). However the volumes of water that have to be treated in scenario 3 are much lower than scenario 2.

A scenario is run to determine the impacts on the Blesbokspruit. It is clear that the sulphate values increase dramatically approximately 20 km downstream due to mining activities. However the concentrations start decreasing thereafter due to the dilution effects of the river.

High ingress areas are a concern in the ERB. Former investigations estimated that the ingress can be reduced by approximately 25% by rehabilitating/sealing these areas (DWA, 2013). Though possible, sealing and stream diversion is costly and this measure require a cost-benefit analysis, should it be considered as part of the treatment solution. In addition the following should be considered with regard to sealing high ingress areas:

- Model results show that high ingress volumes result in a diluted impacting concentration (lower concentration but higher load), which will reduce treatment costs, if the dilution principle is acceptable.
- Sealing will reduce the ingress and delay the flooding process, but it is clear that the mine ingress reduce with a lower of hydraulic gradient. This would lead to higher concentrations and lower loads.

Acknowledgements

The project team would like to thank the Council for Geoscience and more specifically Henk Coetzee and Ugo Nzotto for the opportunity to conduct this research and the funding thereof.

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Saltwater injection into a fractured aquifer: A density-coupled mass-transport model

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Abstract

The Werra-Kali potash mining region has a mining history for more than 90 years. The mining region is situated both in the Free State of Thuringia and the federal state of Hesse, Germany. Since 1925, high saline waters of potash productions have been injected into a confined, deep aquifer of the Permian Zechstein formation (carbonate rock aquifer).

The carbonate rock aquifer is a regional aquifer with extensive natural variations of salinity of geogenic origin, ranging from fresh to saline waters. Its overburden consist of the formation series “Obere Letten” of upper Permian, the Triassic Buntsandstein and Muschelkalk formations. The formation series “Obere Letten” consists of clay- or siltstone and hydraulically separates the carbonate rock aquifer and the Buntsandstein aquifers. The Buntsandstein is subdivided in the lower, middle and upper Buntsandstein, where the lower Buntsandstein is a regional aquifer and the middle Buntsandstein occurs partly as perched aquifer. The upper Buntsandstein is an aquitard and hydraulically separates the underlying middle Buntsandstein from the overburden Muschelkalk. Muschelkalk occurs in the southern part of the region, partly as perched aquifer. Finally, the quaternary sediments occur in river valleys and form local shallow aquifers.

Groundwater levels, salinity, and water levels in the nearby river have been monitored for several decades. The aim of the project was, based on available data and results of geological works and mining investigations, to develop a numerical groundwater model capable of simulating the impact of the injection regime of the past 90 years on regional flow patterns and solute transport underground and identifying possible relations between saltwater injections and the non-point (diffuse) saltwater inflows into the nearby river.

Key words: Mine water, salt water injection, density-dependent saltwater flow and transport, interaction of ground and surface water, numerical modeling, FEFLOW

Historical background

The Werra-Kali potash mining region has a mining history for more than 90 years (Rauche 2015). The mining region is situated both in the Free State of Thuringia and the federal state of Hesse, Germany (fig. 1). Since 1925, high saline production waters have been injected into a confined, deep aquifer of the Permian Zechstein formation (carbonate rock aquifer). Alternating duration, location, and timing, 62 wells were used to inject saline production waters. Injection reached its maximum in the middle of 1960‘s with up to 30 Mio. m³/a. At present, rates are less than 4 Mio. m³/a.

Surface elevations in the mining region vary from 180 m to 700 m above sea level. The carbonate rock aquifer occurs in a variable depth from -800 m below sea level to 440 m above sea level. The Werra rock salt with potash seams occurs below the carbonate rock (Plate Dolomite), separated by impermeable clay formations.

The carbonate rock aquifer is a regional aquifer with extensive natural variations of salinity of geogenic origin, ranging from fresh to saline waters with a total mineralization (TDS) up to 70 g/l (Skowronek, F. et al. 1999). It is overlain by the formation series “Obere Letten” of upper Permian, the Triassic Buntsandstein and Muschelkalk formations. The formation series “Obere Letten” consists of clay- or siltstone and hydraulically separates the carbonate rock aquifer and the Buntsandstein aquifers. The Buntsandstein is subdivided in the lower, middle and upper Buntsandstein, where the lower Buntsandstein is a regional aquifer and the middle Buntsandstein occurs partly as perched aquifer. The upper Buntsandstein is an aquitard and hydraulically separates the underlying middle Buntsandstein from the overburden Muschelkalk. Muschelkalk occurs in the southern part of the region, partly as perched aquifer. Finally, the quaternary unconsolidated sediments occur in river valleys and form local shallow aquifers. Fig 2 schematically shows the hydrogeological situation in the Werra potash mining region.

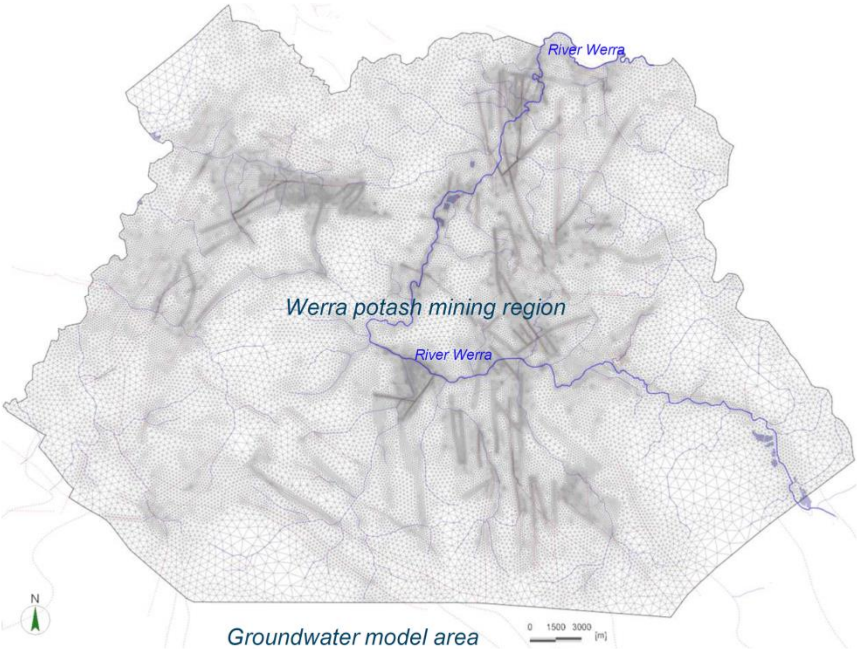

Figure 1 *Location of the Werra potash mining region and groundwater model area.*

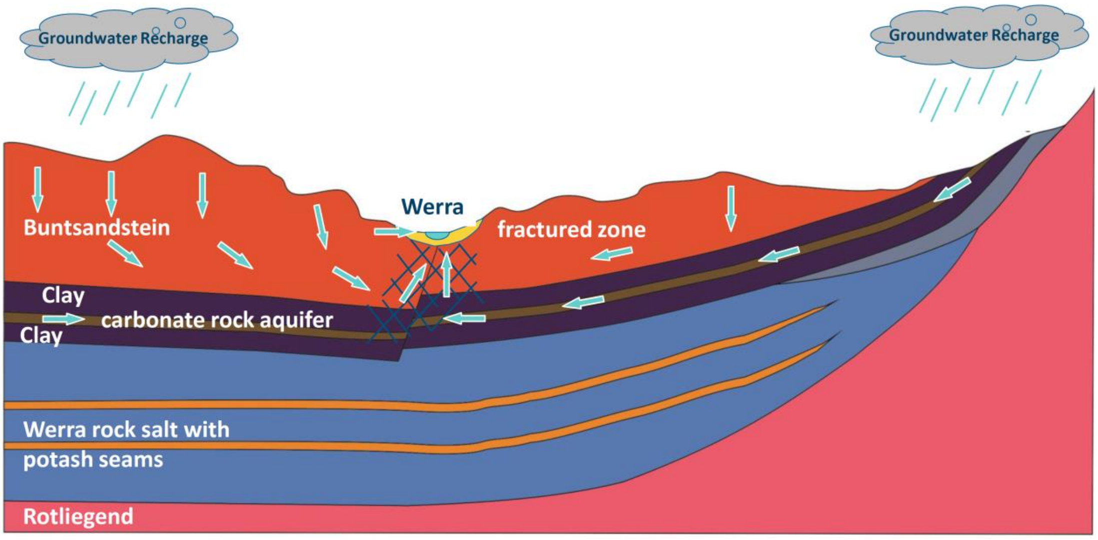

Figure 2 *Schematic hydrogeological situation in Werra potash mining region.*

Groundwater levels, salinity, and water levels in the nearby river have been monitored for several decades. Earlier investigations estimated the fraction of injected saline water, which passes the overburden to form non-point (diffuse) inflows to the main river to amount to app. 30%.

The aim of the project was, based on available data and results of geological works and mining investigations, to develop a numerical groundwater model capable of simulating the impact of the injection regime of the past 90 years on regional flow patterns and solute transport underground and identifying possible relations between saltwater injections and the non-point (diffuse) saltwater inflows into the nearby river.

Model concept and methods

Both a two and a three-dimensional density-coupled flow and mass-transport FEFLOW® model (Diersch 2014) were built based on a hydrogeological model of the region.

The 2D density-coupled flow and mass-transport model with an area of about 1000 km² was firstly established in the year of 2008, consisting only of the confined carbonate rock aquifer. The model was first calibrated for steady state flow conditions and subsequently for transient conditions between 1925 and 2007. The simulation results of the 2D model helped to understand the general system behavior from a modelling point of view and to describe the movement and dispersion of the injected saltwater in the deep carbonate rock aquifer. Yet, a possible up-coning towards the overburden in well-defined small leakage zones could not be analyzed in this 2D space. In the following years, additional boreholes have been explored and hydrogeological studies have been carried out, building a strong basis for the development of a 3D density-coupled mass-transport model.

The development of this 3D density-coupled flow and mass-transport model started in 2011. This model covers a study area of around 1220 km² and considers the complicated multi-layer aquifer system of the carbonate rock aquifer, overlain by siliciclastic Buntsandstein sediments, Muschelkalk and quaternary sediments. The total thickness of the represented hydrogeological formations is up to 1300 meters. The 3D numerical model developed with the code FEFLOW consists of 28 numerical layers with approx. 4 Mio. Finite elements. The density ratio of the density-coupled saltwater flow and transport is up to 1.21 [-].

Objectives of the 3D model developed were:

- Description of the dynamic groundwater levels and concentration developments of TDS in the carbonate rock aquifer and possibly in the overburden formations as a result of the injection activities over the whole period from 1925 to 2010 (transient calibration),
- Description of the movement and dispersion of the injected saltwater (represented by means of TDS) within the aquifer, as well as groundwater movement in the whole model domain,
- Verification of the preliminary 2D-model results,
- Scenario calculations with respect to various injection regimes.

The (from a modelling point of view) highly dynamical injection rates, inevitable density effects in the modelling domain, a large study area and the long simulation period were the main challenges of the project. The model calibration followed the concept shown in Fig 3. The transient calibration of the density-coupled saltwater flow and transport model of app. 90 years was carried out iteratively.

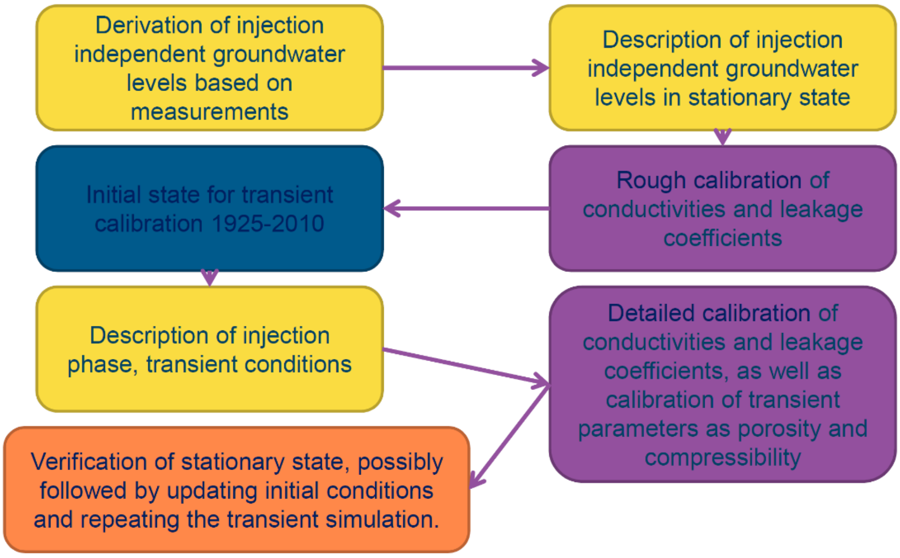

Figure 3 *Concept of the model calibration.*

Main results of the calibration

Evaluation of calibration results was based on:

- Comparison of simulated groundwater levels (hydraulic heads) with measurements in available monitoring wells (75 in the carbonate rock and 138 in the overburden formations),
- Comparison of simulated TDS with measurements in available monitoring wells (52 in the carbonate rock and 134 in the overburden formations),
- Comparison of simulated diffuse inflow (non-point sources) into the river

Fig. 4 exemplarily compares simulated hydraulic heads and TDS with corresponding measurements for a carbonate rock well. The well is situated at the south-western part of the model region and has a distance of app. 10 km to the injection site.

Simulated diffusive inflows to the river in comparison to calculated diffusive inputs based on measured chloride concentrations are shown in Fig. 5.

Fig. 6 shows the subsurface spatial distribution of simulated TDS (end of 2010) (left) in comparison to airborne electromagnetic data (right), where red color indicates comparable high TDS concentrations (left) versus high conductivity (right). Figures 5 and 6 confirm the good agreement of diffuse inflows both in sum over time, as well as at a high spatial resolution.

In general, the calibration results show a good match between simulated and observed heads as well as TDS concentrations in the carbonate rock and overburden formations. A good agreement of simulated diffusive inflows into the river in comparison to calculated diffusive inflows was achieved. The 3D density-coupled flow and mass-transport model reproduces plausible regional distributions of hydraulic heads and TDS in the carbonate rock and overburden formations in Werra potash mining region. The model helps to understand and confirm the general system behavior and to investigate the movement and dispersion of the injected saltwater in the complicated multi-layer aquifer system (Fig. 7).

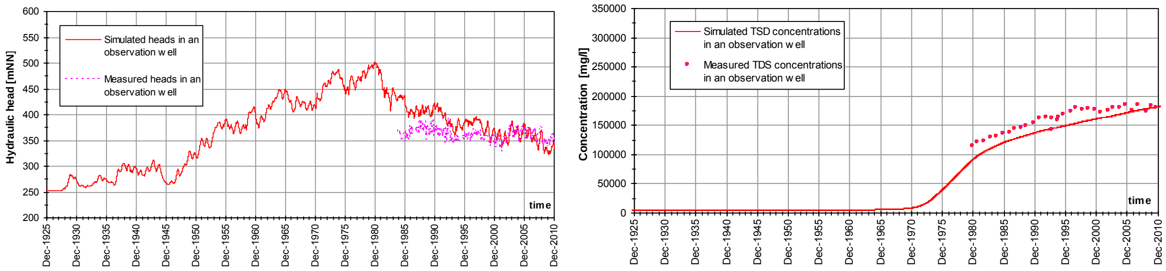

Figure 4 *Comparison of simulated heads and TDS with corresponding measurements in an observation well.*

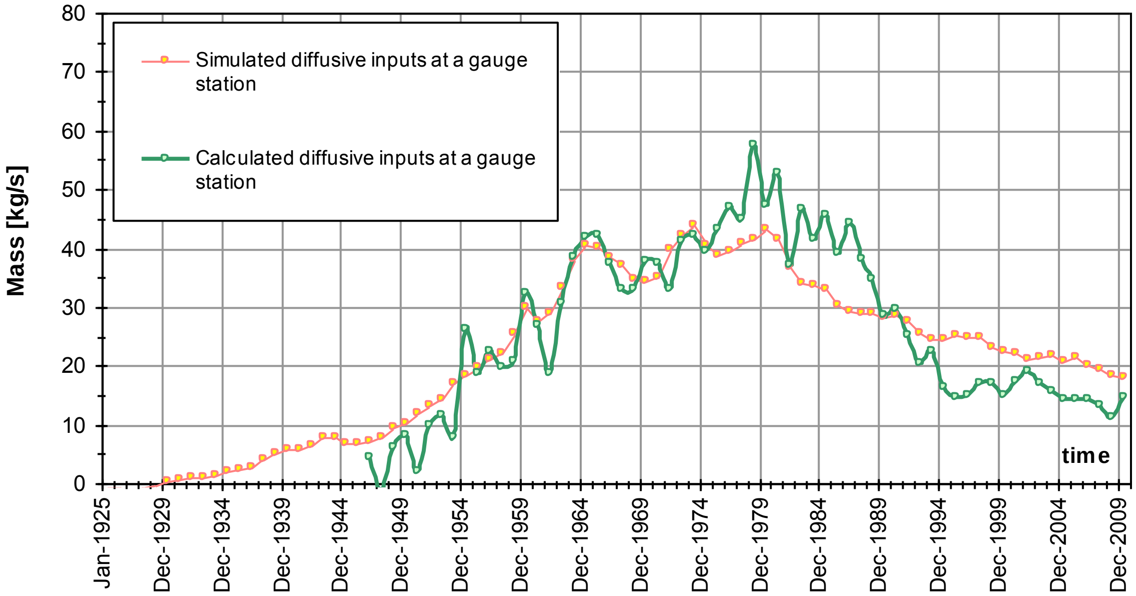

Figure 5 *Comparison of simulated diffusive inflows into the river with the diffusive inflows calculated based on measured chloride concentrations at a gauge station.*

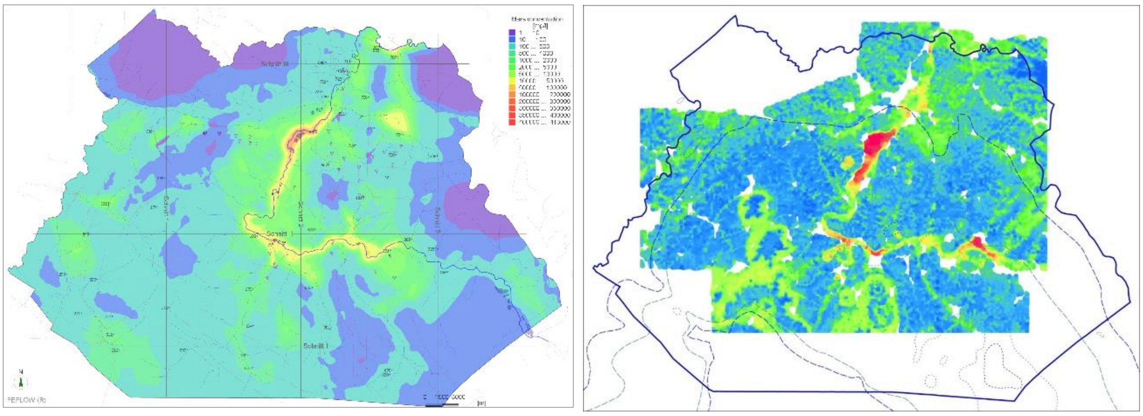

Figure 6 *Comparison of the distribution of simulated TDS near to surface (left) with results of measured airborne electrical resistivity (right), where red color indicates comparable high TDS concentrations or high conductivity, respectively.*

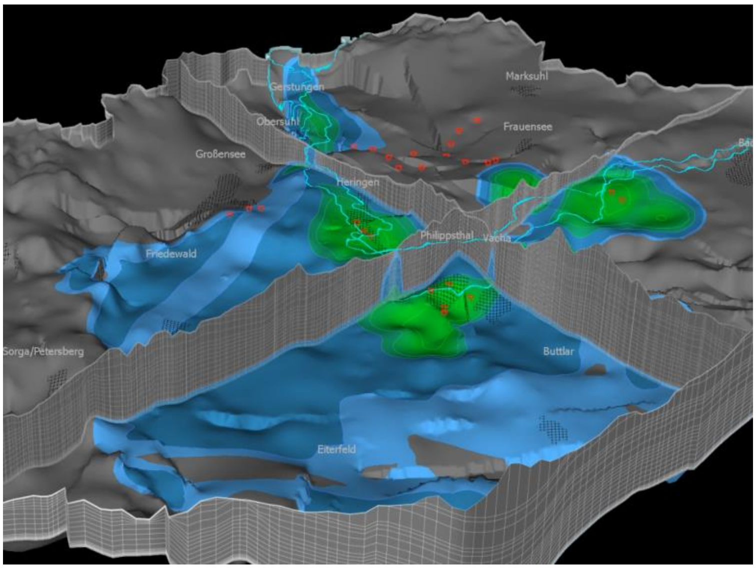

Figure 7 *3D-View of the three dimensional density-dependent salt water transport in the confined carbonate rock aquifer.*

Summary

Although simulations with the 2D model were very useful in tracking the dispersion of injected saltwater in the carbonate rock aquifer, the necessity of the 3D approach was clearly confirmed during the second phase of the project. With the 3D model, further analyses with respect to groundwater recharge in the upper aquifers, which are partly used for drinking water supply, could be conducted. Besides a good match between observed and calculated heads as well as concentrations, the results of the 3D model additionally confirm the observed impact on diffusive inflows. By means of scenario and/or sensitivity studies, the impact of various injection strategies on the whole groundwater system was further analyzed. Accordingly, the following can be stated:

- Potash mining is related to strong environmental constraints;
- In order to meet these environmental demands, a Control Management System should be used;
- For the Werra potash region, part of this Control Management System consists of a 3D density dependent groundwater model based on the FEFLOW modelling framework;
- The model describes heads, concentrations and diffusive inflows into the Werra river on a regional scale and was crucial to confirm and improve the understanding of the long-term processes related to brine injection;
- The model can further be used for scenario simulations of various injection strategies;
- The model is flexible enough to account for future/new measurements and to include further site investigations;
- Nevertheless, only a combined monitoring and modelling approach can represent the whole groundwater system adequately.

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PCGEOFIM – Integrated Modelling of Mining specific Groundwater Dynamics and Soil Water Budget

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Abstract

Post-mining areas in Central Germany are characterized by pit lakes. Therefore, the impact of the expected change of land use may be considerable because changes in groundwater recharge patterns and a possible increase of evaporation from lakes can be important for the total water budget.

A coupled groundwater and soil water budget model based on the groundwater simulator PCGEOFIM and the soil water budget model ArcEGMO was developed. The groundwater model supplies groundwater levels and base flow; the soil water budget model groundwater recharge and river discharge. The exchange time step is typically one day. The model was successfully applied to a site in Central Germany. Model results presented here show good agreement with measured values and first predictions were made. In consideration of the effects of climate change, the model results will have great importance for planning of activities in the region such as recreational use.

Key words: PCGEOFIM, ArcEGMO, groundwater, soil water budget, coupled modeling

Introduction

The complex processes of the water balance can be examined only by models which represent the system in an adequate manner. During the last decades several sophisticated and mature numerical models were created to describe specific parts of the water balance sufficiently. However, for the complex interactions between the different water budget components especially in mining and post-mining areas, their separated consideration is not sufficient for reliable results. Therefore, two separate models, the groundwater simulator PCGEOFIM and the soil water budget model ArcEGMO, were coupled in a bi-directional way.

Groundwater simulator PCGEOFIM

PCGEOFIM (Mansel et al. (2011)) is a numerical groundwater modeling system. It uses the Finite-Volume method to simulate groundwater flow and solute transport. Being developed for more than 25 years, it provides special features to account for mining-related demands and conditions.

Subsurface parameters can be specified as time-dependent to allow for the modeling of excavation of pit mines, filling with overburden, and creation of pit lakes within a single simulation run (Blankenburg et al. (2013)). While working with a regular grid, multiple nested grid refinements that may overlap can be used to get higher resolution in regions of special interest.

In the scope of opencast mining activities and post-mining areas, open pit lakes and surface water such as rivers play an important role in the water management. PCGEOFIM provides a simple but very useful mechanism to account for the interactions between lakes and groundwater. All inflows such as precipitation, groundwater and river infiltration or exfiltration are balanced for each lake. The water level of the lake is computed from a water level-volume relationship which in turn is derived from the spatial geometry (mold) of the lake. That water level is taken as value for the third type boundary condition and is assigned to all cells related to the lake. That relationship is established via vertical and horizontal coupling schemes and is presented in fig. 1.

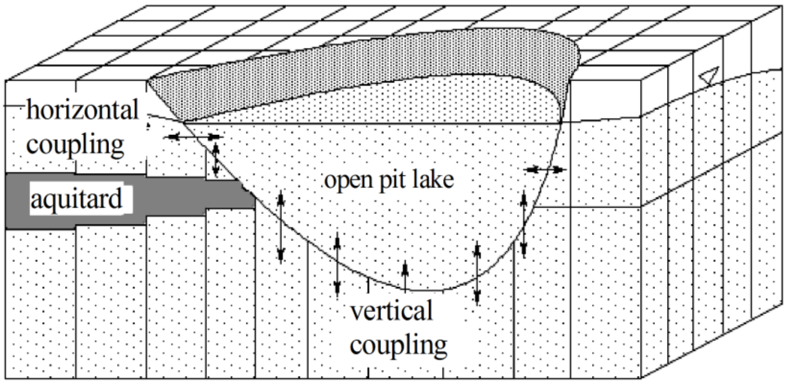

***Figure 1** Implementation of the boundary condition "lake" in PCGEOFIM*

Rivers are represented in a similar manner by using again a third type boundary condition. The flow rate is calculated according to Manning-Strickler's method. In combination with a flow rate-water level relationship the river water level is determined and used as value for the third type boundary condition for each section of the river.

There are a number of additional specific boundary conditions such as wells and HDD-wells across several groundwater layers or controllable connections between rivers and lakes. These connections allow for the implementation of overflows in dependency of user defined conditions. The groundwater recharge rate can be defined in numerous ways with increasing complexity, starting from simply time-invariant or time-dependent, continuing with being a function of the locality, depth to water table in combination with land use and time. In case of coupled modeling, PCGEOFIM gets the groundwater recharge rate from the soil water budget model ArcEGMO.

Soil water budget model ArcEGMO

ArcEGMO (Becker et al. (2002)) is a GIS-based hydrological modeling system. It simulates the spatially distributed hydrological processes in river catchments on different scales. The model consists of two domains:

- Discharge formation which represents the vertical oriented processes and which depends of meteorological parameters as well as vegetation and land use parameters
- Discharge concentration which represents the horizontal processes such as surface runoff or channel discharge, and base flow

In addition to the usual model approaches for describing the lateral surface and subsurface water flows at river basin scales (Becker et al. (2002)), it contains complex growth models for forest and agricultural areas and a detailed soil model (water, carbon/ nitrogen budget). Through implementation of a crop rotation generator, the agricultural land use structure of a region can be well reproduced. Air temperature, precipitation, humidity and global radiation in daily resolution are the required climatic driving variables.

The model domain is discretized in hydrotopes. Hydrotopes are areas with similar or identical hydrological properties, land use, topography, and soil profile. Vegetation dynamics are simulated in dependence on land use in the individual hydrotopes. Four different plant models have been integrated into the model. The groundwater component in ArcEGMO is realized as a linear storage with constant groundwater level. In case of a coupled modeling this groundwater component is deactivated and the groundwater table is imported from PCGEOFIM.

Coupled groundwater and soil water budget modeling

To account for the feedbacks between soil water budget, recharge and groundwater table a bi-directional (online) coupling of the two previously described models PCGEOFIM and ArcEGMO was developed. Figure 2 shows the schematic of the exchange between both models. The groundwater simulator PCGEOFIM supplies groundwater levels and base flow and the soil water budget model ArcEGMO supplies recharge and river discharge. Furthermore, flows at model boundaries are also exchanged if the model domains are not of equal size.

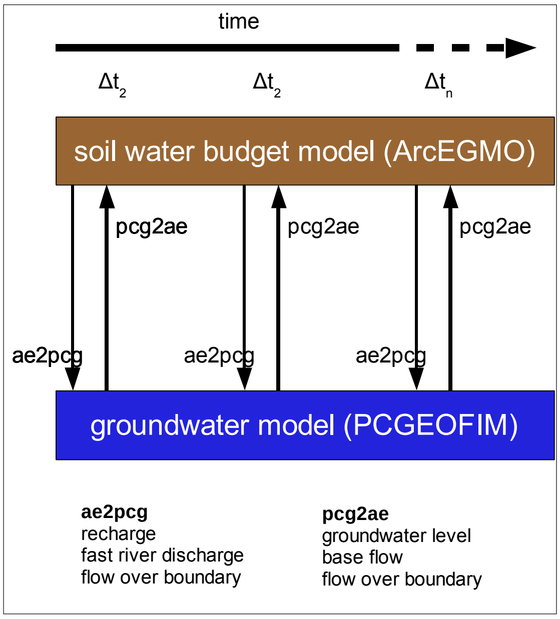

Figure 2 *Schematic of the coupling. The Term ae2pcg characterizes the direction from ArcEGMO to PCGEOFIM; pcg2ae refers to the opposite direction*

All quantities are exchanged with a variable time step that is determined by internal numerical criteria. Time steps will get smaller if river discharge is high. The maximum specific time step is typically one day, which allows for an intensive feedback between both models.

The flow over boundaries in fig. 2 regards to the river discharge that is handed in from the spatially larger model at the boundary to the smaller model. That allows for the modeling of areas where surface and subsurface catchments may not correspond. Climatic changes can be considered directly because ArcEGMO uses meteorological data as input and therefore reacts to changes in climatic conditions.

Soil layers in the soil water budget and groundwater model are of the same size and have the same parameters. If a layer is unsaturated, it will be part of the soil water budget model. As soon as it becomes saturated, it will become part of the groundwater model. That means there is a spatially moving interface between the two models. If the groundwater level reaches the soil surface, all layers will be part of the groundwater model. Groundwater that seeps out at the surface will be put in a surface storage from where it can evaporate or flow into the next river if the storage capacity is exceeded.

Application of the coupled model

The coupled model has been applied to a site in Central Germany in the area of Nachterstedt (IBGW GmbH (2008)). Opencast mining activities lasted from the 19th century to the mid-nineties. The flooding of the open pit lakes began in 1998 by rising groundwater table and supplying of fluvial water. The domain of the groundwater model, colored in green in fig. 3, has an area of 150 km² and incorporates the former opencast pit. The main gaining stream Selke traverses the region from South East to North West. The domain of the soil water budget model has an area of 300 km². It is depicted in orange color in fig. 3.

The discretization step width of both, the groundwater and soil water budget model, was chosen to be identical so that each cell of the top layer of the groundwater model has a corresponding soil budget water cell. Furthermore, the upper two meters of the subsurface are part of both, the groundwater simulator and the soil water budget model, to account for the fluctuating groundwater table.

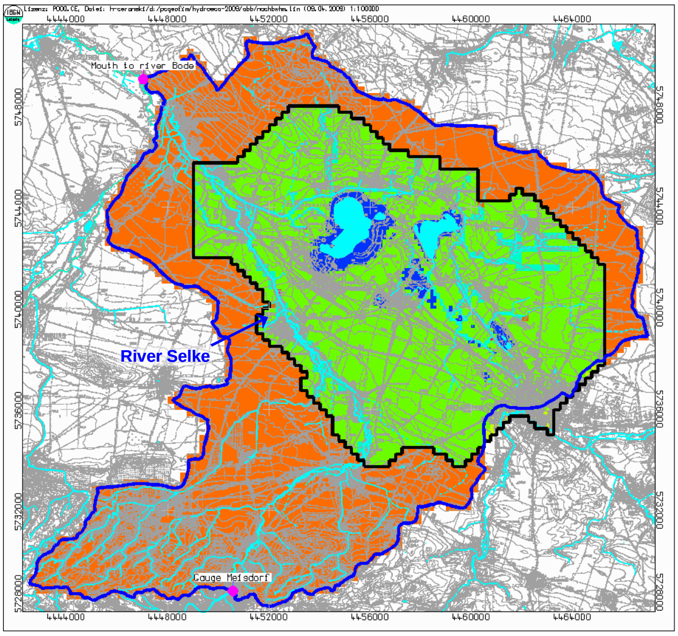

Figure 3 *Groundwater (green) and soil water budget (orange) model domain of site Nachterstedt*

As shown in fig. 3, the extent of the model domain of the soil budget and the groundwater simulator are different. The soil water budget model covers a greater area than the groundwater model. The cyanic areas refer to open pit lakes and rivers. The flow data of the rivers crossing the boundaries between the models are also exchanged at each time step. An exchange time step of one day proved to be useful and allowed stable calculations.

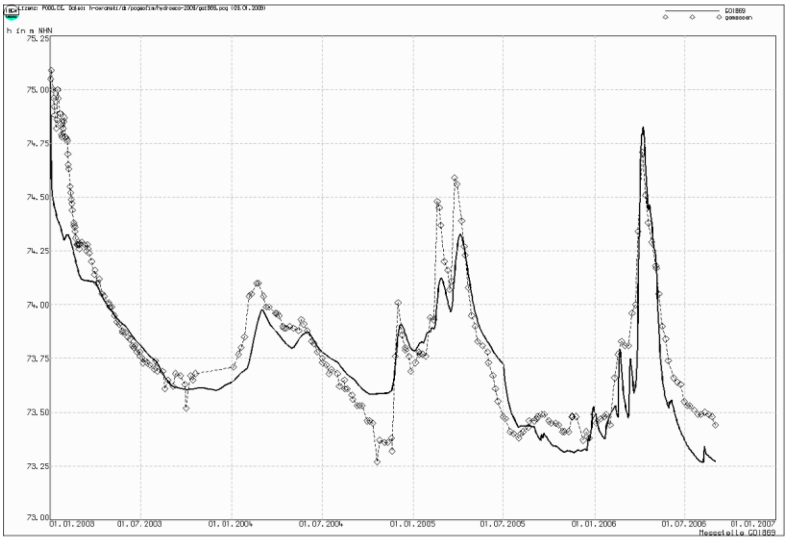

Figure 4 *Comparison of measured and calculated groundwater level at a gauge in the vicinity of the river Selke*

Model runs were carried out in three phases. After a calibration period, the model was run with constant boundary conditions until it reached steady state conditions. Finally, a prediction calculation was done for 25 years starting from steady state conditions. The models could reproduce measured values of groundwater levels and river discharges with good accuracy. Especially in regions with shallow groundwater levels and thus strong interactions between groundwater and soil water significant improvements of model representations could be achieved. Fig. 4 shows good agreement between modeling results and measured values for an observation well close to a river.

Fig. 5 shows the significant change of recharge patterns at the beginning (left) and at the end (right) of the pit flooding. The average groundwater recharge rate is reduced for 23 % (from 53 to 41 mm/a), firstly, due to the conversion of land area into lake area and, secondly, due to shallow groundwater tables where evapotranspiration is increased. The change of the evapotranspiration patterns is shown in fig. 6. Here, the average evapotranspiration increases about 18 % (from 464 to 548 mm/a).

That development of the water balance has negative consequences on the water management of the region. The lakes feed the surrounding streams. The negative water balance leads temporarily to zero-flow rates in some streams, especially in the summer months destabilizing the sensitive hydro ecology of the area. On the other hand, the rising groundwater table causes the formation of shallow surface water bodies interfering with the current agricultural use.

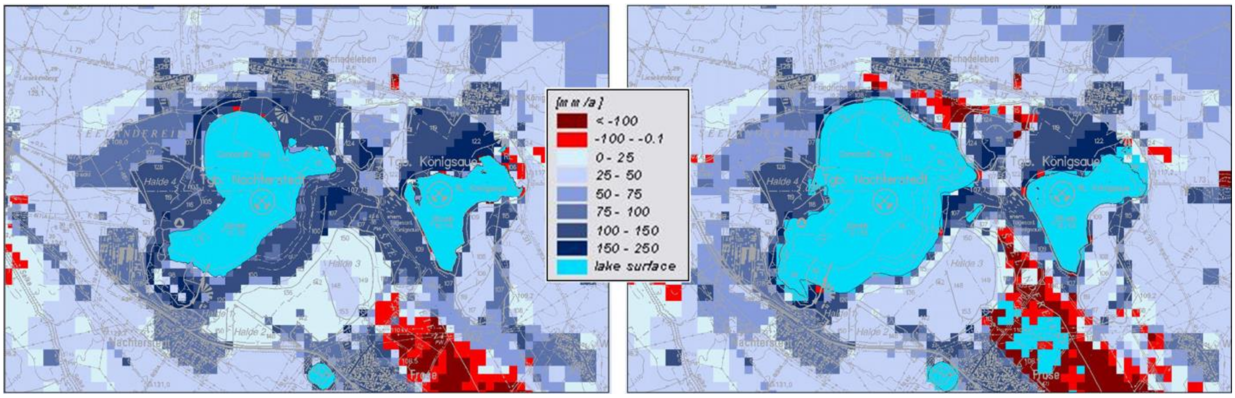

***Figure 5** Comparison of recharge patterns during (left) and after (right) pit flooding*

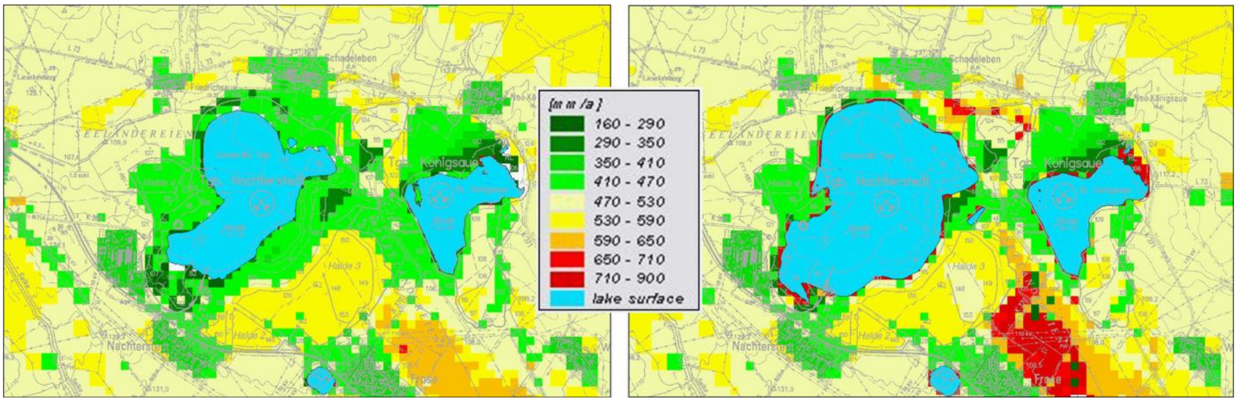

***Figure 6** Comparison of evapotranspiration pattern during (left) and after (right) pit flooding*

Conclusions

The coupled model has proved to be an effective tool for the determination of water management measurements, especially in the case of strong interactions between groundwater and surface waters. Because of the direct processing of climatic data with the coupled model, regionalized data from climate models can be used immediately. By means of scenario runs with the coupled model, different climatic conditions can be simulated and the results are available for statistical analyses. The strong seasonal and long-term volatility of the water balance at the Nachterstedt site in combination with distinctive droughts and wet periods emphasizes the importance of results of the coupled modeling.

In summary, the change of landscape in Central Germany caused by mining activities has a great impact on land use and water management systems. That has to be accounted for by coupled groundwater and surface water modelling. Further investigations of the impact of the climate change are necessary, especially in that region.

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Modeling the changes in water quality of AMD along the flow path

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Abstract

Mine waters enter the environment and spread in groundwater as well as in surface waters. Sometimes they change their characteristics along the flow path several times. By modeling these processes, it is possible to forecast potential environmental damages and to avert them successfully.

AMD flows through various compartments in the environment. In the course of the transition from one compartment to the other, the redox conditions change from anoxic to oxic conditions and vice versa. These compartment transitions and the intrusion of AMD in natural groundwater reservoirs are the focus of the developed model approaches.

Due to compartment transition processes, several fundamental shifts in water quality occur. The displacement of the pore solution of one compartment by the water from an adjacent compartment also provokes changes in water quality. This process is described by the migration of the displacement front.

Simulation calculations allow retracing the observed statistical relation between the acidity and the sulphate concentration. By the use of a connected groundwater flow model, it is possible to forecast the arrival of high iron and sulphate concentrations at sensitive points of the flow path. After the inclusion of microbiological reactions, the developed model concepts based on PHREEQC (Parkhurst & Appelo 1999) will be used for the long-term management of in-situ sulphate reduction.

Key words: Mine water, modeling, groundwater quality

Introduction

During the migration of Acid Mine Drainages (AMD) through different environmental compartments, for example tip, lake or river, their characteristics change. Thereby, undesirable effects and risks may occur because of the acidity and high concentrations of iron, sulphate and heavy metals. Changes in water quality in the course of the spread of AMD in the environment can be understood by the use of several model concepts. In specific cases, they even allow forecasting the relevant changes in characteristics.

Use of neutralization potential to characterize AMD

The oxidation of pyrite and other sulphides generates the acidity of AMD. Using the sum parameter of acid capacity $K_{S4,3}$ the neutralization potential is defined by equation 1 (Evangelou 1995 modified by Schöpke & Preuß 2012).

$$NP \approx K_{S4,3} - 3c_{Al3+} - 2c_{Fe2+} - 2c_{Mn2+} - 2c_{Zn2+} - \ldots \tag{1}$$

Ferrous ions, manganese and aluminum are not included in the titration of $K_{B4.3} = - K_{S4.3}$. Therefore, they must be analysed separately and added to equation 1. Other hydrolyzing cations must also be taken into account. For example, Zn^{2+} will have to be considered if its occurrence plays an important role in the investigated groundwater. Reactions forming AMD (e.g. pyrite weathering), buffering effects and other reactions can be presented as vectors in an acidity/sulphate concentration plane, wherein acidity is represented by –NP (figure 2). Additionally, the processes can be demonstrated in an acidity/pH plane.

Compartment transitions

Changes from anoxic to oxic conditions and vice versa occur by the transition from one environmental compartment to the other. These compartment transitions and the intrusion of AMD in natural groundwater reservoirs are the focus of the developed model approaches (Parkhurst & Appelo 1999).

Figure 1 shows schematically the possible flows of AMD through different compartments. In the course of the transition from one compartment to the other (A to D), the redox conditions change. As a result of these transition processes, several fundamental shifts in water quality occur. The displacement of the pore solution of one compartment by the water from an adjacent compartment also provokes changes in water quality (E). This process is described by the migration of the displacement front.

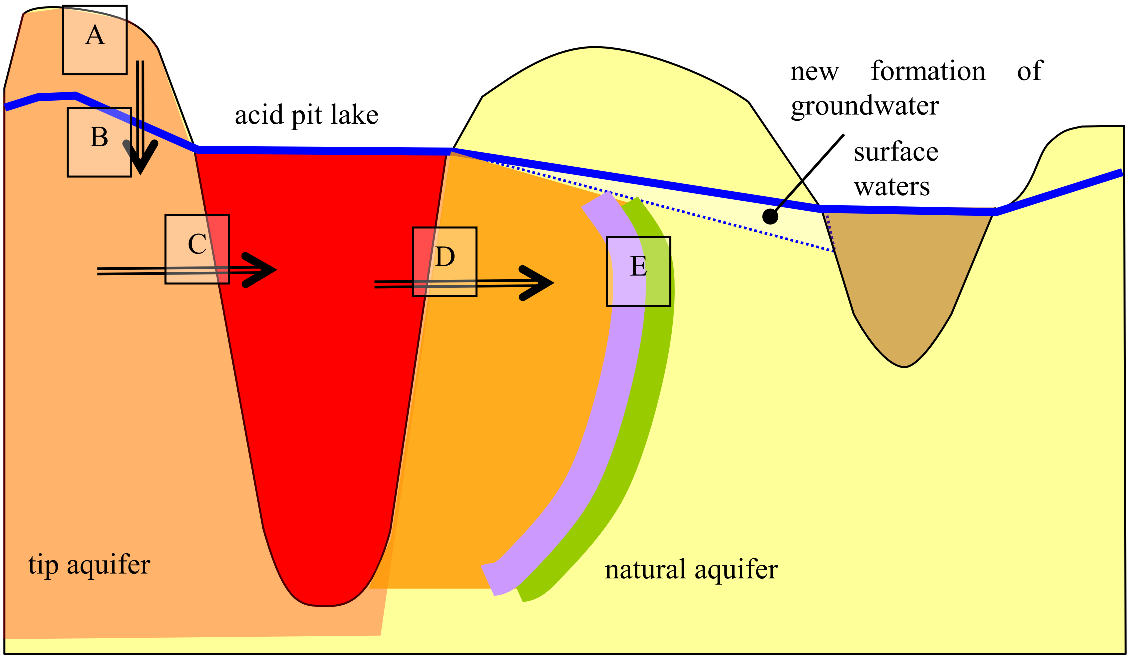

Figure 1 *Scheme of creation and conversion sectors of AMD in the compartments.*

The transitions A-E in figure 1 and figure 2 illustrate:

A: Initial reactions: Pyrite oxidation (A_1) and secondary reactions (A_2) with formation of oxic leachate AMD.

B: Compartment transition: Conversion of oxic AMD in anoxic AMD-groundwater.

C: Compartment transition: Conversion of anoxic tip groundwater in acid pit lake water.

D: Infiltration of acid pit lake water into the aquifer and reconversion in anoxic AMD-groundwater.

E: Migration: Intrusion of anoxic tip groundwater in a natural aquifer with displacement of the original pore solution.

F: Migration: Intrusion of natural groundwater in tip aquifer (not present in figure 1).

By leaching, the oxic AMD with low pH, elevated acidity and high concentration of sulphate will be converted to AMD-groundwater (B). Thus, the acidity will be transformed to ferrous ions and the pH will increase. The produced groundwater will be buffered by hydrogen carbonate while acidity does not change. A statistical linear relationship between the acidity (-NP) and the sulphate concentration is frequently observed in studied areas. Such a statistical relation is found for both oxic and anoxic AMD (Schöpke & Preuß 2012).

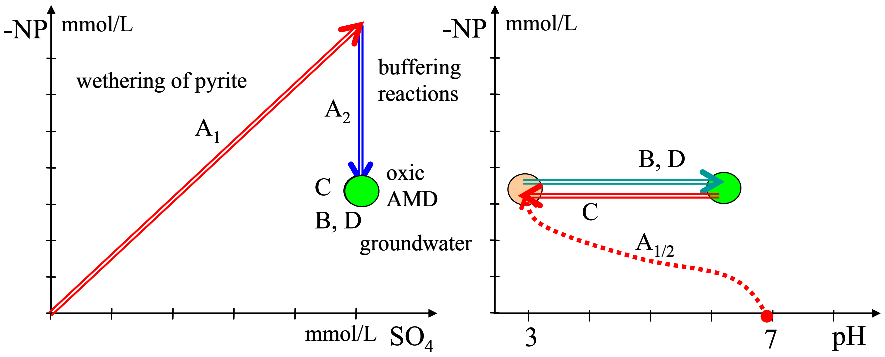

Figure 2 *Reaction vectors in an acidity/sulphate concentration plane.*

At the conversion of anoxic tip groundwater in acid pit lake water (C) and the reconversion in anoxic AMD-groundwater the acidity and the sulphate concentration remain constant while the pH decreases or increases. During the microbial reduction of ferric hydroxides, the acidity and the sulphate concentration change slightly.

Intrusion of anoxic tip groundwater in a natural aquifer with displacement of the original pore solution (E)

After processes B or D, groundwater migrates in a natural aquifer. Thus, the original pore solution of the natural aquifer will be displaced. Naturally, the pore system consists of sand (particles of quartz), silt, clay and natural organic matter (NOM). A chemical equilibrium between the pore solution and the solid matrix will establish only at low flow rates. Decomposition of organic matter is largely completed in natural aquifers. Equilibria with mineral phases and their surfaces primary characterize the change of composition. The equilibria constants of solution complexes and important minerals (calcite, siderite etc.) are known. For simplification, the surfaces of quartz, alumosilicates (silt, clay) and organic matter will be combined to the representative surface sand_wOH defined in PHREEQC. Based on iron oxides (Hfo_wOH in wateq4f) Schöpke et al. (2011) described the surface sand_wOH. Using groundwater monitoring data in the course of treatment experiments the equilibrium constants of surface complexes were adjusted.

To model the relevant processes the aquifer is idealized as a flowed column based on the parameters in table 1.

***Table 1**. Parameters of the aquifer idealized as column*

Parameter	symbol	unit
area of column	A_F	m^2
flow time	t_0, t_1	d
flow length	L	m
reactor (column) volume	V_R	m^3
porosity	n_P	1
specific discharge	v_f	m/d
fluid velocity	v_A	m/d
flowed water column	H	m
amount of exchanged pore volume in the column	PV	1
concentration in the column	c(L)	mol/m^3
amount of substance	n	mol
concentration of inflow	c_0	mol/m^3
capacity function based on volume	$q_V(c)$	mol/m^3
adsorbed concentration with respect to the volume of solution	c_X	mol/m^3

Ions migrate with different specific velocities v_A because of the interaction between the original pore solution and the aquifer matrix. These chromatographic effects can be simulated by the use of the transport model based on PHREEQC.

Via the pore volume n_P, the fluid velocity v_A is linked to the specific discharge v_f.

$$v_A = \frac{v_f}{n_P} \tag{2}$$

By integrating over the specific discharge the flowed water column H will be obtained

$$H = \int_{t0}^{t1} v_f \cdot \partial t \tag{3}$$

In the beginning, $t = t_0$, the pore solution (c_0) is in chemical equilibrium with the solid phases of the aquifer ($q_V(c_0)$). After influx of water column H, so when an ideal jump in concentration ($c_0 \rightarrow c_1$) migrates, the new state of the solid phase ($q_V(c_1)$) standing in equilibrium with c_1 adjusts itself. This leads to mass transfer between the solid phase and the flowed pore solution. As a result, a concentration front differing from the quality of the infiltrated solution occurs. If the solution front has advanced to the length L, the following balance can be used for the flow path (equation 4):

inflow-outflow | solution | matrix

$$(c_1 - c_0) \cdot H_D = \frac{v_f}{v_A(c_0 \rightarrow c_1)} = \frac{\Delta n(t_1)}{A_F} = (c_1 - c_0) \cdot L \cdot n_P + (q_V(c_1) - q_V(c_0)) \cdot L \tag{4}$$

H_D is the already passed water column, when reaching concentration c_1 at length L (breaking point). Thereby, the breakthrough is considered as ideal jump ($c_0 \rightarrow c_1$), which migrates through the column. The amount of substances in the volume of the pore solution is calculated from the reactor length L, the area A_F and the porosity n_P. To calculate the amount of substances adsorbed to the matrix the volume-related capacities of the matrix $q_V(c_0)$ and $q_V(c_1)$ in their respective equilibria are necessary.

As part of the calculations, the processes in filters and in the aquifer refer to the respective reactor volume. PHREEQC indicates the concentration of the adsorbed phase with respect to the volume of the pore solution. The volume-related capacities of the matrix are linked to their concentrations in PHREEQC c_X via the pore volume n_P.

$$q_V(c) = n_P \cdot c_X \tag{5}$$

Unfortunately, the absolute volume-related capacities q_v of real aquifers cannot be indicated because of the different binding forms. However, only the changes are significant to describe the migration processes.

$$R_F = \frac{H_D}{L} = n_P \cdot PV = n_P + \frac{(q_V(c_1) - q_V(c_0))}{(c_1 - c_0)} \tag{6}$$

In contrast to the commonly used definition of the retardation factor R_F, here the often not exactly determinable pore volume n_P is included.

Considering several interacting components instead of just one, for example in a real water, the adjustment of the new equilibrium can take place by several jumps in concentration that occur with each other and/or successively. This transition pattern can be simulated by the use of a mixed-cell-model. For each jump in concentration, characteristic R_F-values are obtained. They allow predicting the further migration assuming defined boundary conditions.

Examples

A simple example is the infiltration of alkaline water from a dump of power plant ash. After infiltrating in the aquifer, the alkaline water is quickly neutralized. During the subsequent displacement of a weakly acidic groundwater by this calcium sulphate-rich infiltrate a complex transition front develops. The inflowing calcium ions thereby replace the cations ferrous and magnesium adsorbed to the matrix of the aquifer. Consequently, a transition front with increased ferrous and magnesium concentrations establishes in the infiltrate. Figure 3 shows the modeling results of this process using a mixed-cell-model. Therein, the progressions of concentrations are plotted depending on the exchanged pore volume PV. Sulphate breaks through immediately running approximately parallel to the hydraulic breakthrough. In previous investigations of pore aquifers in Lusatia, Germany, Schöpke et al. (2011) fitted the parameters of the surface complexes on the aquifer matrix.

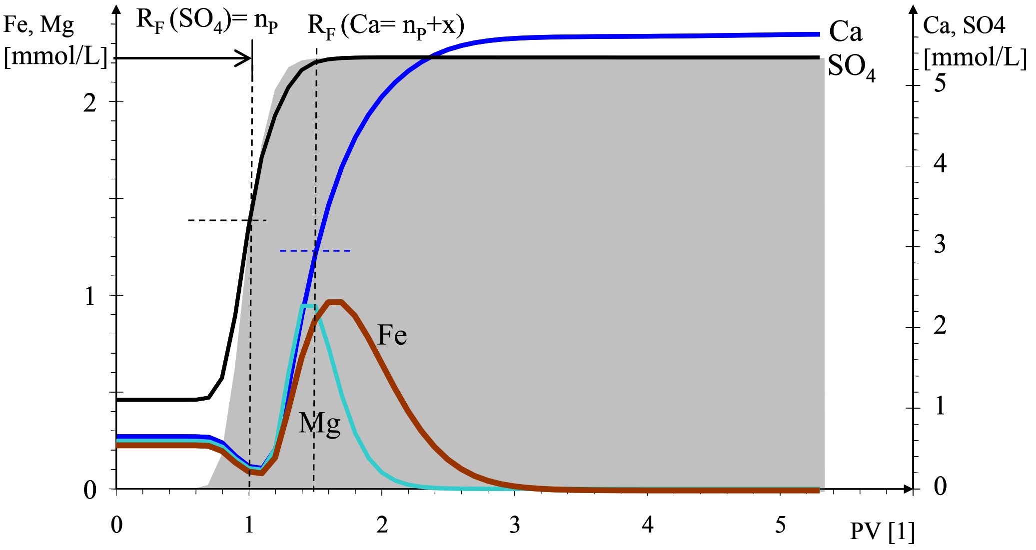

Figure 3 *Modelled concentration patterns due to the displacement of groundwater by a calcium sulphate-rich water as a function of the exchanged pore volume*

However, while the calcium concentration approaches the concentration of the inflow the magnesium and ferrous concentration increase temporarily. In particular, the high amount of ferrous is problematic (Table 2). Anyway, the developed concentration pattern is characteristic of this process. Therein the chemical parameters of the aquifer matrix determine the maximum concentrations and retardations. A result of the modeling is initially a forecast of the expected concentration pattern. The calculated concentration pattern can be divided into sequences of several jumps in concentration. Each jump in concentration migrates in accordance with its characteristic retardation factor $R_{Fi}(X)$. The full passage of such a front can be rarely observed at a single measuring point. To adjust the model the data of a groundwater monitoring network should be used.

***Table 2**. Different water qualities of the displacement of groundwater by a calcium sulphate-rich water*

parameter	unit	neutralised infiltrate	transition front	groundwater
pH	1	5-7	5,1	5,5
$K_{S4,3}$	mmol/L	0	0,13	0,12
NP	mmol/L	0	-2,0	-0,3
Ca	mg/L	225	100 - 150	26
Mg	mg/L	0	20 - 35	6
Fe	mg/L	0	40 - 60	13
SO_4	mg/L	600	400	125

The second example concerns the migration of anoxic tip groundwater in a natural aquifer (E). During this migration in principle the same processes take place, except that the inflow also contains ferrous and acidity. Occasionally calcite and siderite have to be considered as mineral phases in the aquifer matrix. Therefore, the resulting concentration patterns are more complicated than shown in figure 3.

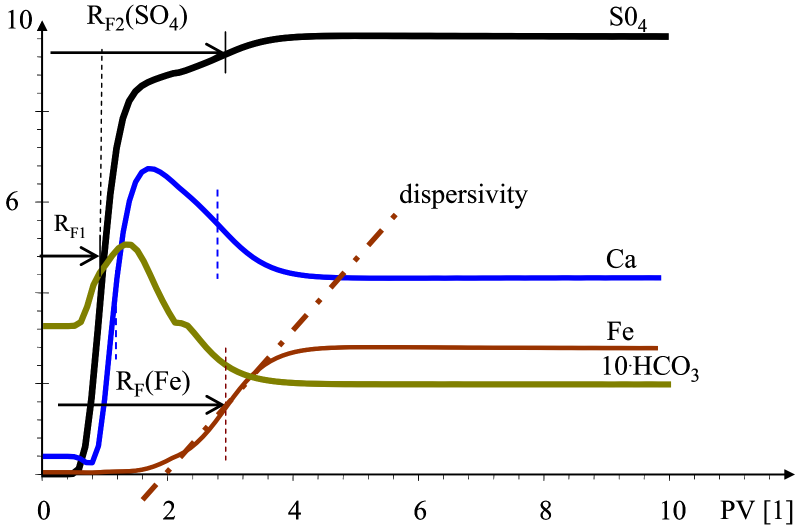

***Figure 4** Modelled concentration pattern due to the displacement of groundwater by tip groundwater as a function of the exchanged pore volume*

The increase in the hydrogen carbonate concentration shown in figure 4 depends on the solution of calcite, which was present in the aquifer. After solving the calcite phase, a jump in concentration follows and a stable groundwater quality establishes. Thereby, the dispersivity of the column determines the steepness of the transitions.

By means of extensive scenario calculations, adsorptive neutralization processes can be traced in tip aquifers (Schöpke & Preuß 2013). They show linear relations between the acidity and the sulphate concentration that deviate from the pyrite weathering stoichiometry (Schöpke & Preuß 2012, Schöpke & Preuß 2015).

Conclusions

When simply changing the redox conditions of AMD (B, C, D), the acidity changes rarely. Oxic AMD are usually acidic, while anoxic AMD are slightly acidic to neutral. In this case, the acidity is mainly caused by ferrous.

During the intrusion of anoxic tip groundwater in a natural aquifer with the displacement of the original pore solution (E), complex quality patterns develop at the displacement front. The individual jumps in quality migrate delayed after the groundwater flow. A transport modeling can approximately predict the quality pattern and their retardation. Hazard scenarios, inter alia for water catchments, can be derived from the comparison between the modeling and the observational data.

Currently, the process of infiltration of acid pit lake water into the aquifer and the reconversion in anoxic AMD-groundwater (D) is still the least understood. In this case, the reduction processes do not end in an equilibrium. At the passage through reducing sediments, a certain pH and the corresponding iron concentration adjust themselves. They decisively determine the concentration pattern that develops during the migration through the aquifer (E).

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Reactive transport modelling of iron-II and sulphate in the former Lusatian lignite mining areas

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Abstract

Decades of dewatering during open pit lignite mining in Lusatia affected geochemistry in the overburden dumps and surrounding aquifers. Due to the groundwater drawdown they became oxidised and act as sulphate- and iron-source. In order to understand the progression and duration of the sulphate- and iron release into the groundwater and the transport into rivers and lakes, reactive transport modelling was applied. Based on preceding projects, the present work utilized reactive transport simulations with an enhanced geochemical concept, that was applied to the latest results of groundwater flow modelling and an improved description of geochemical inventory. First modelling results from the 'Nordraum' site of the current study are shown for the simulated period of 2000 – 2100. They underline the longevity of sulphate storage in the former overburden dumps and also point out the influence of the unworked aquifer parts. Dissolved sulphate and iron-II will have elevated groundwater concentrations over more than one hundred years after the expiration of lignite mining and thus at least until 2100. The mass fluxes of sulphate and iron-II into lakes, rivers and streams in the 'Nordraum' model site decline slowly only towards the end of the simulated period.

Key words: Mine water, Reactive transport modelling, Iron, Sulphate

Introduction

Decades of dewatering during open pit lignite mining in Lusatia affected geochemistry in a large region. Due to the groundwater drawdown not only the sediments in the resulting overburden dumps became oxidized, but also vast parts of surrounding unworked aquifers. Since this massive oxidation cannot not be reversed within a couple of years both of them still act as a source of acidity, iron and sulphur. Aquifers in the Lusatian area are to date typically characterized by concentrations of sulphate from 1300 mg/L to 3800 mg/L, iron from 120 mg/L to 1000 mg/L and moderate pH values from 4.9 to 6.4 (30% and 90% percentile concentration from Bilek 2012). This contamination becomes finally apparent in the downstream rivers and lakes.

In order to describe the (bio-)geochemical processes within these former mining sites, reactive transport modelling is applied within an ongoing series of projects since 2003. Main focus is laid to the progression and duration of the sulphate- and iron release from the geological units into the groundwater and the flux into rivers and lakes. The target is to prove whether the environmental objectives of the European Union's Water Framework Directive can be achieved. The recent project builds on results of the preceding ones and precisifies them. They roughly comprise:

- a methodology to convert results of the complex, PCGEOFIM based hydraulic model into input for the reactive transport simulation code PHT3D (Graupner et al. 2014),
- extensive chemical analysis of groundwater and soil materials,
- the calculation of spatially distributed pyrite oxidation in the modelling area,
- a thereupon based geochemical conception for processes describing the fate of iron and sulphate in dumps and aquifers after pyrite oxidation.

This paper presents the revised modelling methodology and first results from reactive transport calculations based on an enhanced geochemical concept and an improved description of geochemical inventory, that were applied to the latest groundwater flow results.

Methods

Modelling sites

Fig. 1 shows the five considered modelling areas situated in the former Lusatian open pit lignite mining district, each of them comprising multiple dumps and pit lakes. The area encompassed by each model reaches from 540 km² (model area 'Greifenhain/Gräbendorf') to 1214 km^2 (model area 'Nordraum') . The mining history and a more detailed site description are given in Krümmelbein et al. (2012) and Graupner et al. (2012) respectively.

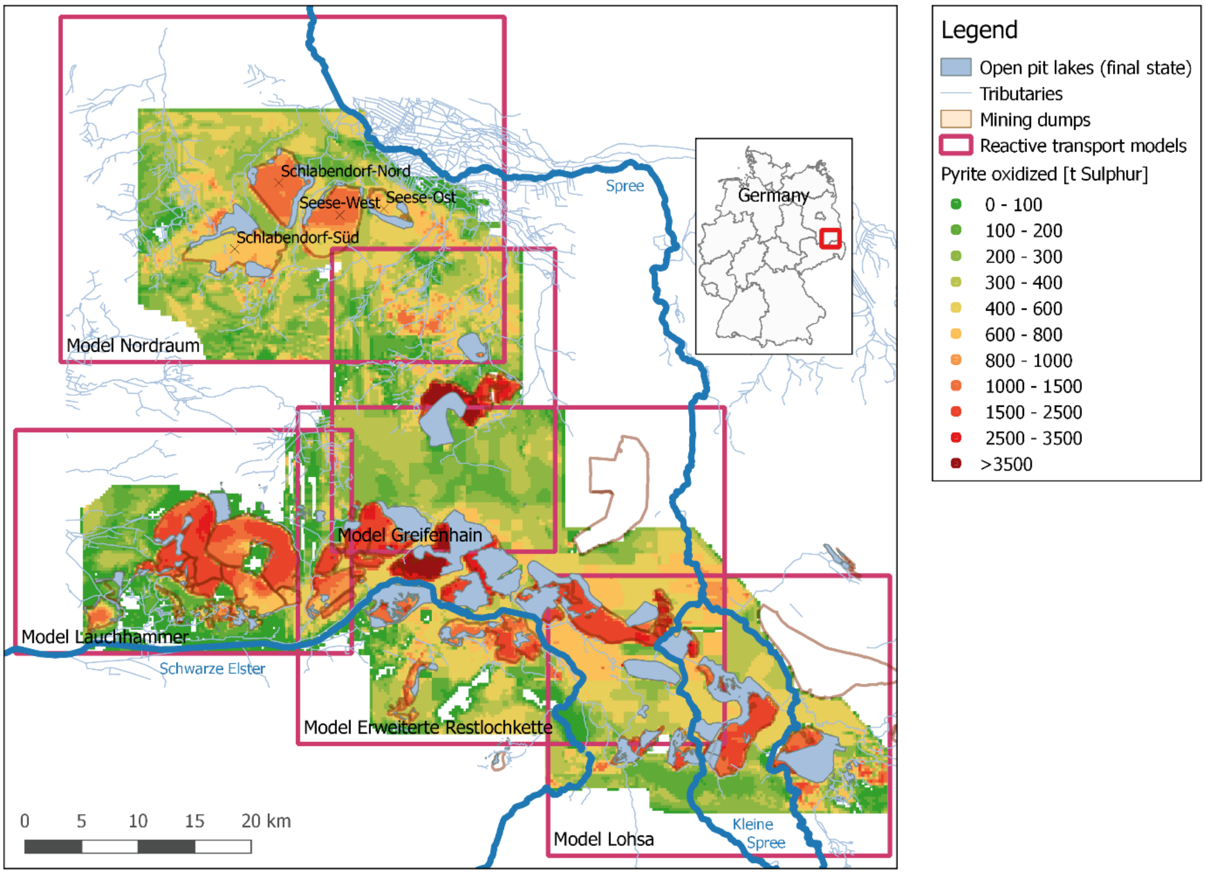

Figure 1 *Overview of study sites location and spatial distribution of sulphur masses from pyrite oxidation in a 200 m x 200 m grid within the scope of evaluation at the year 2000. Former mining sites in the 'Nordraum' model area are labelled.*

Input data and simulation software

Reactive transport modelling was performed using the reactive transport code PHT3D V2.10 (Prommer et al. 2003), which allows the simulation of complex hydrogeochemical processes and refers to the chemical reaction code PHREEQC (Parkhurst & Appelo 1995) and the transport code MT3DMS (Zheng 2005). PHT3D is designed to use flow results from MODFLOW (Harbaugh 2005) simulations. Groundwater flow in the present study sites, however, is described by sophisticated PCGEOFIM flow models already which are continuously maintained since years. In order to use their results they need to be transformed from PCGEOFIMs finite elements approach to PHT3Ds finite differences which was done by the HistoGIS code (Graupner et al. 2014). PHT3D uses the resulting cell based flow rates as **hydraulic input** and calculates reactive transport on them. Applying this procedure avoids the setup of another complex hydraulic model.

As can be seen from fig. 2, particular attention was laid to the determination of **initial geochemical conditions** since they determine the sensitive source term in the predictive modelling. The procedure starts with a historical exploration to gain pre-mining pyrite concentrations assigned to geological layers. Following, PYROX (Wunderly 1994, Wunderly et al. 1996) is applied to calculate the spatially distributed turnover of pyrite by historical groundwater drawdown progression and therewith varying oxygen feeds. The resulting easily mobilised amount of sulphate for the year 2000 is used together with a spatially distributed buffering potential to calculate the hydrochemical starting concentrations (distribution of dissolved species and phases) for the final reactive transport simulation with PHT3D.

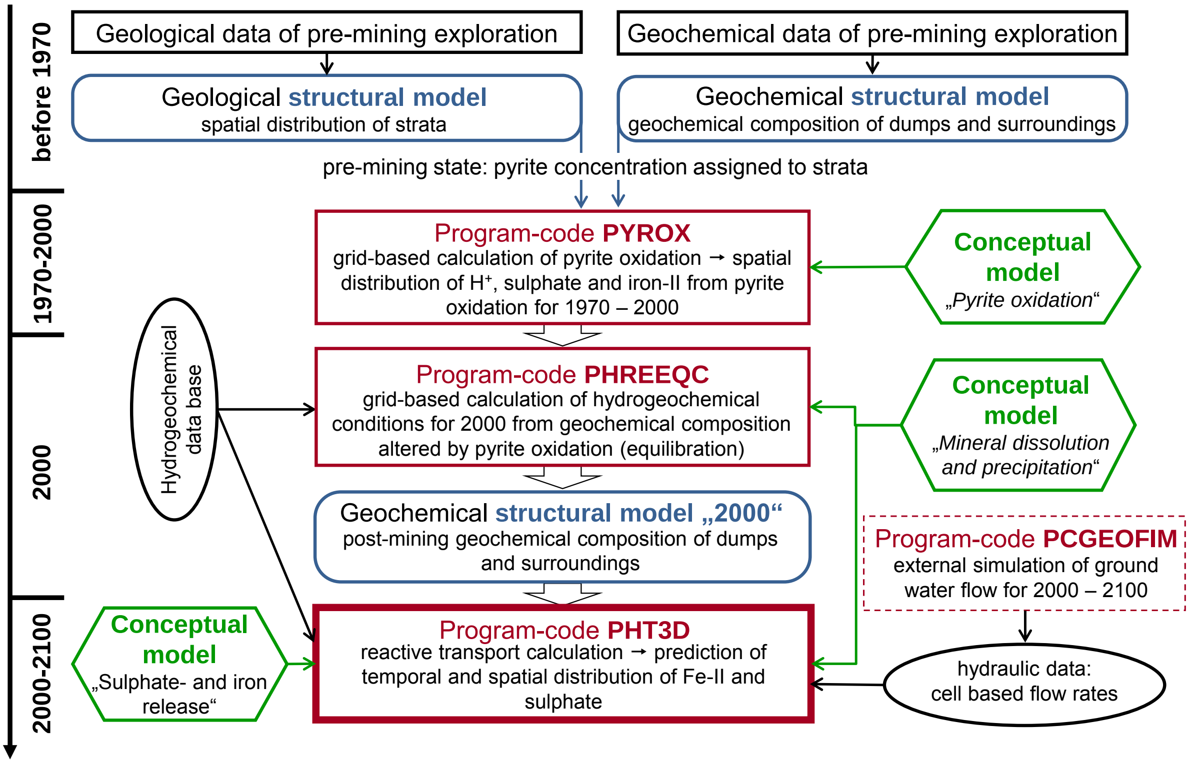

Figure 2 *General work flow for the delineation of geochemical initial conditions in the reactive transport modelling to predict the fate of iron-II and sulphate.*

Geochemical boundary conditions describing the chemical composition of lakes, rivers and streams complete the set of input data for the reactive transport modelling. They were delineated from up to date, long term monitoring data in the area. Future trends were assumed basing on remediation objectives and present trends, but they are less sensitive towards the reactive transport model as most of the surface waters are characterized by effluent flow. Concentration of iron-II and sulphate in groundwater recharge was set to 11 mg/L and 200 mg/ respectively.

Discretization and transport parameter

Each of the five reactive transport models was implemented with a horizontal discretization of 250 m x 250 m, a vertical discretization according to the flow model, excluding vertical refinements. The temporal discretization corresponded that of the flow simulation, with a minimum stress period duration of one year. Porosity was transferred from the flow model, whereas other hydrogeological parameters were assumed to be constant: longitudinal dispersivity (50 m), horizontal transversal dispersivity (5 m), vertical dispersivity (0.5 m), effective molecular diffusion coefficient ($1 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$). Temperature was set to 10 °C.

Geochemical concept

Implemented chemical entities from the standard PHREEQC thermodynamic data base are summarized in tab. 1. Partial chemical equilibrium was assumed with microbial sulphate reduction and feldspar-weathering being kinetically determined. Sulphate reduction rate was described by a Michelis-Menten-kinetic with regard to sulphate, a half saturation constant of $2 \cdot 10^{-4}$ mol/L and a site characteristic reaction rate constant of $6.34 \cdot 10^{-13}$ $mol \cdot L^{-1} \cdot s^{-1}$. Feldspar weathering rate based on results of Bilek (2004) with $1.4 \cdot 10^{-11}$ mol $L^{-1} \cdot s^{-1}$ for pH < 3 with $5.4 \cdot 10^{-12}$ mol $L^{-1} \cdot s^{-1}$ for pH > 4.5 and a linear progression between these values.

***Table 1** Chemical components, minerals and cation exchange species implemented in the reactive transport models.*

Chemical entity	Immobile	Kinetic
Al, C-IV, Ca, Fe-II, Mg, SO_4^{2-}, Si, K	-	-
pH, pe	-	-
$S_{reduced} = Fe^{2+} + SO_4^{2-}$	-	x
Gypsum: $CaSO_4{:}2H_2O_s = Ca^{2+} + SO_4^{2-} + 2H_2O$; $k = 10^{-4,58}$	x	-
Calcite: $CaCO_{3,s} = CO_3^{2-} + Ca^{2+}$; $k=10^{-8,48}$	x	-
Kaolinite: $Al_2Si_2O_5(OH)_{4,s} + 6H^+ = H_2O + 2H_4SiO_4 + 2Al^{+3}$; $k=10^{7,435}$	x	-
$SiO_{2(a)}$: $SiO_{2,s} + 2H_2O = H_4SiO_4$; $k=10^{-2,71}$	x	-
$CO_{2,g}$: $CO_{2,g} = CO_{2,aq}$; $k = 10^{-1.468}$	x	-
Feldspar: $KAlSi_3O_{8,s} + 8H_2O = K^+ + Al(OH)_4^- + 3H_4SiO_4$; $k=10^{-20,573}$	x	x
Cation exchange species: Ca^{2+}, Mg^{2+}, Fe^{2+}	x	-

(Bio-)geochemical processes implemented in the reactive transport models were delineated by explaining present ground-water quality data with chemical equilibrium modelling (Bilek 2014). The major processes cover:

- subsequent delivery of Fe-II, sulphate and H^+ from the immobile storage (gypsum, secondary silicates, cation exchanger),
- dissolution/precipitation of calcite and gypsum according to their solubility product,
- kinetic weathering of K-feldspar as slow buffer reaction after calcite depletion,
- cation exchange of Fe^{2+}, Ca^{2+}, Mg^{2+},
- microbial sulphate reduction with a simplified formulation as a sink for Fe^{2+} and $SO_4^{2-} = FeSO_4$.

Fig. 3 illustrates the connection between the chemical entities by the whole of the implemented (bio-)geochemical processes. They reproduce the dominating processes for sulphate and iron storage, transformation and transport as proven by the reproduction of groundwater quality data. The authors are aware, that especially iron is affected by further complex mineral dissolution and precipitation reactions. But at the present state neither availability of field data nor a thereupon proven concept would allow a more complex implementation.

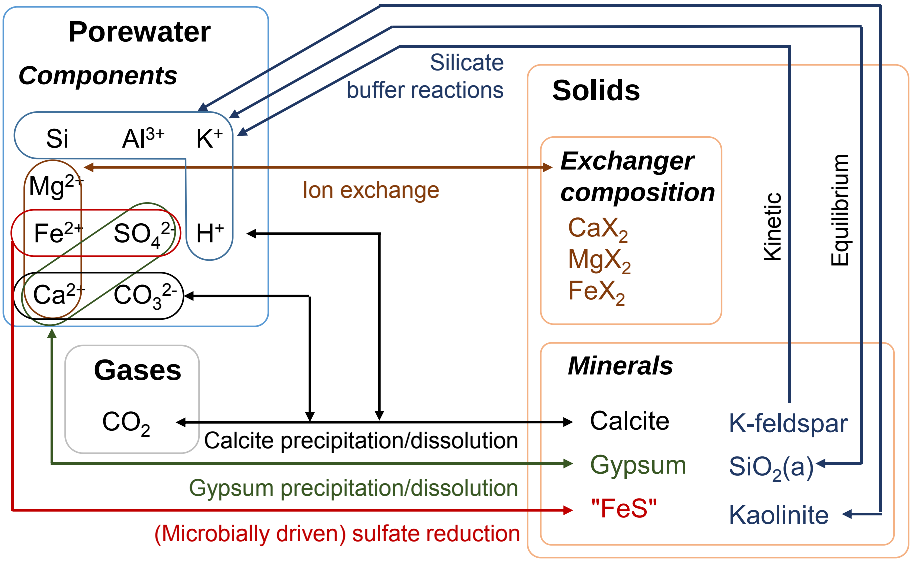

Figure 3 *Geochemical concept of the reactive transport models: reactions after buffering and storage from pyrite oxidation products.*

Results

As an example results from the model area 'Nordraum' are presented in this paper. Fig. 3 shows the spatial distribution of sulphate concentrations in the upper of two model layers at 2010 and 2100. It becomes evident, that not only mining dumps, but also some parts of surrounding unaffected aquifers will be contaminated with high sulphate concentrations at the end of the simulated period. The depletion of sulphate in the model is mainly driven by groundwater recharge (sulphate concentration 200 mg/L) and it's duration depends on the amount of gypsum representing the sulphate source term. Thus the mining dumps Schlabendorf-Nord and Seese-West but also the south-east region in the unworked aquifer with high pyrite oxidation (fig. 1) are subject to sulphate concentrations above 1.7 g/L beyond 2100.

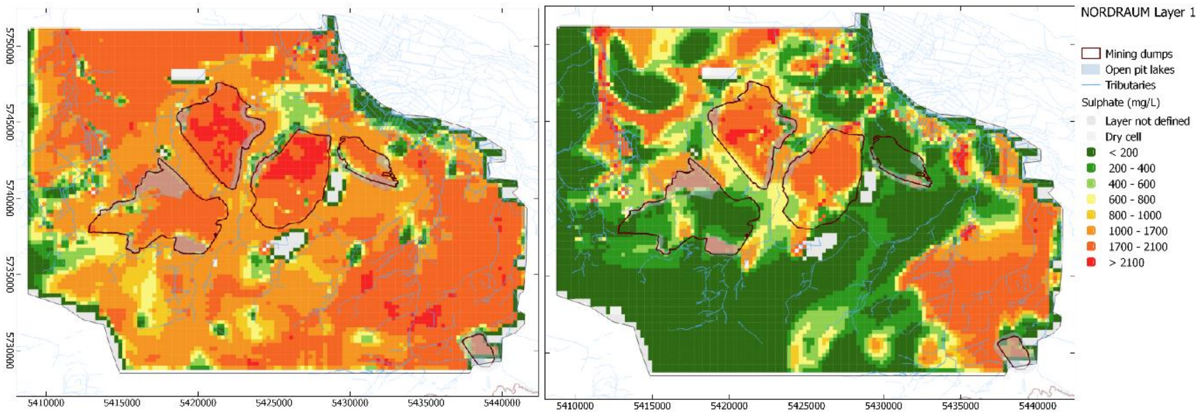

Figure 3 *Spatial distribution of sulphate in the 'Nordraum' area. Left: 2010, right: 2100.*

Fig. 4 illustrates a similar behaviour for the concentration development of dissolved iron-II in the 'Nordraum' area. Comparing sulphate with iron-II, no significant difference is visible for areas subject to elevated concentrations in 2100. For the mining dumps Seese-West and Schlabendorf-Nord and the unworked southeast aquifer region the simulation predicts concentrations above 100 mg/L iron in the groundwater.

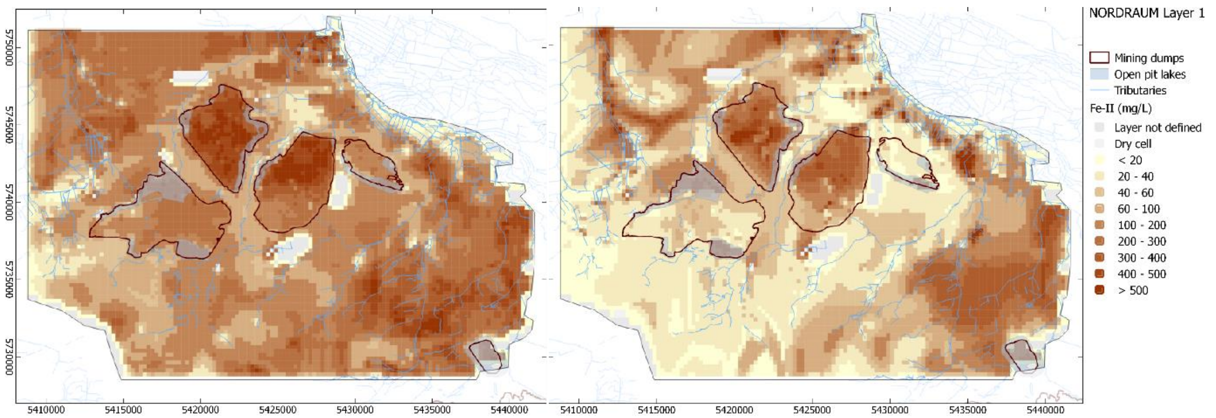

Figure 4 *Modelled spatial distribution of Fe-II in the 'Nordraum' area. Left: 2010, right: 2100.*

In order to illustrate the longevity of the attenuation processes, fig. 5 shows the development of total sulphate and iron-II masses in the 'Nordraum' model area. Gypsum and iron at the exchanger represent the immobile source terms and are slowly depleted only. The dissolved components sulphate and iron-II are – by definition – in equilibrium with these immobile sources and fall below specific equilibrium concentrations when the source term is depleted. Further, sulphate reduction with a typical maximum rate of $6.34 \cdot 10^{-13}$ mol·L^{-1}·s^{-1} influences the attenuation process marginally only.

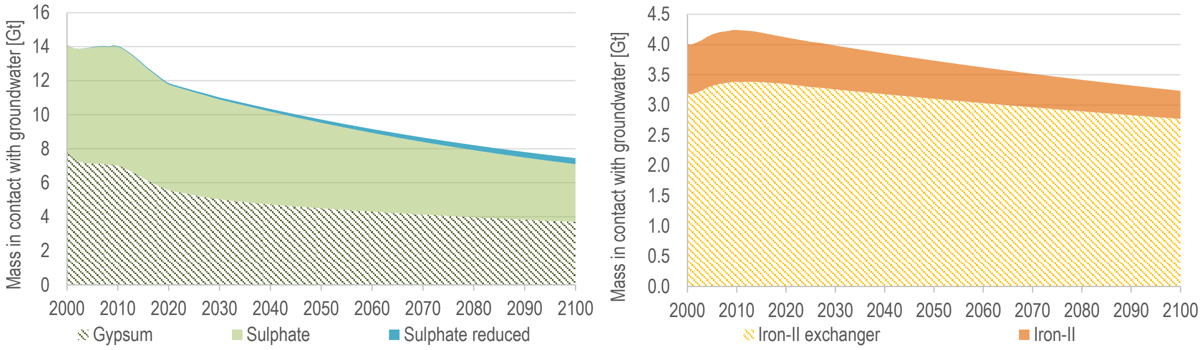

Figure 5 *Modelled development of total masses in contact with groundwater in the 'Nordraum' model area. (The volume saturated with groundwater instead of total cell volumes were used for calculation of total mass, thus representing the mobilizable/mobile masses.)*

Most of the tributaries and lakes are effluent in the 'Nordraum' model area. Following, their water quality is directly influenced by the conditions in the upstream aquifers. Fig. 6 summarizes annual mass fluxes from groundwater into surface water boundary conditions for selected years. The steep decline of fluxes to lakes is caused by the reduced water inflow as the lakes reach their final water table. Rivers and streams, however, get better connected with the groundwater by groundwater table recovery and thus show an increasing flux until to date. This tendency only slowly turns into a decline due to depletion of the sources. Care must be taken transferring these results to the effect on water quality in rivers and lakes. The model describes fluxes out of groundwater but not the processes within the adjacent boundary zone (interstitial) where further transformation reactions occur before the water enters a lake or stream.

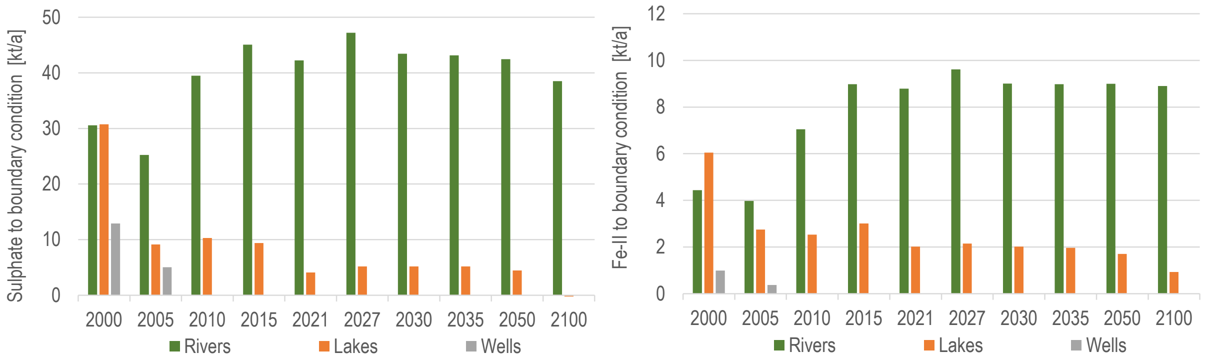

Figure 6 *Modelled total diffuse groundwater borne mass flux into surface water in the 'Nordraum' model area.*

Conclusions

Multi-mine reactive transport models were implemented to determine the effects on both groundwater composition and fluxes into surface waters in the former Lusatian open pit lignite mining district. Their geochemical concept was designed to reflect regional quality effects on a large scale, rather than giving information at specific points. The simulations finally predict, that due to decades of groundwater drawdown pyrite oxidation in the mining dumps themselves, but also in the unworked bedrock constitute a source for elevated concentrations of sulphate and ferrous iron.

Mining affected groundwater quality will be an issue beyond 2100. As an example the overall situation for rivers and streams in the 'Nordraum' area indicates a minor improvement for the water quality until 2100. The results are generally in good agreement with previous work (Graupner 2014, ARGE 2012), added that also unworked aquifers partly constitute a long term source for iron and sulphate. Future work needs to take into account the interaction between the five model areas concerning the mass fluxes across the model area boundaries.

Acknowledgements

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Modelling the Hydrogeochemistry of Decommissioned Opencast Coal Mines

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Abstract

Water quality improvement in underground mines after the initial flush can render these mines as potential water supplies. However, in certain settings, opencast mining is often preferred. With the prospect of an initial flush in backfilled opencast mines, it is essential to study the initial flush in this setting as these mines may also show water supply potential.

Previous work focused on idealised curve fitting to existing mine water chemistry data, analytical calculations, simplified geochemical modelling and numerical transport models. The study presented here combines components of each to predict the initial flush from backfilled opencast mines. An additional component is the calibration of geochemical- and numerical flow and transport modelling data, with existing groundwater monitoring- and laboratory analysis data. A statistically defined mineral assemblage, based on analysis data, is used as input to geochemical models and calibrated using leaching test data. Leaching test data is further compared to speciation calculations and mine water analysis data to ensure representative laboratory data. Long term geochemical modelling results are then used as input to transport models, which are calibrated against groundwater monitoring data.

The study presents a calibrated modelling approach which shows that calibration can provide realistic estimates which is supported by existing work, showing the duration of the initial flush in underground mines to be a few decades. The calculated duration of the initial flush in this study ranged between 20 and 100 years. Results obtained are considered to be more representative than static estimates and can aid in the improvement of rehabilitation techniques and the management of post-mining groundwater quality, with calculated concentrations calibrated up to a 1% error range.

Key words: Mine water, Opencast mining, Hydrogeochemistry, Modelling

Introduction

Various authors have conducted research on the prediction of the initial flush from abandoned underground mines (Appelo and Postma 2005; Banks 1994; Gzyl and Banks 2007; Younger 2000; Younger 2001; Younger and Robins 2002). Calculation of a "first flush", as it was called by Whitehead and Jeffrey (1995), in backfilled, decommissioned opencast collieries, has not been established, even though the extent of this is likely to exceed the temporal magnitude of its underground counterpart. This is attributed to higher reactive mineral surface areas, slower groundwater flow rates and partly the absence of stable mine water stratification found in underground mines (Younger and Sapsford 2004). With mass opencast closure becoming a reality in the future of South Africa (Vermeulen and Usher 2005), the need for a more advanced conceptualisation is evident. Acid-base accounting, which is especially employed in Mpumalanga, South Africa where most of the country's coal reserves are mined (Pinetown et al. 2007), cannot be viewed as a reliable tool to predict temporal ARD variations. Unfortunately, this is occasionally the case with this indicator test (Younger and Sapsford 2004).

This study focusses on the development of a conceptual model approach to numerical geochemical modelling of the initial flush from decommissioned opencast mines. The need for such a study is highlighted by a directive issued to a mine near Carolina, Mpumalanga which required the quantification of the initial flush from its opencast mines as well as the acid rock drainage (ARD) potential of its backfill material.

Methods

An improved understanding of the mine site's hydrogeology, mineralogy and geochemistry was required to address the quantification of the initial flush using a conceptual model based approach. To obtain this information, a review of previous studies and available monitoring data was performed along with sampling of backfill material on site. The material generated on site was sampled from overburden dumps and backfilled opencast mining areas (Figure 1) using a hand auger.

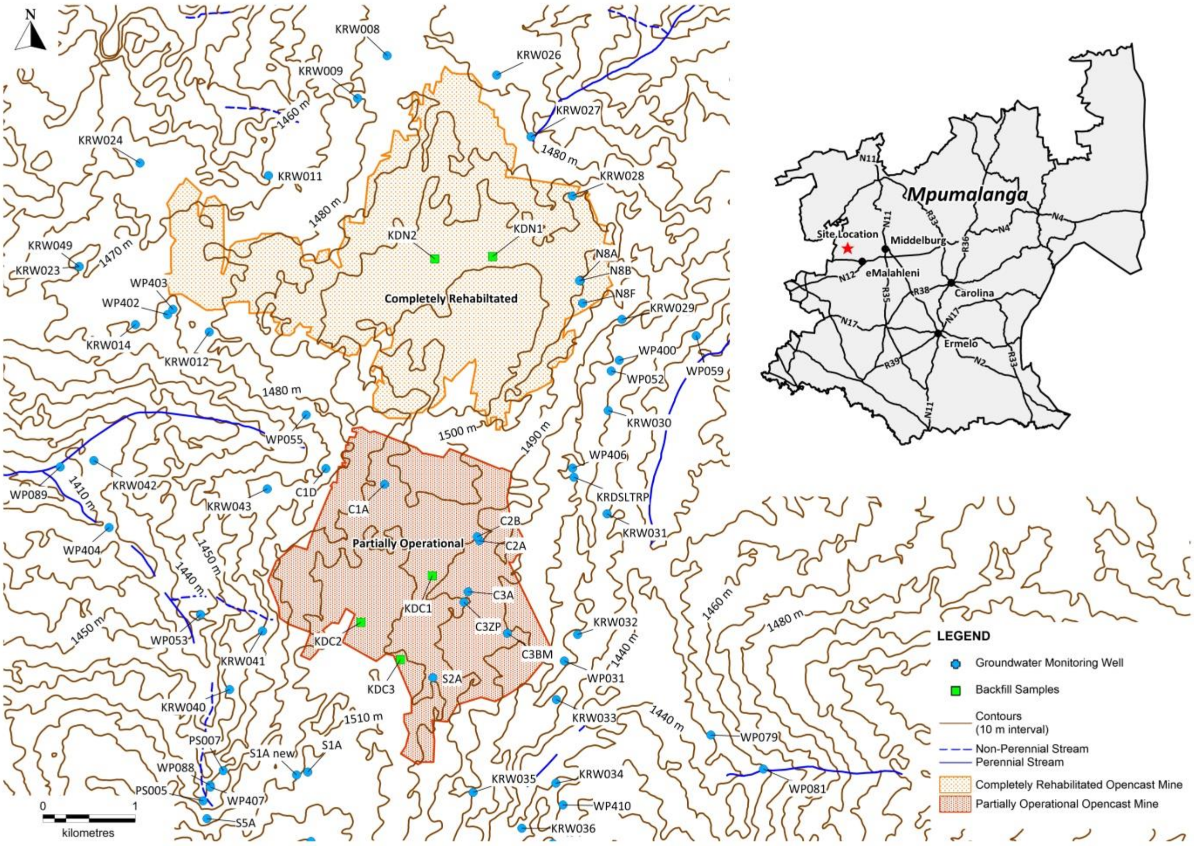

Figure 1 *Geochemical Sampling Locations*

This was followed by submission of the samples for whole-rock X-ray diffraction (XRD) analysis to determine the mineralogical composition of the material. Acid-base accounting was performed on the samples as an indicator test for the presence of potential sulfides to determine the potential for acid generation and to determine the potential sulfate contamination. The samples were analysed for paste pH, total sulfur, acid generation potential, acid neutralisation potential and neutralising potential ratio. Further to this, distilled water leach testing was performed on the samples to demonstrate the possible contaminants that may be leached from the material in the short term under laboratory conditions.

The geochemical modelling interface used for constructing the geochemical model was The Geochemist's Workbench (GWB) 9 (Bethke 2008). This model defines the dynamic geochemical system by using mineral abundances, water qualities, mineral reaction rates and mineral reactive surface areas. The mineral abundances used were calculated based on the XRD results. The average weight percentage of a mineral was calculated along with the standard error associated with it. Standard errors were subsequently added and subtracted from the average to determine the upper and lower limits for the weight percentage of the specific mineral, respectively.

The mineral reaction rates were obtained from literature sources. Additionally, the grain size of the material, as measured on site, was used to calculate a reactive surface area for each mineral. This calculation is based on mineral densities recorded in literature as well as the volume of grains in the sample, assuming most of the mineral grain will be available for reaction with fluids and that grains are spherical (Gautier et al. 2001).

In the event that specific elements were detected during leach testing with no mineral corresponding in the XRD analysis, saturation indices were calculated for specific secondary minerals which may not have been detected by the XRD analysis due to their amorphous nature. Acid-base accounting was also used in this regard to motivate the presence of certain minerals which were undetected by XRD.

Once the mineral assemblage, reaction rates and reactive surface areas were defined, the laboratory leach testing scenario was simulated to calibrate the mineral assemblage. The final simulated concentrations were then correlated with the final leaching test concentrations and if a statistically significant correlation existed ($R^2 > 0.8$, $\alpha = 0.95$) the assemblage was considered to be calibrated. To obtain this correlation, a trial and error approach was used for the geochemical model by adjusting parameters within statistical boundaries to obtain a representative mineral assemblage.

Upon successful calibration of the identified mineral assemblage to the leaching test data, the natural geochemical reaction on site was simulated. Inflow volumes into the opencast mine were obtained from a pre-constructed MODFLOW model. These volumes were then compared to the volume and porosity of each pit to determine the natural fluid to rock ratios over time. The natural conditions on site were then simulated in the geochemical model to provide input to a numerical transport model for a period covering the available groundwater monitoring data for the site.

Inputs generated from the geochemical model were integrated into the numerical transport model using a stress period approach to simulate the conditions within the backfilled opencast mine. The resulting transport solution was then compared to the monitoring data using an error summary graph. This was performed using a trial and error approach, with a successful transient chemical calibration indicating reliability of the geochemical model. In the event that calibration was not achieved, parameters such as oxygen fugacity and fluid to rock ratios within the geochemical model were revised to obtain a more representative input to the transport model. Once transient chemical calibration was achieved within the transport model, long term sulfate concentrations were simulated beyond the period covered by monitoring data to determine potential future environmental effects.

Results

The backfill material consists of quartz, muscovite, K-feldspar, kaolinite, plagioclase, hematite and smectite. Additional minerals assumed to be present, based on visual inspection, acid-base accounting and saturation index calculations, were gypsum and pyrite. The mean mineral abundances, standard errors, reaction rate constants and reactive surface areas (Table 1) were defined using the kinetic reactant function of GWB. The model was calibrated against leaching test constituent concentrations (Table 2).

To calibrate the geochemical model, the distilled water leach tests performed on the material samples, were simulated. Therefore, the mineral assemblage identified in the XRD analysis as well as the subsequent reactive surface areas and rate constants were specified in the model. Leaching of this assemblage by distilled water for 20 h in a 1:4 rock to water ratio was simulated. Simulated concentrations leaching from the mineral assemblage in the geochemical model were then compared to the analysed concentrations from the leaching test (Figure 2). The regression line fitted to the data indicated a coefficient of determination of 0.9943.

Table 1 *Mineral Weight Percentage Statistics*

Mineral Phase Based on Analysis Data	Mean Weight Percentage	Standard Deviation of the Mean Mineral Weight Percentage	Standard Error of the Mean Mineral Weight Percentage	Initial Reaction Rate Constant ($\mathrm{mol\cdot cm^{-2}\cdot s^{-1}}$)	Initial Reactive Surface Area ($\mathrm{cm^{2}\cdot g^{-1}}$)#
Hematite	0.77	0.46	0.19	5×10^{-11} [a]	57
Kaolinite	16.56	8.32	3.39	1×10^{-17} [b]	58
K-Feldspar	10.87	2.57	1.05	1.7×10^{-17} [c]	58
Muscovite	6.01	1.59	0.65	2.9×10^{-15} [d]	53
Plagioclase	2.03	4.53	1.85	1.0×10^{-16} [e]	55
Quartz	45.25	11.15	4.55	5.0×10^{-14} [f]	22
Smectite	36.22	2.26	0.92	3.0×10^{-15} [g]	60
Mineral Phase Assumed Present				Reaction Rate Constant ($\mathrm{mol\cdot cm^{-2}\cdot s^{-1}}$)	
Pyrite	0.03*			2.8×10^{-12} [h]	104
Gypsum	0.05*			1.3×10^{-04} [i]	26

[a]Hersman et al. (1995); [b]Huertas et al. (1999); [c]Oelkers and Schott (1998); [d]Oelkers et al. (2008); [e]Gudbrandsson et al. (2014); [f]Gautier et al. (2001); [g]Marty et al. (2015); [h]Malmström et al. (2006); [i]Jeschke et al. (2001); *Estimated based on field observations, acid-base accounting, saturation indices and literature reaction rate constants; #Calculated from sample average grain size and mineral density, assuming entire surface is available for reaction. See Brantley (1998); Gautier et al. (2001); and White and Brantley (2003).

Table 2 *Chemical Constituent Concentration Statistics, all concentrations in mg/L, TDS: Total Dissolved Solids*

Chemical Constituent	Mean Concentration	Standard Deviation of Element Concentrations	Standard Error of Element Concentrations
Al	0.23	0.42	0.17
Ca	9.17	14.30	5.84
Fe	0.14	0.30	0.12
K	3.55	2.22	0.91
Mg	4.67	4.89	1.99
Mn	1.38	3.08	1.26
Na	2.67	1.37	0.56
Si	4.93	2.29	0.94
TDS Calculated	90.83	115.49	47.15
Alkalinity (CaCO3 eq.)	0.00	0.00	0.00
Cl	1.00	2.45	1.00
SO_4	33.40	70.34	28.72
NO_3	0.25	0.22	0.09
pH	4.92	0.75	0.30

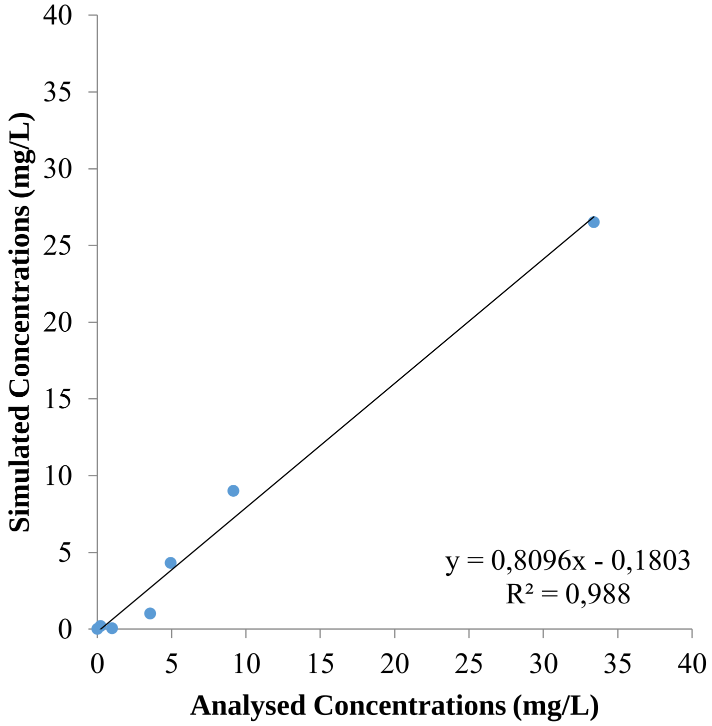

Figure 2 *Correlation Graph of Average Constituent Concentrations Measured During Leaching Test Analyses vs. Constituent Concentrations Simulated in a Geochemical Model Simulating the Leaching Test Procedure*

After simulation of the leaching test, the natural conditions on site were simulated in the geochemical model for the period of groundwater monitoring. The resulting solution was integrated with the transport model as specified. The transport simulation was performed for the period which monitoring data was available. Once the simulation was completed, a transient calibration graph was constructed to determine how well the simulated sulfate concentrations compared to monitoring data. An error range of 50 mg/L was used as concentrations of sulfate observed in the monitoring wells reach levels of over 500 mg/L in some areas. Therefore, a 10% error of the monitoring concentrations for sulfate was deemed applicable (Figure 3). Results show that most of the simulated concentrations were within the specified error margin, for the simulated time period. The initial flush breakthrough curve can also be observed in certain monitoring points. Based on the chemical calibration of the numerical transport model, representative input of sulfate into the model was assumed. Therefore, long term sulfate transport could be simulated in an attempt to determine the sulfate concentrations that could potentially be released from the rehabilitated opencast mines in the long term.

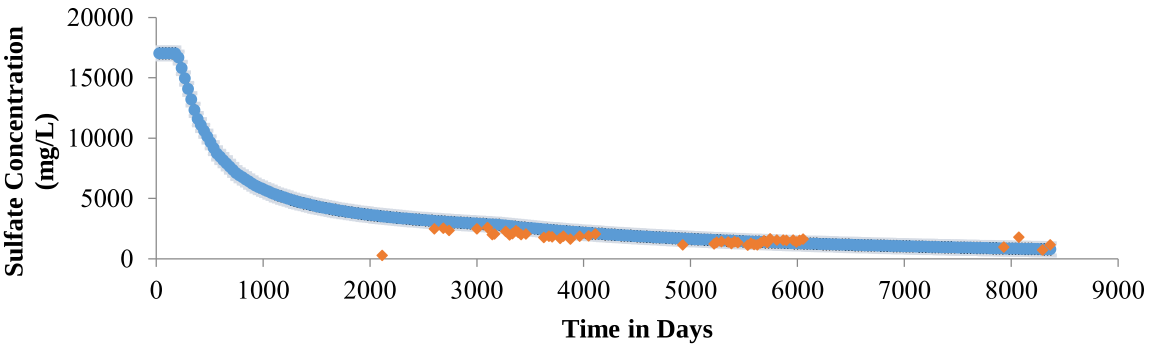

Figure 3 *Example of Simulated Sulfate Concentrations at an Observation Well in the Numerical Flow Model vs. Measured Sulfate Concentrations Obtained from Monitoring Data for the Same Well in Reality (Blue dots indicate simulated concentrations. Red diamonds indicate measured concentrations).*

Discussion

Modelled constituent concentrations in the geochemical and numerical models corresponded well with measured concentrations within the identified error ranges, especially in areas with higher sulfate concentrations. This shows that the focus of this modelling method depends on the controlling parameters of the site geochemistry. Pyrite oxidation and weathering, as well as carbonate mineral weathering were identified as the main controls on solution pH and chemistry, with major mineralogy playing a secondary role. Therefore, the calibration of pH and sulfate is essential for modelling representative values and was the main focus of geochemical model calibration. As pyrite and carbonate mineral weathering are the primary controls on mine water chemistry in the Mpumalanga coalfields, the correspondence of the modelled and measured constituent concentrations is explicable. Further to the identification of the primary controls on the mine water chemistry is the enhancement of calibration accuracy with abundant measured data. As a large monitoring data set was available, it was deduced that monitoring data plays an essential role in the prediction of long term mine water chemistry. This observation is based on clearer concentration trends observed over longer periods, which gives a better indication of how calculated concentration trends should behave if they are based on defensible model inputs.

Conclusions

Findings in this study illustrate that a simplified conceptual model as well as an improved understanding of mineralogy and geochemistry in decommissioned opencast mines can provide improved prediction of transient mine water chemistry. Constant source modelling and acid-base accounting can be regarded as a worst-case estimate but may prove less useful in a closure and mine water management scenario. Therefore, this methodology can be employed to provide an improved estimate of the initial flush from opencast mines as well as its subsequent duration and concentrations. This data can in turn be used to plan mitigation measures to be implemented for realistic time frames, as mining wastes are decaying contaminant sources and should therefore be treated as finite. Although defensible results have been obtained in this study, further refinement is achievable. It is suggested that the influence of microbiology as well as transient meteorological conditions be integrated into future modelling processes to improve calculations. Based on refined models, improved rehabilitation techniques and mine water management measures can be developed possibly turning opencast mines from sources of contamination to functional groundwater reservoirs.

Acknowledgements

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Decision Making For Sustainable Tailings and Water Management – A Dynamic Modelling Approach

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Abstract

The water system of a mine is complex and its behavior depends on a great number of variables. To obtain a holistic understanding of the water system it is necessary to link all elements in the system together. In this sense, a dynamic modelling of a mine water system needs to integrate the tailing storage facility together with relevant production parameters in the plant, the clarification pond and its interaction with external water sources. Traditionally, the water management for a mine is established through water and mass balances. These balances for tailing storage facilities does not account for the changes in water volumes. This constitutes the main reason why advanced water quality modelling often is omitted for the storage. Hence, a fundamental part and the link between the plant and the clarification pond is missing. This has forced the development of forecasts and prognostics based on simplified assumptions and methodologies for the tailings ponds and do not consider properly its evolution over time. This paper focus on the development on a methodology to build a dynamic model for the tailing storage facility through a coupled hydraulic and a water chemical model, which is integrated as the link between the plant and the clarification pond. The result is a more precise modelling tool that creates the base for decision making to minimize the impact on the environment during both the design and the operation of the system.

Key words: dynamic modelling, integrated model, tailing storage facilities, tailings, water quality

Introduction

The need for dynamic modelling in mining systems is clear. A large number of variables intervene in the operation and can only be properly considered in a dynamic modelling. The mine system should though include the tailing storage facility (herein denominated TSF) in a more detailed manner. A method has been developed by the authors that enables an integrated water balance and water quality modeling that includes essential aspects for the dam safety at the same time. The method is based on the fact that the TSF is a series of an infinite number of storage areas. This method brings light to fundamental parameters that are discussed for the design of the TSF. This is also a requirement to perform advanced modelling of the water quality in the TSF, which explains variations in the outgoing water quality to the clarification pond. The conclusions can be used to optimize the mine water system, to identify critical aspects that could occur during the operation.

Dynamic modelling of mine water systems

Dynamic modelling of mine water systems is discussed by Nalecki and Gowan (2008) and by Lauzon and Paget (2011). Dynamic modelling is required to better understand the mine water system and it needs to integrate essential parameters already during the planning phase of the project but also for the operation of the mine. Mine water systems are composed by production plants, which generates tailings and delivers the slurry to the TSF. The operation of the TSF must take into consideration many factors related to the tailings disposal strategy, dam safety and the management of the water elevations in the storage. The TSF ensures that the water reach an adequate quality before it is delivered further to the clarification pond. From the clarification pond, the water is being pumped up again to the production plant. To the system, the need for additional water make up is also planned.

However, the tailings disposal strategy is a crucial part for the planning of the storage, which affects the storage area's geometry continuously. This influence the management of water elevations and water volumes. Inversely, the change in water volumes affect the tailings slopes, which also affect the storage geometry. Consequently, the water quality is also affected by variations in both the tailing disposal strategy and the management of the water elevations in the TSF.

Given the implications of the water management in the tailings storage facility it is convenient to take into consideration parameters related to the dam safety such as required beach widths, maximum flood elevations, dam heights and spillway structures and its varying capacity over time. Beach widths may have a limiting factor on the water volumes that can be stored in the TSF and hence a direct impact on the water quality that leaves the pond. The minimum required beach widths depends on the tailings disposal strategy.

A dynamic model for a mine water project should consider all the above parameters in order to be able to produce future forecasts for the operation of the system. All these parameters varies over time and can adopt a range of possible values. Therefore, and to cover properly possible future scenarios, the authors have adopted Monte Carlo Simulation techniques that enables probabilistic variations of important variables in the system. The result is an interval of possible results that are an essential part in the decision-making during the design and/or operation of the system.

Characterization of the Tailing storage facility

Nalecki and Gowan (2008) and Lauzon and Paget (2011) consider a continuous tailings disposal throughout the mine projects lifetime. However, it is not clear how the modelling of the tailing storage is performed or how the water volumes evolve with time. TSF need to integrate the tailings disposal strategies for the future operation periods. Past and future geometries of the TSF are necessary to be able to make historical analysis, planning of new projects or for an upcoming maintenance period.

A TSF can be described as an infinite number of storage areas (SA) each of them are associated to a specific time (t, t+1,…, t+n), i.e. SA_t, SA_{t+1},…, SA_{t+n}. Each storage area per time step can be described using conventional stage-storage and stage-area curves (fig 1). In the figure, it can be observed how the bottom line of the storage area, i.e. elevation for volume equal zero, increases continuously with time.

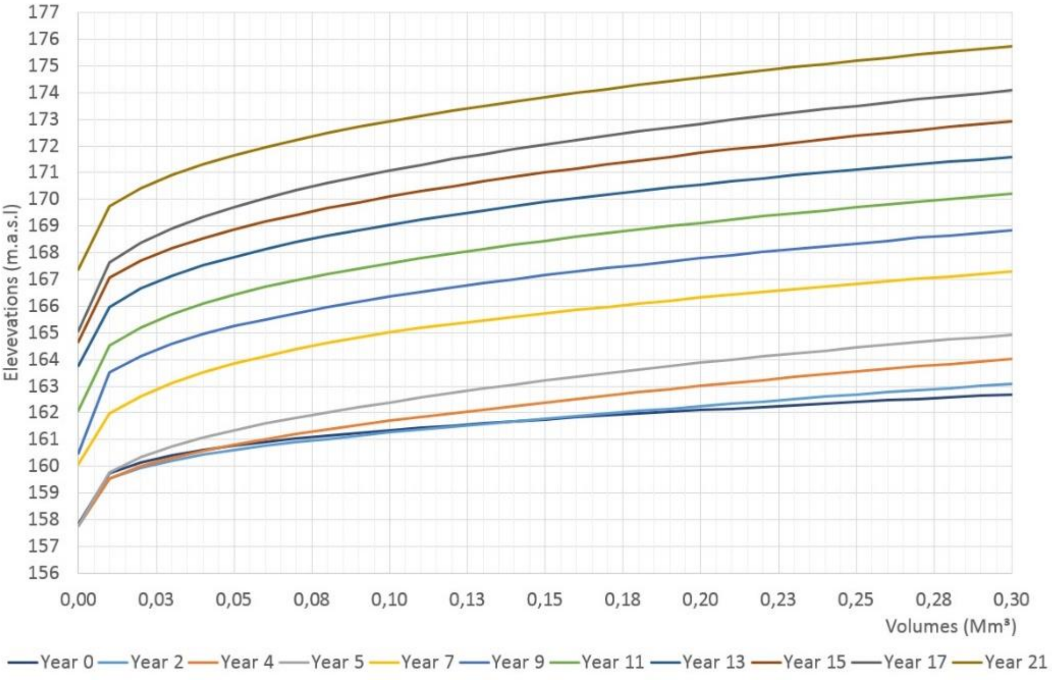

Figure 1 *Examples of a set of stage storage curves for a fictive tailings storage facility. Own elaboration.*

Having the set of stage storage curves defined for a period of time (fig 1), it is possible to carry out a regulation study of the TSF. For a specific volume and time, the water elevation, Z_{water}, can be obtained through a bilinear interpolation between the set of storage curves (fig 2).

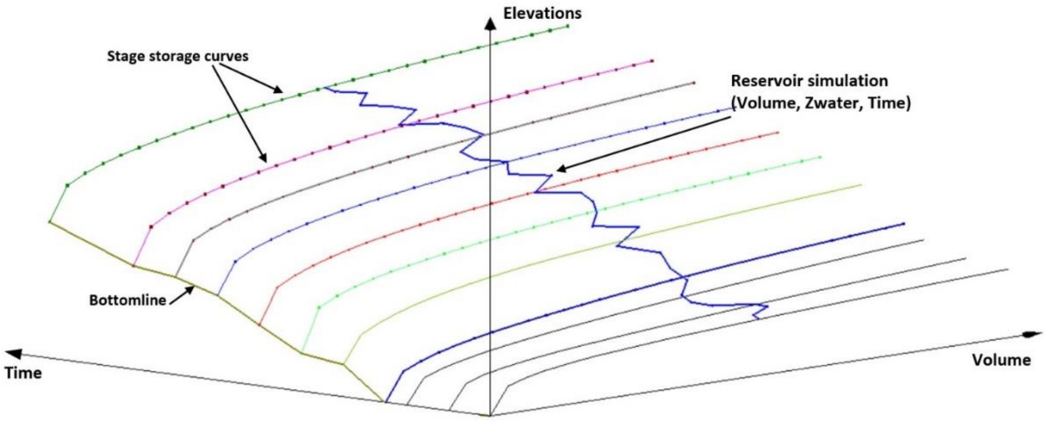

Figure 2 *Example of a reservoir simulation for a period of time for a fictive tailings storage facility. Own elaboration.*

Tailings Storage facility – Regulation study

Current Guidelines ICOLD (2011) indicate that the water balance for a TSF has to consider all potential inputs and outputs to ensure successful operation of the facility. These guidelines also mention that change of storage in the TSF is a potential threat and should be accounted for in the design. Furthermore, the TSF pool storage should be verified for rise in pool levels for change of storages and this can be done for selected intervals during the operation. Established minimum beach widths for each TSF shall be maintained during the any flood event.

The proposed method herein enables traditional reservoir regulation studies, or water balance modelling, for TSF. This study can be done for the TSF's entire lifetime rather than for selected time intervals as indicated in ICOLD (2011). The main objective of such a study consists of defining a design that, on one hand, contains an adequate amount of water to ensure satisfactory functioning of the TSF from a water quality perspective and, on the other hand, to ensure that maximum flood levels are not exceeded. A regulation study for a TSF should take into consideration several aspects such as all inflows and outflows, water levels, minimum operation levels, emergency spillway levels, beach width levels, maximum flood levels, dam crest elevations and the staging of the project (fig 3).

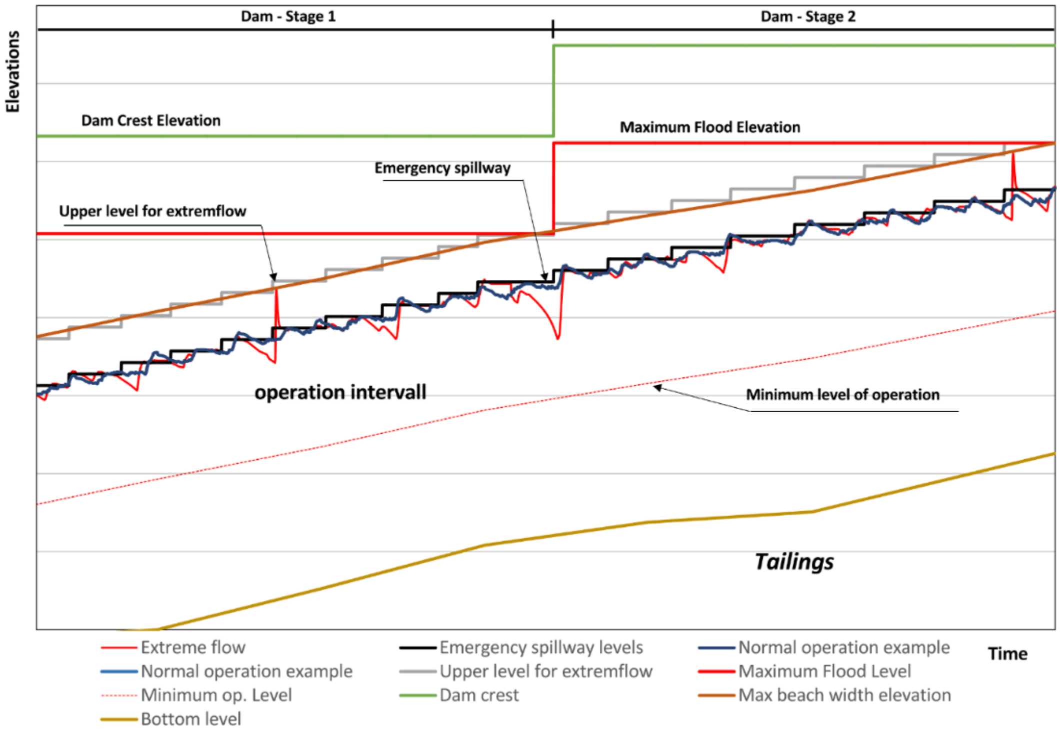

Figure 3 *Example of a design of a fictive tailing storage facility. Own elaboration.*

The construction of TSF is divided into stages and the maximum flood level is normally set to one level per each stage (fig 3). This maximum flood is however only reached in the end of each phase but the flood event can occur at any time during the projects lifetime. This means that the water operation levels could be tested for design floods a long its lifetime. This would generate the Upper Level for Extreme flow limit (fig 3), which should be compared, for instance, with the minimum beach width elevation. In the end of each stage the upper level of extreme flow would coincide with the maximum flood level. This information is important to consider when determining the planning of the different constructions stages of the dam.

What is an adequate interval of water volumes in the TSF, how shall it be determined and what limitations must be taken into consideration? The interval of volumes is the result from an iterative process between tailings management, water quality and water balances. The necessary water volumes could follow from a water regulation study based on limiting factors from the tailings management, which should be verified through detailed water quality analysis. For instance, the result from the water quality results adjustments might be necessary for water volumes and tailing disposal strategy. The disposal of tailings throughout time changes the geometry of the TSF, which for instance means that a constant water level would generate a loss of water volume for a certain time period. The authors have implemented this method in two projects in Sweden. Both studies included an analysis on possible future water operation levels considering probabilistic sampling of relevant parameters in the study. This applied for instance for different substances and for hydrological variations in the rainfall to evaluate the sensitivity of certain results such as water elevations and water volumes in the TSF. The analysis was useful to determine critical periods and levels for the operation.

The quantity of tailings and the amount of process water that reach the TSF has to be considered in the dynamic model. The production rates in the plant such as the amount of incoming product from the mine, percentage of ready product, which finally gives the amount of tailings, varies considerably. The quantity and characteristics of the tailings influence the water quality in the mine water system.

Water quality modelling

Water quality modelling of mine water systems is generally considered a challenging topic, both because of its technical complication and inherent uncertainties (Maest et al. 2005) but also because of natural phenomena and their variability.

A TSF or a clarification pond can be considered to work as a continuous stirred tank reactor (CSTR) in the ideal case. This means that the concentration of a substance is equal everywhere in the tank and that the effluent water has the same concentration.

The material balance equation for such a reactor looks like:

$$In + Prod = Out + Acc$$

This means that for a certain substance that what goes in (*In*) and what is produced (*Prod*, usually through chemical reactions) must equal what goes out (*Out*) and what is accumulated (*Acc*) in the reactor.

For substance A the equation can be written:

$$Q_0 \cdot C_{A,0} + r_A \cdot V = Q \cdot C_A + V \cdot \frac{dC_A}{dt}$$

where Q_0 and Q denote the volumetric flow in and out of the system respectively and $C_{A,0}$ and C_A the concentration of A in the inflow and outflow respectively. r_A is the reaction rate for the conversion of substance A and depends on the concentration of A if the chemical reaction is of the first order.

A study of the equation reveals that both the volume of the reactor (in this case the TSF, the clarification pond or for that matter a lake that receives effluent water) and the concentration of substance A influence the chemical processes in the system. Substance A can be involved in several reactions, for example ammonium (NH_4^+) is involved in nitrification (transformation of NH_4^+ by bacteria to NO_2^-/NO_3^-), volatilization ($NH_4^+$is transformed to gaseous ammonia which goes off to the air), ammonification (NH_4^+ is produced when organic material is decomposing) and also taken up as a nutrient by vegetation, plankton et cetera. All of these processes depend more or less on the concentration of ammonium in the water, which in turn depends on the volume of water. Considering this, it is evident that from a water quality modelling perspective it is of greatest importance that volumes of the different ponds in a mine water system and the water flows between them are as correctly estimated as possible. As seen above (fig 2 and fig 3) the water volume in a TSF can vary considerably over time. This also means that the volumes of other ponds and the flows in the system will vary and hence influence the chemical reactions. Many reaction rates do not only depend on concentrations of the reactants, other physical and chemical characteristics of the water such as e.g. temperature but also pH are important and change when flows are mixed or a flow is emitted into a lake.

An example from a study of an existing mine water system is shown (fig 4). In this case only inert suspended solids were modelled, but also from this rather simple case it is evident that the water volume in the TSF plays a major role for the overall cleaning performance of the system. In this case the production was fluctuating which has not been shown separately in the figure. The zero concentration values stem from production intermissions. It should be noted that the observed concentrations were analyzed in one single grab sample.

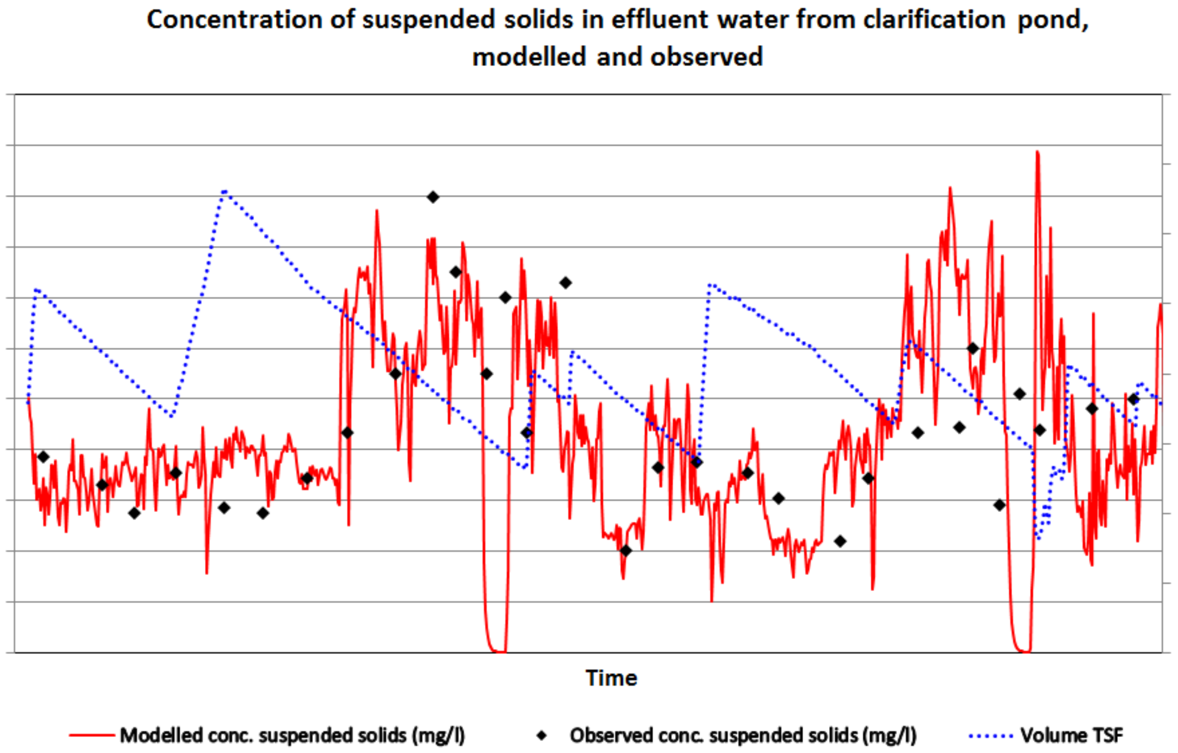

Figure 4 *Example of results from an actual project where the described method of combining detailed water regulation studies with water quality calculations.*

Results from another water quality example where the proposed method has been used is shown below (fig 5). In this case, the water quality modelling is more complex since it involves the nitrogen cycle with both chemical reactions and biological processes, but the production scenario in the mine is less varying than in the former case (fig 4). The nitrogen model was developed from a model presented by Chlot et al. (2011). The influence of the volume in the TSF can be seen even clearer in these model results, also in the recipient (fig 5), which is a lake of notable volume. For easily realized reasons these model results have not been validated.

Uncertainty in models that involve the natural environment is usually significant. Uncertainty can be divided into two types, variability, the uncertainty that comes from nature's true fluctuations and true uncertainty, uncertainty due to lack of knowledge. The size of both types must be quantified, but normally only true uncertainty can be reduced. Variability can best be described as the natural randomness, e.g. in weather conditions. Variability cannot be reduced by more extensive studies, but it is possible to describe better. Uncertainties that have to do with our knowledge and our models can in many cases be reduced by more studies or by using expertise. It is therefore important to follow up on model results to verify (or falsify) the model results but also to gain more knowledge of how the system works in order to continuously improve the models and the understanding.

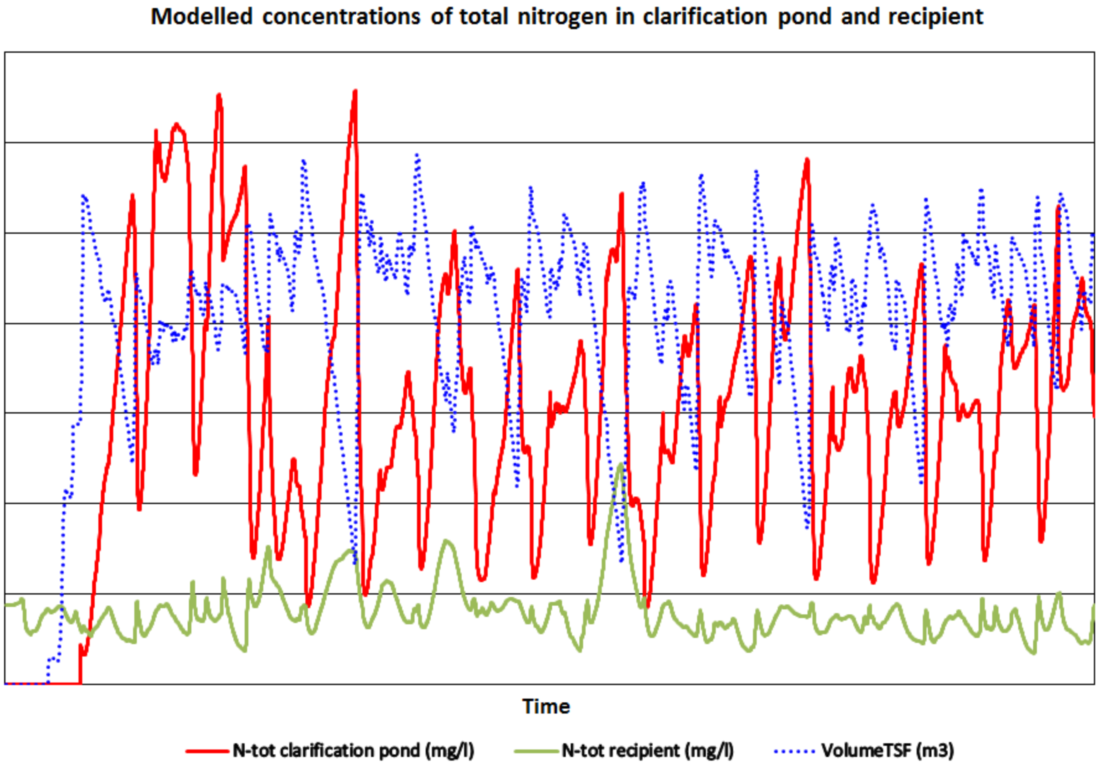

Figure 5 *Example of model results from a project aiming at evaluating the performance of the water system in a planned mine.*

Conclusions

The method developed by the authors consists of considering the tailings pond in the system as a conventional dam storage together with the clarification pond. The TSF is characterized using past and future geometries of the tailings storage, rather than using a mass transport approach, why dynamic hydraulic and water chemistry modelling of the whole system of ponds can be made and is necessary. The geometries of the tailings pond are based on the tailings disposal strategy, why the study includes relevant and limiting factors such as minimum required beach widths etc. and its variation with time. Future operation strategies can be tested and optimized; staging of dam raisings can be done considering the production in the plant, tailings management, water resources and water quality questions. Hence, future deficiencies in the system can be identified and efficient remedial measures proposed ensuring that environmental conditions and requirements are fulfilled.

This method has been tested in one existing and in one new project. From an environmental point of view, the water quality variations in the tailings pond can be determined adequately and related to parameters in the plant and hence how it influences the water quality in the clarification pond and the discharged waters. From a dam safety perspective, both operation rules and an extreme flood event may be “tested” throughout the entire lifetime of the project ensuring thus that spillways works adequately during normal operation and flood events. The interaction between the operation- and tailings disposal strategies is decisive since it affects beach slopes and hence the geometry of the pond.

The functioning of a tailings pond is a close interaction between tailings management, water quantities and water quality. Through an iterative approach, an optimum operation strategy can be determined. The dynamic modelling approach is useful to not only ensure that the environmental requirements are met but its level of detail also provides mining companies with a complete tool for holistic planning and design approach of sustainable mine water systems. Decision-making processes regarding issues such as predicting future needs for raisings of tailings dams, the effect of increased production rates, etc. can now be made environmentally sustainable. It is the authors opinion that an integrated operation strategy of tailings ponds is important to ensure that water volumes in the tailings pond is maintained within an acceptable interval in order to improve the control of concentrations of contaminants in the effluents.

Acknowledgements

We would like to thank the mining companies that supported this initiative and allowed us to develop integrated solutions for their projects.

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Reactive transport modelling based on velocity fields obtained on drill core scale

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Extended Abstract

The objective of the EU project *BioMOre* is the development of new technological concepts for in situ recovering metals from deep European Kupferschiefer deposits using controlled stimulation of pre-existing fractures in combination with in-situ bioleaching. Considerable parts of the project are leaching experiments on lab scale and on small field scale at a selected location in an existing copper mine, as well as the related reactive transport modelling tasks including the required backcoupling from chemical reactions on the hydrodynamics as well as the upscaling. These tasks shall assist in the optimization of the bio-leaching efficiency, stimulating processes, as well as the environmental impact and sustainability assessment. Here we introduce our most recent technical advancement. It allows us to accomplish two tasks in one line of action: The extraction of effective hydrodynamic parameters in 3D for downstram modelling, and the upscaling from molecular process observations to reactive transport simulations on drill core scale.

For more than a decade a spatiotemporal visualization tool for transport process observations in dense material by means of PET (positron emission tomography) was developed [1-5]. Such quantitative GeoPET images are exceptionally sensitive to displacements of pico molar tracer quantities detected within 1 mm grids on laboratory/drill core scale. Now we reached a strategic milestone: A custom made image analysis algorithm is capable of quantitatively extracting velocity and porosity fields from such GeoPET image time series, even if the 4D image information includes discontinuous flow patterns (due to bottle neck effect related detection limits) and localized image artifacts. We present our approach with the aid of a) the data set with which the algorithm was validated, and b) provide an outlook for its application in the context of this EU project: the bio-leaching of Kupferschiefer.

From an observed fluid flow process in a dense core material by means of GeoPET (Fig. 1 left) the effective porosity and velocity field is extracted by our image analyis algorithm and this data is used in a forward numerical transport simulation and compared with the original fluid flow process (Fig. 1 right). Next steps will be the evaluation of non-reactive flow process observations in fractured calciferous sandstone from the Kupferschiefer ore deposit (Fig. 2), and the respective porosity and velocity field extraction for 3D reactive transport modelling in fracture and porous matrix by means of iCP [6] - an interface coupling the finite element based code COMSOL Multiphysics® with the geochemical code PhreeqC.

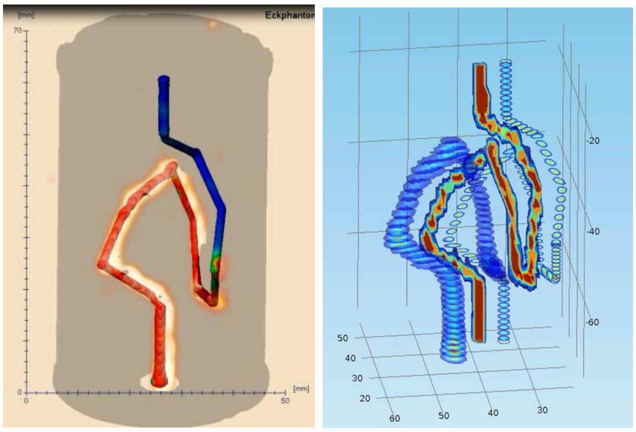

Fig. 1, left: *Snapshot of a visualized fluid transport inside a tube embedded in a cement core by means of GeoPET;* ***right:*** *From right to left: extracted absolute value of v(x,y,z) and extracted effective porosity n(x,y,z); simulated c(x,y,z,t) as obtained from a model with an unstructured grid. The observed and modelled transport processes agree well. The 3D velocity field extraction from experimental observations is therewith validated.*

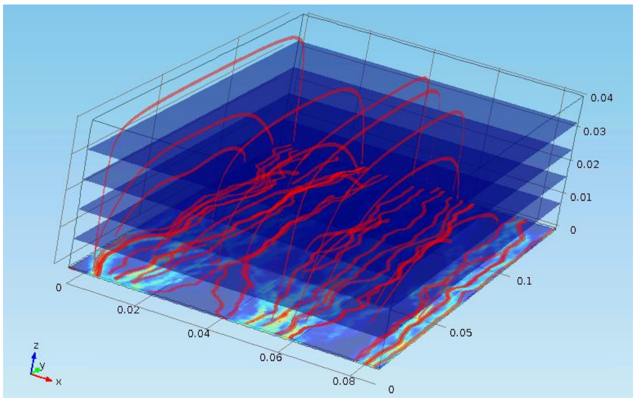

Fig. 2: *Simulated velocity distribution (rainbow colour) and flow lines (red lines) inside a heterogeneous fracture (bottom) and adjacent porous calciferous sandstone (block above fracture): Outlook: Effective fracture velocities extracted from flow monitoring in fractured cores will be used in a 3D reactive transport model for estimating e.g. the effect of porosity/permeability change due to calcite dissolution and gypsum precipitation.*

Key words: 4D image analysis, reactive transport modeling, in-situ leaching

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AcquaTailings: A Tool for Streamlining Mining Water Budget

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Abstract

Acquatailings is a Graphical User Interface (GUI) tool developed in-house by GeoHydroTech Engineering to streamline the assessment and prediction of mining water budgets in tailing dams. It enables the quick examination of the sensitivity of the results to the various input variables used in this type of study, such as the physical characteristics of the watershed and of the spillway, dry/bulk density of the mined material and the solid rate of the processed pulp, as well as water fluxes captured from adjoining streams or lost through infiltration.

Acquatailings is capable of resolving monthly predictions of several mining water parameters that are important in the design, construction schedule, and operation of tailing dams. These variables include: the dam water level, flooded area, water volume, storage capacity, water deficit, meteorological balance, water/sediment occupation, and the spillway water volume, as well as a three-dimensional, cross-sectional illustration of the water level in the dam. This tool also enables the visualization of other graphical outputs, such as normal intervals for precipitation and evaporation, and elevation-area-volume plots.

Simulations are obtained using three climatic scenarios that span the entire spectrum of likely environments that this mining site may observe: dry threshold, normal, and wet threshold. The former scenario yields a combination of reduced monthly precipitation and enhanced monthly evaporation, albeit at the limit of what can be climatologically considered normal. The latter scenario is created with the opposite setup (increased monthly precipitation and suppressed evaporation), whereas the normal scenario uses monthly median values for these variables.

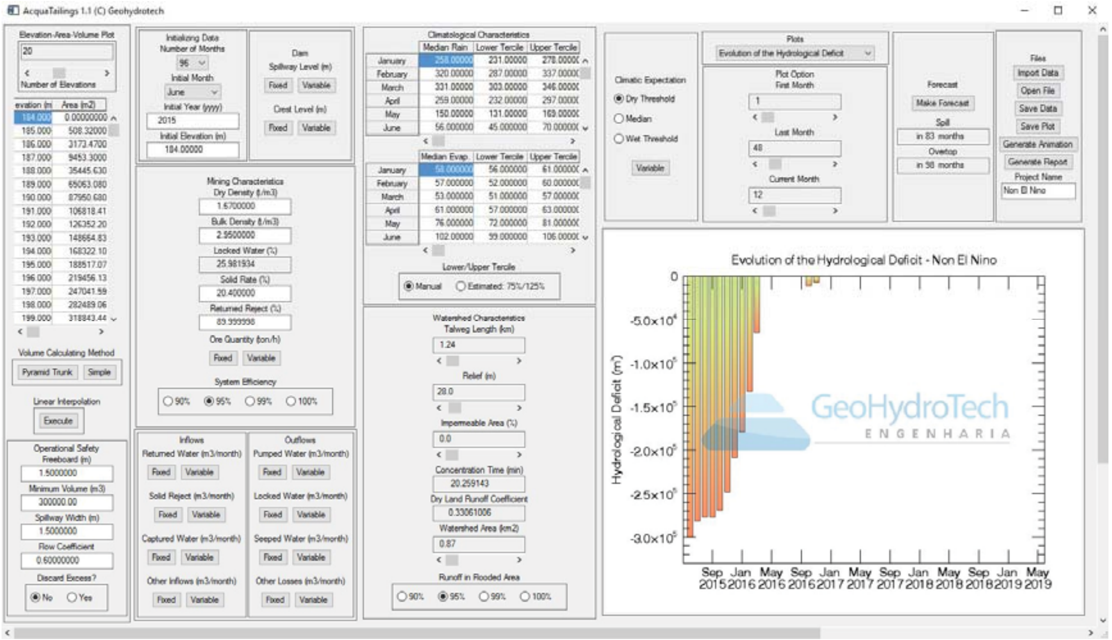
The capabilities of this new tool are showcased in this study, using a dataset from a mining site in the northern part of Brazil. The region is characterized by a tropical savanna climate, with warm temperatures year-round, abundant annual rainfall, and pronounced wet and dry seasons. The precipitation in the region is also heavily influenced by cycles of the El Niño Southern Oscillation. Thus, Acquatailings was used to enable the proper long-term planning of mining water budgets for a tailings dam in the aforementioned region, ahead of the current 2015-2016 El Niño cycle.

Key words: mine water, simulation, tools, water budgets, climate

Introduction

Water balance studies are a fundamental step in the design, construction schedule, and operation of the tailings management facilities used in the mining industry. They are paramount not only to determine the stability of the balance in a given site, but they also allow for project managers to better understand the likelihood of scenarios where water scarcity or excess can develop. According to Papageorgiou et al. (2003) the vast majority of failures in tailings dams during the 1980s and early 1990s were a result of inappropriate water management. Consequently, examining the volatility of water budget results to the various contributing factors used in their calculation is essential to fully grasp the range of conditions for which a site manager must prepare, such as variations due to climatic oscillations.

In order to expedite the sensitivity of our hydrological balance studies to various mining and hydrometeorological conditions observed at tailing dams, GeoHydroTech Engineering spearheaded a project to develop, in-house, a new software tool in the form of a user-friendly Graphical User Interface (GUI): *AcquaTailings*. This tool is useful to assess the uncertainty of the results due to climatic variation and unmeasurable empirical parameters, such as the system's efficiency and runoff coefficients. This software was designed to quickly simulate monthly forecasts for a myriad of mining water variables, such as the dam's water level, flooded area, and water volume, as well as its storage capacity (for sediment and water), and the reservoir's proportional occupation by water and sediment. It also calculates any potential water deficits at the dam site, the meteorological balance (i.e. the total monthly natural gain/loss of water at the reservoir solely due to precipitation and evaporation), and any volume of water released through a spillway. *AcquaTailings* is capable of producing an animation illustrating a three-dimensional cross-section of the water level in the dam, as well as the normal intervals for precipitation and evaporation, and elevation-area-volume plots. Figure 1 displays a picture of the *AcquaTailings* GUI workspace.



Elevation-Area-Volume Plot: 20

evation (m	Area (m2)
184.000	0.00000000
185.000	508.32000
186.000	3173.4700
187.000	9453.3000
188.000	35445.630
189.000	65063.080
190.000	87950.680
191.000	106818.41
192.000	126352.20
193.000	148664.83
194.000	168322.10
195.000	188517.07
196.000	219456.13
197.000	247041.59
198.000	282489.06
199.000	318843.44

Operational Safety
Freeboard (m): 1.5000000
Minimum Volume (m3): 300000.00
Spillway Width (m): 1.5000000
Flow Coefficient: 0.60000000
Discard Excess? ● No ○ Yes

Initializing Data
Number of Months: 96
Initial Month: June
Initial Year (yyyy): 2015
Initial Elevation (m): 184.00000

Mining Characteristics
Dry Density (t/m3): 1.6700000
Bulk Density (t/m3): 2.9500000
Locked Water (%): 25.981934
Solid Rate (%): 20.400000
Returned Reject (%): 89.999998
System Efficiency: ○ 90% ● 95% ○ 99% ○ 100%

	Median Rain	Lower Tercile	Upper Tercile
January	258.00000	231.00000	278.0000
February	320.00000	287.00000	337.0000
March	331.00000	303.00000	346.0000
April	259.00000	232.00000	297.0000
May	150.00000	131.00000	169.0000
June	56.000000	45.000000	70.00000

	Median Evap.	Lower Tercile	Upper Tercile
January	58.000000	56.000000	61.00000
February	57.000000	52.000000	60.00000
March	53.000000	51.000000	57.00000
April	61.000000	57.000000	63.00000
May	76.000000	72.000000	81.00000
June	102.00000	99.000000	106.0000

Lower/Upper Tercile: ● Manual ○ Estimated: 75%/125%

Watershed Characteristics
Talweg Length (km): 1.24
Relief (m): 28.0
Impermeable Area (%): 0.0
Concentration Time (min): 20.259143
Dry Land Runoff Coefficient: 0.33061006
Watershed Area (km2): 0.87
Runoff in Flooded Area: ○ 90% ● 95% ○ 99% ○ 100%

Climatic Expectation: ● Dry Threshold ○ Median ○ Wet Threshold

Plots: Evolution of the Hydrological Deficit
Plot Option
First Month: 1
Last Month: 48
Current Month: 12

Forecast
Spill: in 83 months
Overtop: in 98 months

Project Name: Non El Nino

Figure 1 *Screen Capture of the AcquaTailings Graphics User Interface.*

Data & Methodology

The method for calculating the bulk of the prognostic variables in *AcquaTailings* is fundamentally based on the continuity equation. As such, the reservoir's water budget is calculated as:

$$V_f = V_i + C_1 \cdot \frac{P \cdot A_D}{\Delta t} + C_2 \cdot \frac{P \cdot A_F}{\Delta t} + Q_{RW} + Q_{RJ} + Q_{NW} + Q_{OG} - Q_{PW} - Q_{OS} - Q_{LW} - \frac{E \cdot A_A}{\Delta t} - Q_{OL}$$

Where:
V_f = final volume at the beginning of each month (m^3);
V_i = initial volume at the end of each month (m^3);
C_1 = runoff coefficient over dry land;
C_2 = runoff coefficient over flooded areas;
P = monthly precipitation (mm);
A_D = dry watershed area (m^2);
A_F = flooded watershed area (m^2);
Q_{RW} = water flowing back into the reservoir (m^3/month);
Q_{RJ} = solid reject flow into the reservoir (m^3/month);
Q_{NW} = new water captured into the reservoir (m^3/month);
Q_{OG} = other inflows (m^3/month);
Q_{PW} = flow of water pumped out of the reservoir to the mining plant (m^3/month);
Q_{OS} = outflow of water due to seepage (m^3/ month);
Q_{LW} = water flow locked in the reject (m^3/ month);
E = monthly evaporation (mm); and
Q_{OL} = other outflows (m^3/month).

The simulations presented in this study are based on a tailings dam built for a copper mining site in the Brazilian State of Pará. This mining site, developed and operated by Avanco Resources Limited, and its watershed are characterized by the following general conditions:

- Dry Density: 1.67 t/m^3
- Bulk Density: 2.95 t/m^3
- Solid Rate: 20.4%
- Returned Reject: 90%
- Watershed Area: 0.87 km^2
- Talweg Length: 1.24 km
- Relief: 28 m

For this site, we chose to make use of monthly precipitation and evaporation data for the city of Marabá, Brazil (obtained from the Brazilian Meteorology National Institute - INMET) as it meets the requirements of a reference station that can be used for climatic studies (World Meteorological Organization 1986). The Oceanic Niño Index (ONI) was obtained from NOAA's Climate Prediction Center to define the periods of El Niño. Warm episodes of the El Niño Southern Oscillation (ENSO), commonly known simply as El Niño, are characterized by ONI values greater or equal to 0.5 ºC (Kousky and Higgins 2007). The monthly precipitation and evaporation data were then divided into two groups. The El Niño dataset contains solely the monthly data during periods when that climatic phenomenon was identified in the ONI dataset. The other group, labeled "Non El Niño", contains the remainder of the dataset. Three statistical parameters were calculated for each of these two data groups to define the range of most likely monthly meteorological conditions: the median, the lower tercile, and the upper tercile. The latter two parameters represent the limits of what could be considered climatologically normal to expect in an El Niño vs. a non El Niño month. In addition to developing forecasts using the median precipitation and evaporation during El Niño and non El Niño years, simulations were also made using a combination of the lower tercile of precipitation and upper tercile of evaporation (dubbed the "dry threshold"), as well as a combination of the upper tercile of precipation and lower tercile of evaporation (hereby named "wet threshold").

The statistical results for the precipitation and evaporation data are presented, respectively, in Tables 1 and 2. In broad terms, Table 1 shows that El Niño years in the region of Marabá are characterized by lower precipitation than non El Niño years, with statistically significant differences ($p < 0.05$) observed between March and June, as well as in December. Trends in the evaporation data (Table 2) are not so obvious, but statistically significant differences are seen during the peak rainy months of March and April, both of which display higher evaporation rates in the region during El Niño years.

Table 1 *Precipitation climatology (in mm) for Marabá, Brazil between 1973 and 2011 during El Niño years and during years without El Niño.*

Month	Lower Tercile		Median		Upper Tercile	
	El Niño	Non El Niño	El Niño	Non El Niño	El Niño	Non El Niño
Jan	230	231	248	258	285	278
Feb	266	287	282	320	319	337
Mar	234	303	246	331	251	346
Apr	170	232	184	259	193	297
May	56	131	67	150	98	169
Jun	12	45	19	56	42	70
Jul	12	15	19	19	25	26
Aug	15	14	25	24	32	26
Sep	46	39	57	46	64	61
Oct	60	80	80	92	100	120
Nov	109	132	133	147	150	193
Dec	170	191	184	213	189	231

Table 2 *Evaporation climatology (in mm) for Marabá, Brazil between 1973 and 2011 during El Niño years and during years without El Niño.*

Month	Lower Tercile		Median		Upper Tercile	
	El Niño	Non El Niño	El Niño	Non El Niño	El Niño	Non El Niño
Jan	58	56	60	58	63	61
Feb	54	52	55	57	59	60
Mar	57	51	58	53	61	57
Apr	67	57	70	61	74	63
May	74	72	78	76	83	81
Jun	98	99	99	102	105	106
Jul	119	118	123	124	132	134
Aug	123	119	131	129	138	142
Sep	109	115	110	124	130	136
Oct	92	95	94	102	104	111
Nov	78	73	82	78	83	85
Dec	65	61	68	64	72	67

In this study we showcase three of the products generated by *AcquaTailings*: The Reservoir's Water Level, the Reservoir's Water Volume, and the Reservoir's Occupied Volume. These products will be initially assessed in a situation when no additional new water is captured from an adjoining stream into the reservoir (i.e. all water in the reservoir is the result of the rainfall and runoff). Five-year forecasts will be generated under El Niño and non-El Niño meteorological conditions for the dry and wet thresholds. Based on these results, a schedule for capturing new water from the stream is proposed and a new set of forecasts is generated.

Results

Figure 2 reveals the monthly forecasts generated by *AcquaTailings* for the Water Volume (in cubic meters) inside the tailings dam reservoir. The top panel shows the 5-year simulation using the dry threshold of El Niño years, which corresponds to the driest scenario in our study. It reveals a grave drought situation in the reservoir, which displays significant water accumulation only during the first half of 2016. Using the dry threshold for Non El Niño years (second panel), a slightly better picture emerges, with water accumulating during the wet season and depleting during the dry season in the middle of each calendar year. The third panel exhibits a marginally improved condition for the El Niño wet threshold, albeit one where water is still fully depleted in the reservoir during the first few dry seasons. Lastly, using Non El Niño wet threshold conditions, the reservoir manages to store water starting in January 2016, and peaking at $1.5x10^6$ m^3 of water at the of the simulation in May 2020.

Figure 3 presents the same set of simulations as the previous figure, but displays the monthly water level. In the absence of any water, the values represent the reservoir floor level (which will progressively rise as the tailings are deposited each month). The red line denotes the elevation of the dam's crest, which undergo two planned heightening construction phases, while the yellow line corresponds to the level at which water from the reservoir begins to flow out through the spillway. It reveals that water levels remain safely under the spillway level in all four simulations, the closest situation being observed in mid-2018 and mid-2020 using the wet threshold of Non El Niño years (bottom panel).

The percentage volume occupation of reservoir by tailings deposits and water is presented in Figure 4. It unveils a time-lapse forecast of the proportional occupation of the reservoir. It is important to keep in mind that every time the dam undergoes a heightening period, the reservoir capacity increases, driving downward the reservoir's occupation percentage values. Once again, in the top panel (El Niño dry threshold) we observe a situation of water scarcity that would, in practice, not allow the mining plant to operate. The second and third panels once again illustrate when the reservoir's water is depleted whilst the tailings accumulation forecasts do not change (even though, in practice, exhausting the water supply would effectively shut down the plant and cease the tailings deposits in the reservoir). Only in the wet threshold for Non El Niño years (bottom panel) we observe a situation where water is consistently present and the reservoir's capacity is near 100% at the end of the simulation.

The aforementioned results reveal the necessity of developing a new water capture plan, from an adjacent stream into the reservoir, in order to maintain a volume of water that can safely enable the continuous operation of the mining plant under all potential climatic scenarios simulated here. An examination of the meteorological balance product in *AcquaTailings* (not shown), indicated that the period from June to November of each year is the most conducive for natural water losses in the reservoir. Thus, we proposed the monthly capture of 40000 m^3 of new water from the adjoining stream during these 6 months for the first 3 years of operation of this tailings dam.

Figure 5 presents the same product displayed in Figure 4, but the monthly forecasts are obtained while incorporating the proposed plan for new water capture. The top panel of Figure 5 (El Niño dry threshold), which represents the case where the hydrological setup of the reservoir is most strained, demonstrates that the suggested plan is sufficient to maintain some water stored in the reservoir even under this difficult scenario. Conversely, by looking at the simulation that uses the wet threshold of Non El Niño years, the proposed schedule of new water capture maintains the water level just below full capacity during its projected peak occupation months (January 2018 and April 2020). Therefore, one can conclude that this would be an ideal plan to prepare for the entire array of climatic conditions under which the tailings dams at this site may need to be ready to operate.

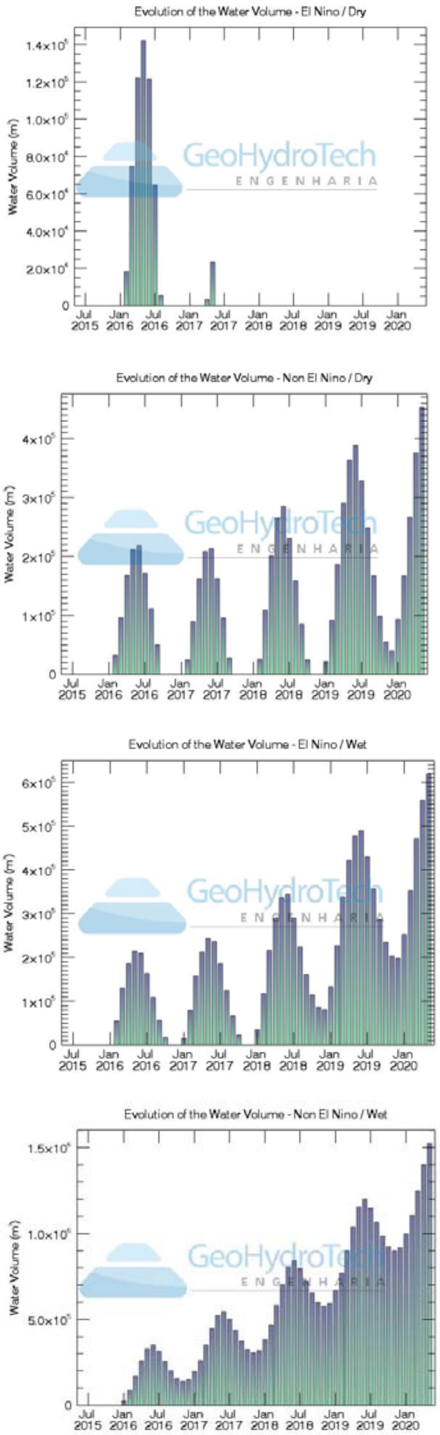


Figure 2 Monthly forecasts for the Reservoir's Water Volume under 4 scenarios (top to bottom): Dry Threshold in El Niño Years, Dry Threshold in Non El Niño Years, Wet Threshold in El Niño Years, and Wet Threshold in Non El Niño Years.

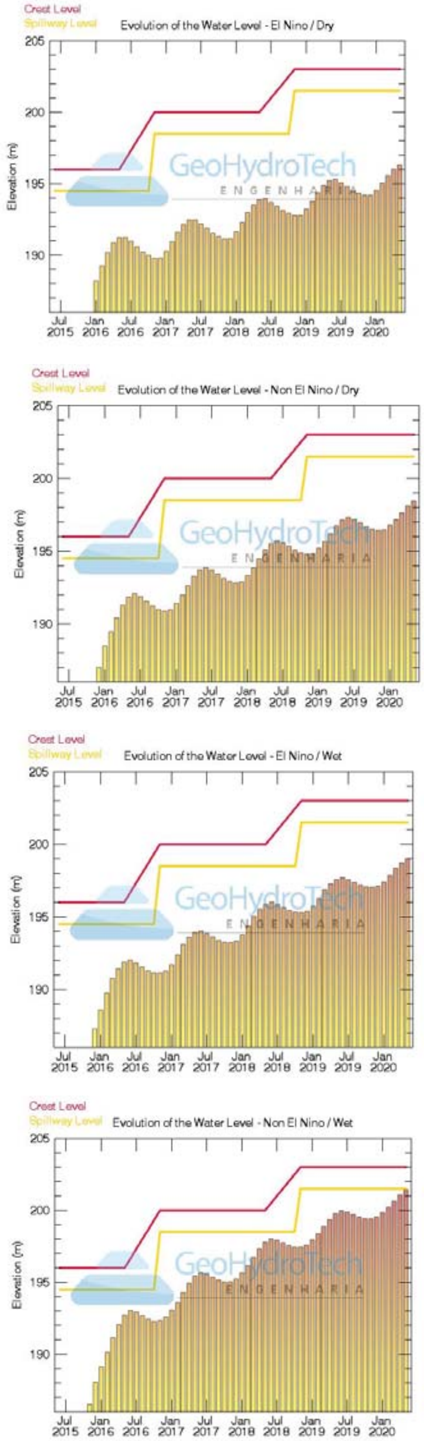


Figure 3 Monthly forecasts for the Reservoir's Water Level under 4 scenarios (top to bottom): Dry Threshold in El Niño Years, Dry Threshold in Non El Niño Years, Wet Threshold in El Niño Years, and Wet Threshold in Non El Niño Years. The red line represents the dam's crest level, and the yellow line represents the spillway base level.

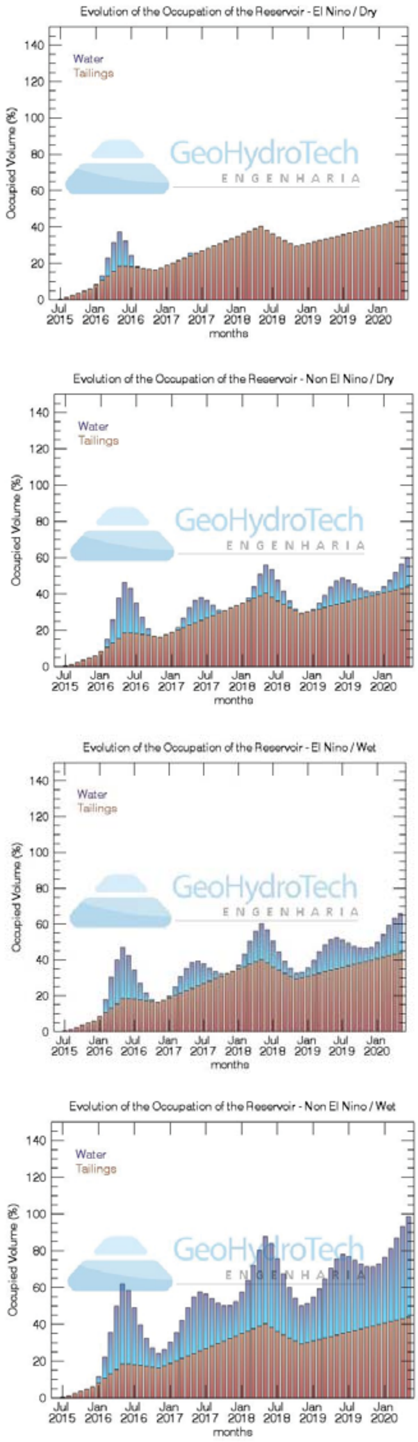


***Figure 4** Monthly forecasts for the Reservoir's Occupied Volume under 4 scenarios (top to bottom): Dry Threshold in El Niño Years, Dry Threshold in Non El Niño Years, Wet Threshold in El Niño Years, and Wet Threshold in Non El Niño Years. The brown shading indicates percentage occupied by tailings, and the blue shading indicates the percentage occupied by water.*

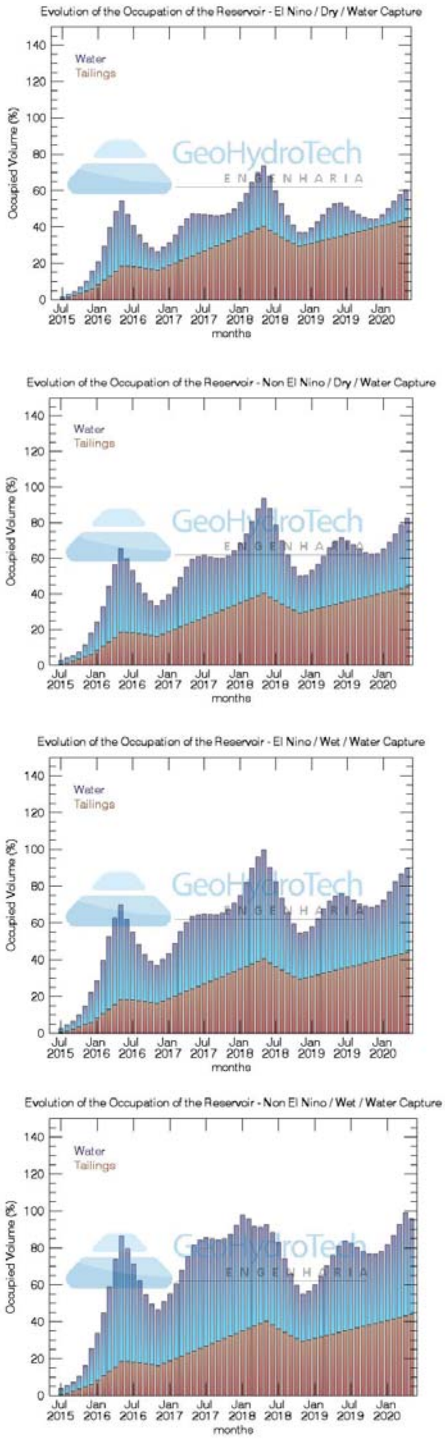


***Figure 5** Same as Figure 4, but including a proposed schedule of new water capture from an adjoining stream into the reservoir.*

Conclusions

Acquatailings is a tool newly developed by GeoHydroTech to produced monthly forecasts of mining water parameters that are useful in planning and operating tailings dams. The usefulness of this tool is showcased for a tailings dam located in the northern part of Brazil, a region known to be significantly impacted by the climatic cycles of ENSO. Warm ENSO episodes (i.e. El Niño) are characterized by below normal precipitation during the rainy season at this tailings dam site. Consequently, we examined the susceptibility of mining water budgets at this location under four climatic scenarios: El Niño dry threshold, Non El Niño dry threshold, El Niño wet threshold, and Non El Niño wet threshold.

The results of this study reveal that this tailings dam, as it was designed, would not be able operate without the capture of a new water. While the dry and wet threshold represent the upper and lower limits of what could be considered climatologically normal in a region, observing five consecutive years of El Niño-like conditions is far less reasonable and, as such, the El Niño simulations represent a more extreme situation under which this mining site may need to operate. Nonetheless, examining these four scenarios provide a safe margin for the mining operator to plan their production. The simulation for the El Niño dry threshold produced the hydrologic setup with greatest water scarcity, whereas the Non El Niño wet threshold generated the environment with greatest abundance of water.

Using the reservoir water volume, water level, and occupied volume products, it was possible to determine that an adequate water budget balance can be reached by capturing 40000 m^3 of new water per month, in the first three years of the simulation, between the months of June and November. The forecasts obtained using this proposed water capture plan was capable of providing a constant supply of water at the reservoir while maintaining the water level within safety regulations (i.e. beneath the spillway base level).

One of the other capabilities of *Acquatailings* that was not explored here, is the ability to quickly determine the sensitivity of the results to various unmeasurable empirical parameters used in the forecast, such as the efficiency of the system, the runoff coefficient in flooded areas (which is impacted by the uneven distribution of tailings and the presence of dead pools). The usage of all features in *AcquaTailings* enables the time-efficient development of sound hydrological balance studies. Furthermore, *AcquaTailings* offers a tool to quickly obtain a better alternative to deterministic studies that are solely based on mean values for all the various components used in this type of study.

Acknowledgements

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Reactive Transport Modelling of the contaminant release from Uranium Tailings using PhreeqC/Excel-coupling

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Abstract

Between the early 1950's and 1990, uranium mining and processing produced large quantities of radioactive mill tailings in Eastern Germany. Presently, the tailings sites are remediated according to the strategy of dry in-situ stabilization. Due to recontouring of the tailings, pore water is squeezed out resulting in a significant contaminant release. A multi-layer type soil cover will finally minimize the water infiltration, gas transport and seepage in the future.

The release of contaminated seepage water into ground and surface waters cannot be completely avoided due to lack of base sealing. For planing and monitoring of the remediation works geochemical models are essential in order to evaluate the long-term development of the contaminant release and to forecast future challenges for the water management and treatment at the site. In fact, the geochemical conditions within the tailings are highly complex due to the history of processing and discharge regime which resulted in a large heterogeneity of hydraulic and geochemical properties within the tailings impoundments.

This paper summarizes the current state of the development of a geochemical transport model in order to identify the geochemical processes responsible for the contaminant release in seepage water based on available lab-test data. For this purpose a 1-dimensional multi-component transport model was developed using the hydro-geochemical transport code PhreeqC and the spreadsheet program Microsoft Excel®. The coupling was realized using a Microsoft COM (component object model) enabling the simple manipulation of the PhreeqC input via Visual Basic for Applications (VBA) macro. Two infiltrative column experiments with tailings material from the tailings management facility (TMF) Culmitzsch (Seelingstädt) were used to validate the model approach by computing the effluent water composition of the columns.

Key words: uranium tailings, transport modeling, PhreeqC, column experiments, oxygen diffusion

Introduction

In 1990, the uranium production of SDAG Wismut in Eastern Germany was stopped. 45 years of uranium mining left behind legacies of ore mining and milling. Between 1960 and 1990, ores extracted in the Thuringian mining district were hydrometallurgically processed in the uranium processing facility at Seelingstädt. The tailings were disposed in the former open pits of Trünzig and Culmitzsch. In the course of the remediation of the tailings management facilities (TMF) at the Seelingstädt site a dry in-situ stabilization of the about 100 Mm³ tailings material is underway. An essential part of this remediation strategy refers to the catchment and treatment of contaminated pore and seepage water, which also represents a precondition for the geotechnical stabilization.

For planning and monitoring of the remediation activities geochemical models are necessary. They are used to understand the complex geochemical processes within the tailings body and to forecast the long-term development of contaminant release from TMF seepage water and thus the necessity of water catchment and treatment.

The structure of the tailings ponds is very complex resulting in heterogeneous hydraulic properties based on the tailings discharge technology. Moreover, various geochemical processes interact with each other depending on the small-scale variations of the environmental conditions. Several 2D/3D reactive transport models have already been developed on behalf of WISMUT. However, their complexity limits the detailed understanding of single processes responsible for the contaminant release. Therefore, the applied model should be kept as simple as possible with the main focus on the geochemical processes while reducing the description of hydraulic conditions to the essential aspects.

Thus, a simple 1-dimensional geochemical transport model was developed to describe the contaminant release and transport in the vadose zone of the tailings material. The model implementation comprises the coupling of the hydrochemical transport code PhreeqC (Parkhurst and Appelo, 1999) with the spreadsheet program Microsoft Excel®. In order to calibrate this model approach, data from infiltrative column experiments in the laboratory were used. With these experiments, processes of the long-term contaminant release from tailings material of the TMF Culmitzsch were examined.

Site characterization

The TMF Culmitzsch comprises two tailings ponds A and B occupying 158.1 ha and 75.8 ha, respectively (Fig. 1). The total volume of the tailings amounts to 61.3 Mm³ for pond A and 23.6 Mm³ for pond B with corresponding maximum thicknesses of 72 m and 68 m.

***Figure 1** Tailings management facility (TMF) Culmitzsch, Seelingstädt, Germany (November 2015).*

The discharge of tailings from the uranium processing facility Seelingstädt into the TMF started in 1967, immediately after termination of the uranium ore mining in the Culmitzsch open-pit. The dam structures were already constructed during the ongoing open-pit mining operation before tailings discharge.

Tailings pond A was filled with silicate tailings from the sulfuric acid ore processing via annular discharge pipes. The discharge was accomplished from certain points along the pipes both into the pond interior as well as in direction of the south/southeast dam. Due to a changing discharge regime and the relocation of the discharge points during the operation period, a strong lateral and vertical differentiation in soil-physical and structural composition of the disposed tailings resulted over time.

In the tailings pond B, the residues of soda-alkaline uranium ore leaching were disposed. Later on in the operation period, lime mud from the water treatment was disposed in the northern part of pond B. The discharge of tailings was finished in 1991.

Since 1991, remediation activities have been conducted at the TMF Culmitzsch with the aim of dry in-situ stabilization of the entire impoundment. The applied remediation technology comprises an interim cover, geotechnical stabilization as well as contouring and covering of the facility with material from nearby mine dumps. Contaminated pore water and seepage water is collected and treated.

Methodology of model development

Experimental data basis

Two column experiments were conducted for the duration of roughly one year using tailings material from drillings in tailings pond A (CA68) and pond B (CB36-8). Mixed material from different depths was filled in PVC tubes (40 cm high, 19 cm in diameter) and compacted in layers. Once a week, the columns were irrigated on the top with 0.5 l infiltration water (CA68: distilled water, CB36-8: seepage water from dump material used for contouring of the TMF Culmitzsch) over a period of 24 h. Bulk samples of the column effluents were analyzed every two weeks. The experiments were conducted at room temperature, and the columns remained open in contact with the atmosphere in order to assess the effects of oxygen diffusion on geochemical reactions in the tailings material. With an initial water saturation of 36.7 % the tailings of column CA68 were unsaturated whereas column CB36-8 showed almost saturated conditions. In the latter case, a residual gas proportion of 2 % of the total porosity was assumed for modelling. Table 1 summarizes the main soil physical parameters of both column experiments.

***Table 1** Soil physical parameters of the column experiments CA 68 and CB 36-8.*

Parameter	Units	CA 68	CB 36-8
Material level in column	cm	38.5	31.0
Soil type (German class.)	-	Ss	Su3
Density (wet)	g/cm³	1.554	2.118
Density (dry)	g/cm³	1.374	1.762
Initial water saturation	-	0.367	0.98
Total porosity	%	49.1	35.6
Gas phase	%	31.1	0.7
Mobile water	%	9.2	17.4
Adhesive water	%	8.8	17.5
Immobile water	%	6.6	14.0
Dead water	%	2.4	3.5
Duration of experiment	days	336	315
Infiltration water	-	Distilled water	Dump seepage water
Mean drainage	l/week	0.447	0.490
Permeability	m/s	2.03E-07	2.76E-07

Solid samples of the tailings underwent full geochemical analyses using ICP-OES and XRD in order to determine the initial mineral phase assemblage (Tab. 2).

***Table 2** Mineral phase assemblage calculated from geochemical analyzes and identified by [a]XRD.*

Mineral phase	CA68 [ppm]	CB36-8 [ppm]	Mineral phase	CA68 [ppm]	CB36-8 [ppm]
Albite [a]	10 000	10 000	Magnetite [a]	10 000	-
Anorthite [a]	10 000	10 000	Manganite	213	619.8
Barite	143	565.9	Millerite	60.0	229.3
Calcite *	40 096	60 753	Pyrite *	12 332	618
Chalcopyrite	367	-	Pyrolusite	105	306.4
Chlorite [a]	40 000	70 000	Quartz [a]	500 000	370 000
Dolomite *	9 033	110 641	Rhodochrosite	278	810
Galena	31	-	Siderite *	21 698	52 581
Gibbsite	11 828	22 900	Smithsonite	41	-
Greenockite	0.8	-	Sphalerite	144	-
Gypsum	14 089	39 889	Strontianite	71	164.4
Iron hydroxide (amorph.)	17 000	28 417	Uraninite	29.6	35.4
Kaolinite [a]	20 000	20 000			

**kinetic approach*

The column effluent immediately collected after the first irrigation step is assumed to represent the initial pore water composition in the tailings material. Before modelling, the chemical composition of the initial pore water was balanced out using PHREEQC (Tab. 3).

***Table 3** Initial aqueous species concentrations in the tailings pore water and infiltration water (IW) [mg/l].*

Species	CA68	CB36-8	IW*	Species	CA68	CB36-8	IW*
Temp [°C]	22	-	-	As	0.068	0.220	0.005
pH	8.2	8.4	7.85	Ba	0.026	0.029	0.031
Eh [mV]	370	440	525	Cd	0.002	0.002	0.001
$O_{2(aq)}$	7.03	9.20	8.77	Cu	0.035	0.027	0.020
Na	4 290	5 656	14	Fe	0.10	0.039	0.070
Mg	1 235	549	120	Mn	14.17	0.632	0.681
K	126	129	3	Ni	1.04	1.215	0.020
Ca	445	461	180	Pb	0.02	0.020	0.020
SO_4	13 370	12 872	490	Si	5.30	3.864	3.203
Cl	1 121	1 379	16	Sr	6.05	5.336	0.187
HCO_3	243	648	543	U	4.34	12.973	0.550
Al	0.10	0.146	0.055	Zn	0.037	0.029	0.001

** Dump seepage water used for column experiment CB36-8*

Conceptual model setup

The 1-dimensional geochemical transport model was created by coupling of the geochemical reaction code PhreeqC (Parkhurst and Appelo, 1999) and the spreadsheet program Microcsoft Excel® via a Microsoft COM (component object module). The PhreeqC input can be optionally adapted after each batch reaction by the help of a Visual Basic for Applications (VBA) macro (Charlton and Parkhurst, 2011).

Since PhreeqC alone is only suitable for modelling saturated flow or aqueous diffusion, it does not consider gas transport in unsaturated conditions. However, the gas phase composition especially in the column experiment CA68 is influenced by interactions with the liquid phase (i.e. HENRY-exchange, O_2 and CO_2 consumption or production by chemical reactions) as well as by gas transport. The latter one can be controlled by convection and/or diffusion. With respect to the grain size distribution of the tailings material, gas convection can be neglected in these column experiments. The O_2 and CO_2 replenishment by diffusion was computed in MS Excel according to FICK's law for each time step (batch reaction) and each model cell. The effective gas diffusion flux is calculated from the gradient between the gas concentration in the considered model cell (c_i) and the previous cell (c_{i-1}) taking also into account the simultaneous gas transport into the following cell (c_{i+1}) (Eq. 1).

$$q_{O2} = D_{eff} \cdot \frac{c_{i-1} - c_i - c_{i+1}}{\Delta x} \cdot \Delta t \qquad \text{(Equation 1)}$$

Thereby, D_{eff} is the effective diffusion coefficient, Δt is the time step of the batch reaction and Δx is the length of each model cell. The effective gas diffusion coefficient was set to 1E-06 m^2/s for all model cells in accordance with Eckart et al. (2006). The resulting molar amount of O_2 (CO_2) in the gas phase of each model cell after the batch reaction and diffusion step is transferred from the Excel balance calculation into the PhreeqC input for the next reaction step using a VBA macro.

The residence time of the percolation water reproduced by the model is crucial for the contaminant release. In accordance with the conceptual approach in TENSIC (Eckart et al., 2006) or HYDRUS (Jacques et al., 2013) it is therefore assumed that the liquid phase is subdivided into a mobile and an immobile phase depending on the geotechnical properties of the tailings (Tab. 1). The immobile phase comprises the adhesive water, which entirely moisten the solid particle surface (Fig. 2). The dead water in isolated pores is assumed not to contribute to the contaminant release. The essential geochemical processes, as for example pyrite oxidation, mineral dissolution/precipitation, ion exchange and sorption, are assumed to take place in the immobile phase.

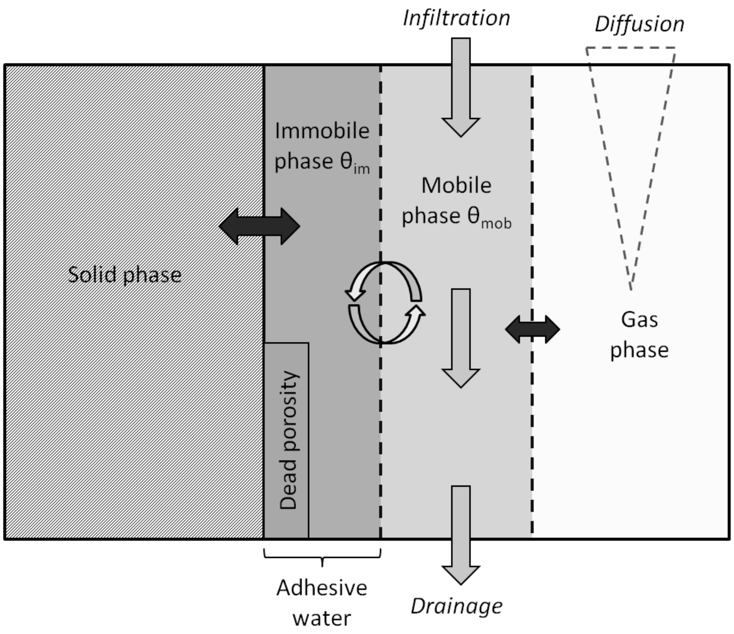

***Figure 2** Conceptual structure of a model cell with physical non-equilibrium (mobile-immobile water) transport.*

The mobile phase will be permanently exchanged by the input of infiltration water (Tab. 3). It represents the medium of solute transport in the strict sense. The mobile and the immobile phase stay in a mixing equilibrium. The mass exchange rate between both phases is given by their mixing ratio. Additionally, after each batch calculation a balance with the gas phase is enforced so that oxygen and carbon dioxide can be solved in or degassed from water according to HENRY's law.

For simplification, it was assumed that the gas volume in the unsaturated pore space of the tailings material is equal in all depth of the column and remains constant over time.

Both columns are discretised into three equally sized model cells (CA68: 12.8 cm; CB36-8: 10.3 cm). Initially, each model cell contains pore water with the chemical composition of the first effluent (Tab. 1) both in the mobile and the immobile phase.

The hydraulic transport is realized by shifting the water composition of the mobile phase from one to the next model cell after each reaction step (Fig. 2). The allocation of the mobile phase water composition is realized using the VBA script language in Excel.

The immobile water remains in each model cell and its composition is newly calculated after each reaction step (Fig. 2).

The time resolution (*Δt*) for a single reaction step depends on the permeability of the tailings material (k_f) and the effective porosity (n_{eff}) which is assumed to be equal to the proportion of the mobile water (Tab. 1).

$$\Delta t = \frac{n_{eff}}{k_f} \qquad \text{(Equation 2)}$$

Modelling results and discussion

The general flow conditions within the tailings columns could be well reproduced even by a simple hydraulic approach based on the geotechnical properties and physical non-equilibrium transport using a mobile-immobile model. The hydraulic calibration was performed by adjusting the mixing ratio between mobile and immobile phase to 0.4 in consideration of the volumetric ratios based on soil physical properties (Tab. 1) for both column experiments in order to fit the chloride release curve with the experimental data (Fig. 3). The geochemical data of the column experiments and the modelling results for pH- and redox (pe) conditions as well as for Na, Cl, Mg, Ca and SO_4 concentrations are compared in Figure 3. The concentrations of the columns' effluent could be fitted quite well by the model calculations. However, uncertainties still exist with regard to the Mg release from the CA68 column.

The dissolution and/or precipitation of most minerals contained in the solid tailings assemblage was considered to occur under equilibrium conditions in contact with the immobile water phase (Tab. 2).

The oxidation of pyrite with oxygen is assumed to be kinetically controlled depending on the amount of oxygen diffusing within the unsaturated pore space into the column material. The specific oxidation rate for pyrite is considered within the PhreeqC database *wateq4f.dat* according to Williamson and Rimstidt (1994).

Despite ongoing dissolution of pore water by infiltrating water, the measured SO_4 concentrations reach a stable level of roughly 2000 mg/l in both columns which could be predominantly modelled by gypsum dissolution and less by pyrite oxidation (ca. 1400 mg/l in the model).

The model approach has shown that the adjustment of the calcite equilibrium is inhibited in the experiments. However, the kinetic calcite dissolution according to the mechanistic approach from (Plummer et al., 1978) did also not fit well because it is based on experiments on synthetic calcites. However, natural calcites which can be assumed to occur in the tailings material contain impurities which lead to sorption processes on the crystal surface. This, in turn, inhibits the calcite dissolution (Svensson and Dreybrodt, 1992). Thus, the kinetic for the calcite dissolution was implemented according to Chou et al. (1989).

In addition, it was found that also the Mg concentration strongly depends on the dissolution kinetic of dolomite. Another important factor controlling the HCO_3-content in the model simulation was found to be the kinetics of siderite.

Table 4 *Kinetic rates (r) for mineral dissolution and precipitation considered in the model.*

Mineral phase	Kinetic equation	Constants	Reference
Pyrite FeS_2	$r = 10^{n} \cdot m_{DO}^{k1} \cdot m_{H+}^{-k2}$ $[r] = \frac{mol}{m^2 \cdot s}; [m] = \frac{mol}{kg}$	$n = -8.19\ (\pm 0.10)$ $k_1 = 0.50\ (\pm 0.04)$ $k_2 = 0.11(\pm 0.01)$	Williamson and Rimstidt, 1994; Parkhurst and Appelo, 1999
Calcite $CaCO_3$	$r = k_1 \cdot a_{H+} + k_2 \cdot a_{H2CO3} + k_3 \cdot a_{H2O} - k_4 \cdot a_{Ca+2} \cdot a_{CO3-2}$ $[a_i] = mol/cm^3$	$k_1 = 8.9 \cdot 10^{-5}$ mol cm^{-2} s^{-1} $k_2 = 5.0 \cdot 10^{-8}$ mol cm^{-2} s^{-1} $k_3 = 6.5 \cdot 10^{-11}$ mol cm^{-2} s^{-1} $k_4 = 1.9 \cdot 10^{-2}$ mol cm^{-2} s^{-1}	Chou et al., 1989
Dolomite $(Ca,Mg)CO_3$	$r = k_1 \cdot {a_{H+}}^{n} + k_2 \cdot {a_{H2CO3}}^{n} + k_3$ $[a_i] = mol/cm^3$	$n = 0.75$ $k_1 = 2.6 \cdot 10^{-7}$ mol cm^{-2} s^{-1} $k_2 = 1.0 \cdot 10^{-8}$ mol cm^{-2} s^{-1} $k_3 = 2.2 \cdot 10^{-12}$ mol cm^{-2} s^{-1}	Chou et al., 1989
Siderite $FeCO_3$	$r = k_{H+} \cdot {a_{H+}}^{n}$ $[a_i] = mol/cm^3$ (pH = 2...4, T = 25°C)	$k_{H+} = 1.79 \cdot 10^{-8}$ mol/cm^2 s^{-1} $n = 0.75$	Golubev et al., 2009

Distinct differences between experimental data and model results occur for Mg in the column CA68. The measured concentrations slightly decrease, but do not reach zero. Hence, they do not represent a pure washout effect. Taking into account the kinetic of dolomite dissolution (Tab. 4) instead of equilibrium conditions resulted in better model results for CB36-8 compared to CA68. The still remaining difference between modelled and measured concentrations especially for CA68 might be caused by the input parameters for the mineral assemblage of the tailings which were deduced from geochemical analyses of the borehole material. The column material can show slight differences which might be sensitive to the model results.

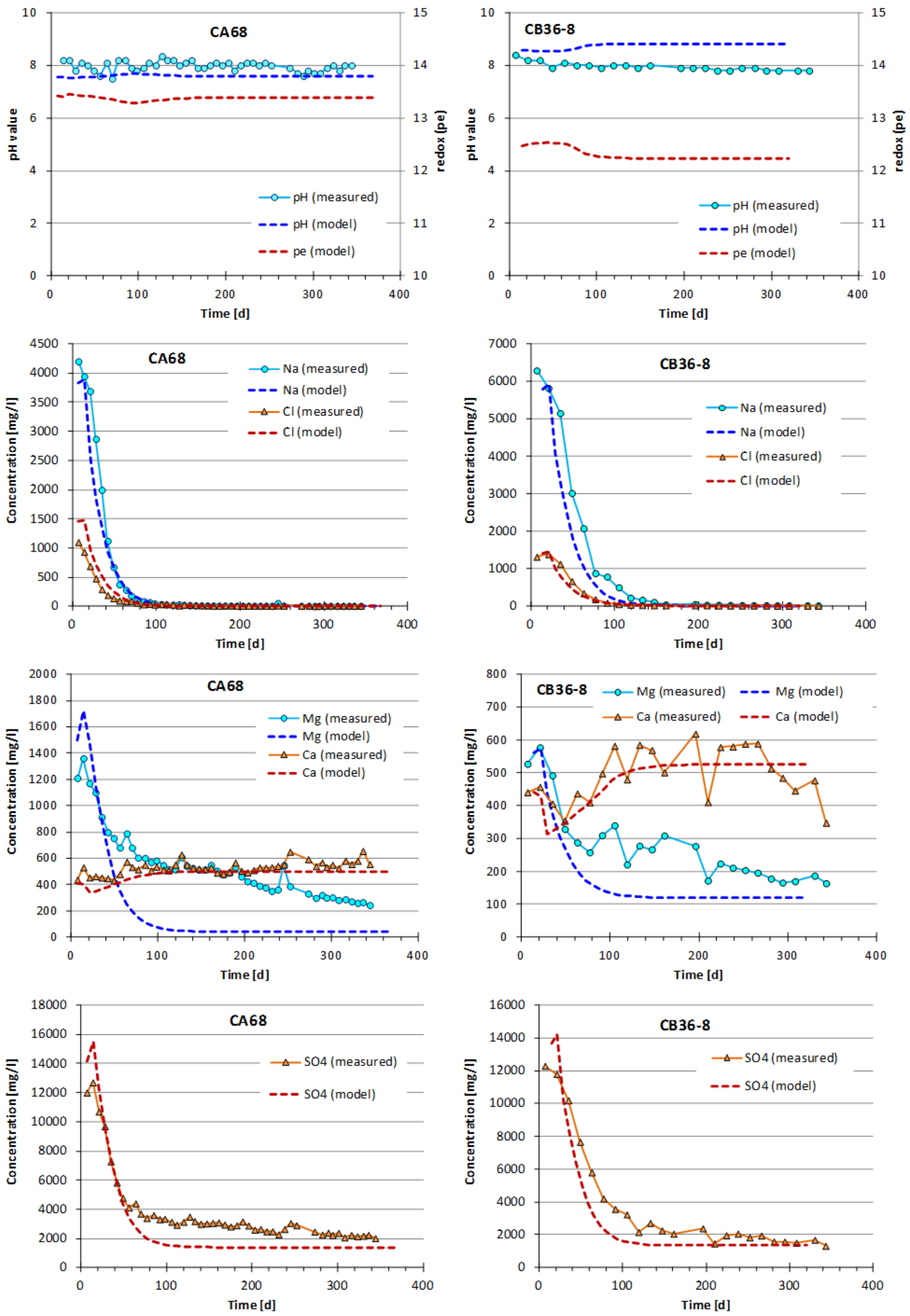

Figure 3 *Comparison of measured and modelled concentration developments of major constituents for the column experiments CA 68 (left) and CB 36-8 (right).*

Conclusions

The general model approach by coupling PhreeqC and MS Excel is appropriate to simulate the general geochemical processes and the 1-dimensional contaminant transport with consideration of gas transport by diffusion within tailings material of the TMF Culmitzsch.

At present, the major processes of mineral dissolution and precipitation under equilibrium or kinetic conditions are considered in the model. The geochemical milieu in the column experiments is strongly determined by gypsum equilibrium as well as the kinetic dissolution of carbonates (calcite, dolomite, siderite) and to less extent pyrite oxidation.

Next efforts will be undertaken to examine the sensitivity of the initial mineral assemblage and pore water composition with respect to the modelling results.

Future tasks will deal with the impact of sorption (e.g. on amorphous $Fe(OH)_3$ or AlOOH) and ion exchange reactions on trace metal concentrations in the effluent as well as the presence of organic matter (e.g. humic acids) on redox reactions in the column experiments. Furthermore, the formation of alkaline earth uranyl carbonate species (Bernhard et al., 2001) is supposed to influence the uranium speciation and thus its sorption and transport behaviour in the tailings material which needs verification, too.

Up-scaling of this 1-dimensional model approach to the field scale of the TMF Culmitzsch needs further efforts with regard to the extension of the current conceptual model as well as data acquisition for model parameterisation.

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Validating WRD conceptual models and implications for mine closure in semi arid environments: a high level assessment using field data

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Abstract

The prediction of how waste materials will evolve geochemically within waste storage facilities in semi arid environments requires a coherent and detailed understanding of the mechanisms that control oxidation reactions, and seepage generation. As part of a large scale investigation to improve the understanding of waste rock geochemistry at macro scale in semi arid environments O'Kane Consultants (OKC) has had the opportunity to lead two large scale waste rock storage facilities (WRSF) drilling programs at different sites in Western Australia. A range of WRSFs were investigated to include both active facilities and historical closed facilities of around 10-30 years in age. These investigations included approximately 2,000 m of sonic drilling, the recovery and detailed analysis of over 2,000 samples of core material and the installation of over 200 sensors at depths between 5 and 140 m within the waste which have provided over 5 million points of monitoring data to date and are still actively generating data.

The quantity and quality of materials testing and in situ monitoring data collected has provided OKC the opportunity to determine the specific factors related to in situ field conditions that act as the main controls on geochemical evolution of waste materials in semi arid environments. Data has been used to develop a detailed conceptual model for the geohydrology of WRDs within a semi arid environment. In addition OKC has developed field calibrated analytical AMD loading models.

The extensive data gathered as part of the assessment has allowed OKC to determine the geochemical, hydrological and geophysical evolution of the waste rock facilities as a result of 10-30 years of exposure. This valuable site data has been used to both back test the results of predictive models made for the waste facilities, and to optimise predictive models for future scenarios.

Key words: Semi arid environment, pyrite oxidation rate, stored acidity

Introduction

A typical conceptual model for oxygen ingress is that gas flux occurs as a result of air ingress occurring through the WRD at the bottom of the pile in rubble zones, and moving upwards through the free draining coarse material layers by the process of thermal advection. The conceptual model for the hydrology of waste rock dumps is that the infiltration of water enters the WRD at the top of the pile, percolating down through areas of fine grained materials due to their ability to retain water and the low air entry value of course grained material. During heavy rain events such as cyclones, water will also enter the WRD in coarse grained sections quickly percolating to depth.

On a conceptual level this kind of understanding of internal waste rock dynamics can be easily determined, the challenge is to take this conceptual understanding and make quantitative predictions about the geochemical and geo-hydrological evolution of the WRFS over time and understand AMD risk.

As part of a large scale investigation (Pearce and Barteaux 2014, 2014b) to improve the understanding of waste rock geochemistry at macro scale in semi arid environments O'Kane Consultants (OKC) has had the opportunity to lead two large scale WRSF drilling programs at different sites in Western Australia. A range of WRSFs were investigated to include both active facilities and historical closed facilities of around 10-30 years in age. These investigations included approximately 2,000 m of sonic drilling, the recovery and detailed analysis of over 2,000 samples of core material and the installation of over 200 sensors at depths between 5 and140 m within the waste which have provided over 5 million points of monitoring data to date and are still actively generating data.

Key findings from the data analysis and modelling have been summarised herein

Moisture cycling

Matric potential and temperature sensor data indicates that significant moisture cycling through the waste rock dumps occurs as a result of advection forced drying. The process results in transfer of oxygen and moisture through waste dumps in the vapour phase that stimulates oxidation reactions in material buried deep within the waste dump that would be considered as being "oxygen and moisture limited" based on theoretical understanding of waste dump geohydrology. Up to 100mm per year of net percolation may be redistributed as a result of this process.

A key consequence of advective drying is to significantly increase theoretical timeframes for "wetting up" of waste rock to occur as the overall water balance for the WRD is significantly impacted by this process that is not commonly included as part of traditional water balance calculations. In addition wetting up has been shown to not be a homogeneous process so the concept of a defined "wetting front" is not supported, rather preferential flow and drying occurs through the waste even after 30+ years of exposure.

Oxygen ingress

Air flow rates calculated based on site data indicate that where coarse basal zones are present air flux rates through waste mass of around $1\text{–}2 \times 10^{-4}$ m^3/m^2s can be expected. Based on typical sulphide oxidation rates the oxygen flux that derived from gas flux of this magnitude is sufficient to allow oxidation to occur at unconstrained rates (Pearce et al 2015). Advective airflow rates through the waste are the primary control on oxidation rates for sulfides. This process has been linked to waste dump structure with basal rubble zones providing significant sources of continued oxygen ingress. In many cases due to segregation of waste as a result of end tipped structures, oxygen ingress is significant through the entire profile of the waste and oxygen ingress through the base is linked to internal flow pathways.

Given the above observations it may be inferred that oxidation reactions within the WRDs studied may not be O_2 limited, but are more likely to be limited by the supply and movement of H_2O. Geochemical analysis of drill core supports this conjecture as there is a significant presence of secondary sulfate minerals which are indicative of precipitation of sulfate bearing minerals as a result of stationary pore fluids (and therefore a very low L:S ratios). The geochemical system can therefore be best thought of as semi closed in that oxygen and H_2O (possibly supplied from internal evaporation rather than matrix pore water flow) can enter the waste but very limited leachate leaves the system. This results in a buildup of secondary sulfate minerals.

It is interesting to note that even with the very low L:S ratios observed in the WRSFs that oxidation reactions have proceeded to 60% or greater completion over 30 years (Pearce el 2015).

Predictive modeling

Based on the field investigation and ongoing monitoring data from the instruments placed within the waste a predictive model was established to determine the potential AMD discharge profile for the waste (Pearce et al 2015). The majority of acidity production is stored as secondary mineral products over the first 40 years of the assessment period and so is not likely to be reported in basal seepages. After 40 years however significant impacts on seepage quality are noted as both seepage rates increase as a result of "wetting up" and stored acidity products are released (Figure 1).

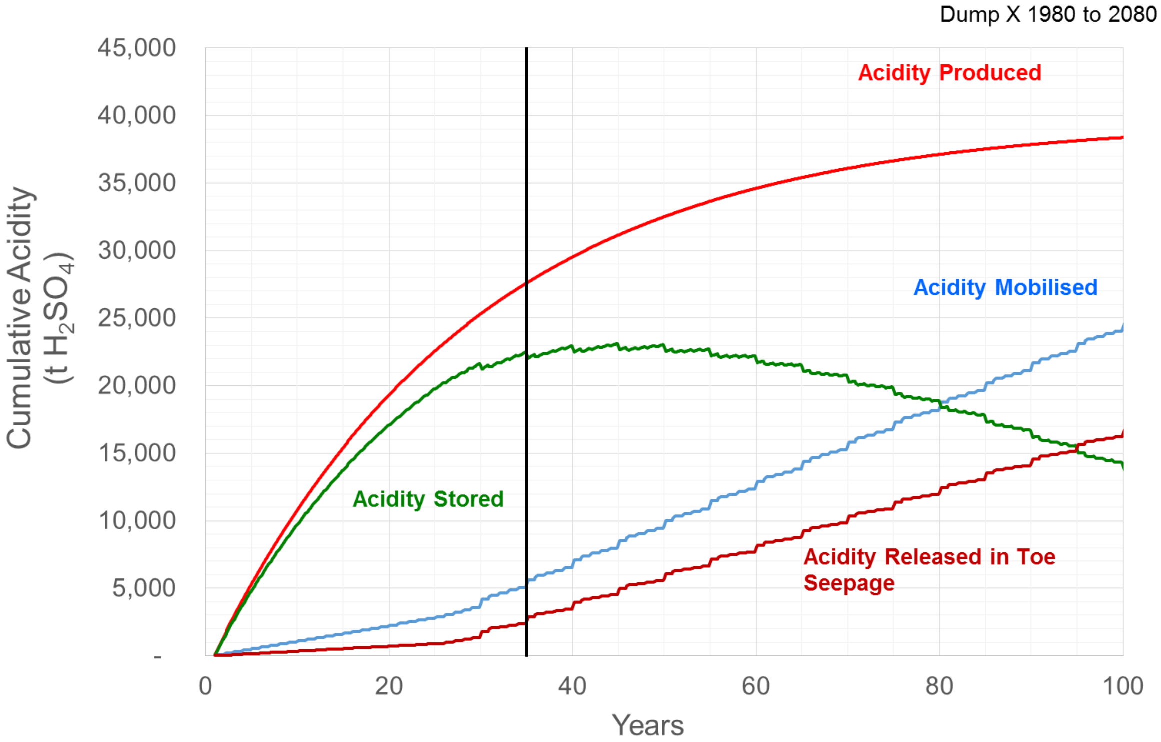

Figure 1 *AMD load predicted from field calibrated model*

Conclusions

In semi arid climates such as the Pilbara, low rainfall environments create conditions of very low liquid to solid ratios where high levels of oxygen ingress are indicated to occur. Field data from a number of historical WRD containing pyritic material indicates internally the waste materials have not reached a “wetted up” state even after 30 years of storage. However even in such low moisture environment oxidation reactions have proceeded to 60% or greater completion indicating that water supply is not an overriding oxidation reaction limiting factor. Air flux rates are indicated to be significant as a result of large advective gas fluxes resulting from the unsaturated nature of the material and large temperature gradients. The field data indicates that in semi arid environments limited seepages are likely to occur in the short term (<30 years) due to the low amount of net percolation occurring and high moisture losses from the WRD as a result of evapotranspiration from the surface and advective drying at depth.

An AMD load model built on conceptual model formed from the field data gathered indicates that in semi arid environments stored acidity loads are likely be generated a relatively high rates only limited by oxygen ingress rates for periods of up for decades. Over this timeframe significant pore water flushing and vertical drainage through the waste (and production of seepages) are not likely to occur and so >60% of the AMD is stored as semi volatile acid salts within pore spaces. Once “wetting up” conditions are reached and seepages begin, AMD loads are likely to be significant as the dissolution of the stored products will be at low L:S ratios and concentrations will be close to solubility constraints for key metals and sulfate.

It is notable that the lack of AMD seepages from waste dumps in semi arid environments is often used as proof that AMD is risks are limited, and that cover systems are an appropriate risk mitigation measure. However the implications of the work presented in this study extend to a significant reappraisal of the potential AMD risks of reactive waste rock stored in semi arid environments, and further to the effectiveness of cover systems as a “panacea” to manage AMD risks in these environments.

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3D geological modelling for geo-environmental characterization of mineral deposits and pragmatic management of geochemical risks.

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Abstract

An understanding of geochemical risks associated with mineral deposits and how they can be managed often begins with an investigation of the conceptual environmental geological model. Previously this was generally based on geological cross-sections and analysis of drillcore logs. 3D geological modelling software has been widely used for mineral resource applications but its value for use investigating acid rock drainage risk of projects is still relatively limited. This poster outlines how 3D geological modelling software can be used on a wide range of mining projects to quantitatively manage geochemical risks associated with mine operation and closure. The 3D geological modelling software, Petrel (Schlumberger), although originally developed for oilfield settings, has since 2008 been applied in geo-environmental characterization, geochemical risk assessments and waste rock management planning for more than 100 new mining projects and operations globally. The principal applications for which the software has been used include the development of defensible sampling plans for static and kinetic testing, elucidation of the spatial and temporal variability of ARD/ML risks during operation and closure, and optimization of the scheduling and distribution of waste rock to backfill, reactive waste or 'inert' waste storage facilities. A particular strength of the 3D modelling approach is the ease with which ARD classifications may be visualized in conjunction with economic (commodity assay or rock value), geo-mechanical and other variables of relevance to the wider mine planning process.

Key words: ARD, Petrel, Geostatistics, 3D geological models

Introduction

Successful characterization of the environmental geology of mineral deposits, including the identification of representative sample populations for assessment of acid rock drainage (ARD) and metal leaching (ML) risks at the design stages of new mining projects, relies fundamentally on a capacity to visualize and classify in three dimensions the rock units present. Traditionally, this information has been obtained through geo-statistical analysis of drill core logs, or through the construction from such logs of cross-sections to depict the distribution of discrete lithology-alteration-mineralization (LAM) units within an area of proposed open pit or underground mine development.

While 3D geological modelling software has been used for more than a decade for interpolation of exploration drill hole information of relevance to mineral resource estimation, the adoption of such software within the realm of environmental geology has been suprisingly limited. The use of 3D modelling software allows, however, rapid integration, geostatistical analysis and visualization of multi-variable datasets (such as those relating to lithology, alteration and mineralization type) in a manner which substantially improves the confidence level with which representative sampling programs for industry-standard static and kinetic testing may be undertaken and for the practical incorporation of the results of such tests into activities such as mine design optimization and operational waste rock handling.

Software application

Software used for 3D modelling of mineral resources has previously been reported for use within ARD/ML studies (Linklater et. al. 2015). The 3D geological modelling software, Petrel (Schlumberger), although originally developed for oilfield settings, has since 2008 been applied in geo-environmental characterization, geochemical risk assessments and waste rock management planning for more than 100 new mining projects and operations globally. The principal applications for which the software has been used include:

- Statistical interrogation of geological block models in conjunction with mine plans (for example, annual pit shells) to develop defensible sampling plans for static and kinetic testing.
- Incorporation of ARD/ML classification systems into geological block models, thus allowing the spatial and temporal variability of ARD/ML risks to be elucidated when interrogated in conjunction with mine plan information (for example annual pit shells as shown in Figure 1).
- Dynamic calculation of changes in the magnitude of ARD/ML risks during progressive inundation of open pit and underground mines at closure.
- Optimization of the scheduling and distribution of waste rock to backfill, reactive waste or ‘inert’ waste storage facilities through mine life, based on differential ARD/ML classifications.

In many instances, the incorporation of ARD/ML classifications into a 3D geological model can be performed on the basis of only one variable (for example sulphide S, see Figure 2). However, Petrel has also been applied for complex situations in which waste rock behaviour is a function of multiple variables. A particular strength of the 3D modelling approach is the ease with which ARD classifications may be visualized in conjunction with economic (commodity assay or rock value), geo-mechanical and other variables of relevance to the wider mine planning process. This effecivtively enables coupling of ARD/ML studies with resource models, pit design and mine scheduling tools. Ultimately, the benefit of this approach has been an improved awareness of the risks associated with ARD/ML throughout the life of mining projects, and an improved capacity to pro-actively avert or mitigate.

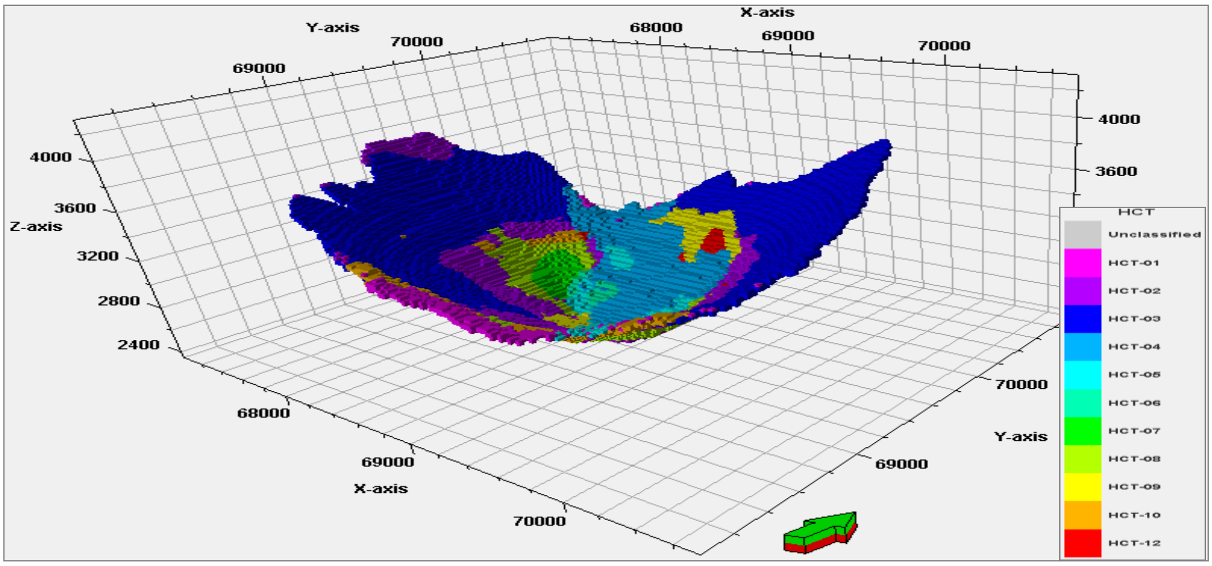

Figure 1 *3D representation of a pit shell defined by geochemical kinetic tests*

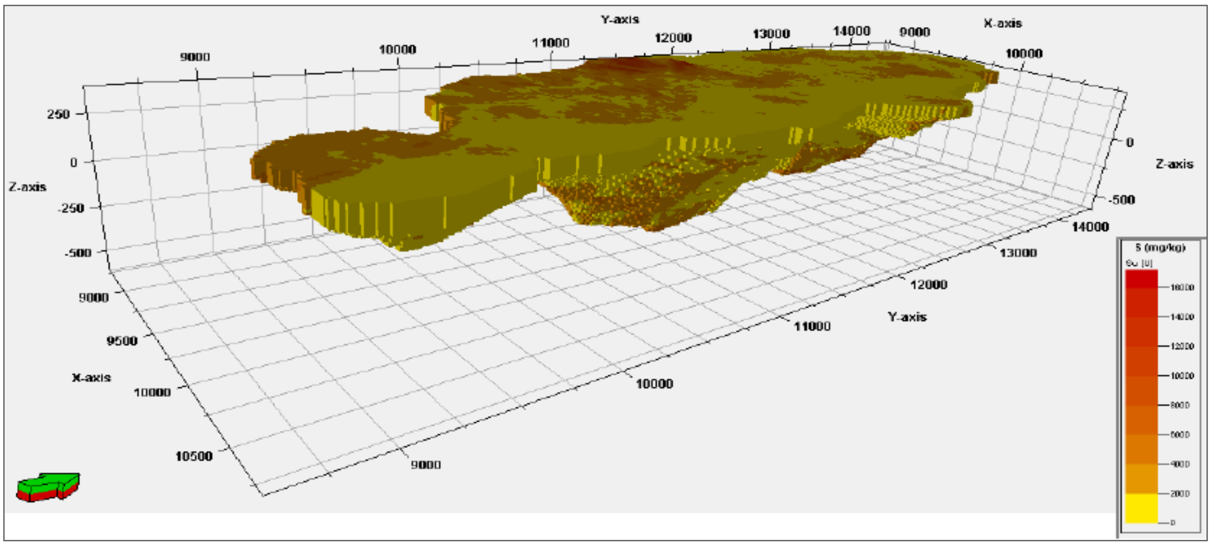

Figure 2 *Sulphur model defining ARD risk within a deposit*

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Fate of radium in river and lake sediments impacted by coal mining sites in Silesia (Poland)

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Abstract

The Upper Silesian Coal Basin has been extensively mined since the beginning of the 20th century. Wastewaters released from Polish coal mines contain radium (Ra) in ionic form as well as in suspended matter. Although co-precipitation of Ra into radio-barite ($(Ba,Ra)SO_4$) has been enhanced for reducing the impact of mining activities on water quality, sediments in rivers and lakes surrounding mining sites still show relevant activities of both ^{226}Ra (1600 y half-life) and ^{228}Ra (5.7 y half-life) isotopes. The management of this contamination currently relies on natural attenuation.

This study focuses on assessing the long-term impact of Ra which has been trapped into river and lake sediments in the vicinity of coal mining sites in Poland. Two geochemical interfaces have been surveyed by sampling sediment, surface and pore waters downstream from coal mining sites: (1) the hyporheic zone of a river, where groundwater tends to mix with surface waters within the river bed; and (2) the water-sediment interface in a lake which was formerly used as a settling pond. Both represent redox interfaces where radium-bearing solid phases (barite, metal oxyhydroxides) can undergo various geochemical processes which have not been quantified yet.

Our preliminary results show that pore water geochemistry within the hyporheic zone of the studied river is impacted by diffuse and direct wastewater releases from an operating settling pond. A geochemical model built with JCHESS® suggests that mixing of surface waters with wastewaters favors witherite ($BaCO_3$) precipitation within the riverbed. Additional investigations are planned to assess the consequences of this suspected process on Ra behavior through the hyporheic zone. Moreover further investigations are performed for studying the fate of Ra trapped into $BaSO_4$ within pond sediments where sulfate-reducing conditions could occur with depth due to organic matter degradation and where ^{210}Po (^{226}Ra decay product) is detected into surface waters.

Key words: radium, coal mines, barite, witherite, polonium

Introduction

The Upper Silesian Coal Basin in southwestern Poland has been extensively mined since the beginning of the 20th century (Chałupnik et al. 2001). Almost 30 underground coal mines are currently operated which has led to the release of brines (Total Dissolved Solids ≈ 200 g/L) in surface waters, naturally enriched with radium (up to a few Bq/L), barium (up to several g/L) and metals (Zn, Sr, Pb, Cu, Ni, Co). Since the beginning of the 1990s, a wide range of counter-measures were taken in order to decrease the impact of mining activities on surface water quality (Leopold et al. 2007; Chałupnik & Wysocka 2008a&b). These basically consisted in reducing infiltration of meteoric waters into the underground galleries and enhancing co-precipitation of Ra into radio-barite ($(Ba,Ra)SO_4$). Although these actions led to the reduction of Ra releases to surface waters by 60% (Chałupnik & Wysocka 2008a&b), sediments in rivers and lakes surrounding mining sites still show relevant activities of both ^{226}Ra (1600 y half-life) and ^{228}Ra (5.7 y half-life) isotopes (Leopold et al. 2007).

Over many mining sites, radionuclides and heavy metals usually migrate through several water pathways as dissolved phases, colloids and suspended particles. Before these contaminants reach fast-flowing water systems, bottom sediments in streams and lakes can act as geochemical barriers and long-term sinks of radionuclides (Winde & van der Walt 2004) and heavy metals (Fuller & Harvey

2000). On the one hand in ponds and lakes, this natural attenuation results from scavenging by sedimentation and early diagenesis. On the other hand in watercourses, this attenuation is driven by dilution in fast-flowing waters and geochemical processes that occur in the hyporheic zone defined as the redox transition interface where groundwater tends to mix with surface waters (usually more oxygenated than groundwater; Gandy *et al.* 2006). Because of this attenuation, diffuse releases via groundwater from point or diffuse sources (tailings disposals, settling ponds, etc.) to adjacent water courses are difficult to monitor and quantify while it can lead to a substantial contamination of sediments by radionuclides and co-contaminants (Winde & van der Walt 2004). Understanding the way in which aquatic interfaces (like water/sediment interface in lakes or aquifer/river interface in streams) interfere on radionuclide transport through the aqueous pathway is thus of importance for assessing the impacts of radioactive substances on aquatic ecosystems and consequently human populations.

In order to contribute to the characterization effort of Polish mining sites for future radio-eco-toxicological researches, this study focuses on assessing the long-term impact of Ra which has been trapped into river and pond sediments in the vicinity of coal mining sites in Poland. Two geochemical interfaces have been surveyed by sampling sediment, surface and pore waters in the vicinity of an operating coal mining site: (1) the hyporheic zone of a river, where groundwater tends to mix with surface waters within the riverbed; and (2) the water-sediment interface in a lake which was formerly used as a settling pond. Whereas the hyporheic zone is advection-dominated, the water-sediment interface in lakes is usually diffusion-dominated. However, both represent redox interfaces where radium-bearing solid phases (barite, metal oxyhydroxides) undergo various geochemical processes which have not been quantified yet.

Methods

The vicinity of an operating underground coal mine was selected for sampling (1) the hyporheic zone of a river adjacent to a settling pond (where mine wastewaters are temporary stored before being discharged into the river), (2) the water-sediment interface in a lake which was formerly used as a settling pond by the same mine operator (from 1977 to 2002). Two field campaigns were performed: a first one in Nov. 2014 for selecting the site and undertaking preliminary water and sediment characterizations; a second one in May 2015 for further investigating the hyporheic zone and the former settling pond.

Surface water sampling was performed in both the current and former settling ponds of this site as well as into the river adjacent to the current settling pond (both upstream and downstream from the direct discharge). The hyporheic pore water was sampled into small piezometers disposed into the riverbed (2-cm wide pipes slotted over 5 cm at their bottom and installed at 0.5 meter below the water/sediment interface into the riverbed). In order to ensure that pore water samples were representative of a mixing zone between groundwater and surface waters, the pipes were installed into coarse riverbed sediments composed of sand and pebbles and were subjected to initial pumping tests in order to monitor how quickly the water level returns to the pre-pumped level. Sampling was performed when the water level into the small piezometers was higher than the river level (*i.e.* when groundwater is drained by the river). In order to check that no mixing with surface waters occurred during pore water sampling into the hyporheic zone, the small piezometers were sampled at very small rates (< 50 mL/min), more than 24 hours after their installation and initial testing, while the electrical specific conductivity of pore water was measured in line for ensuring that it was held constant. Groundwater representative of the main shallow water table connected to the river was also sampled into a piezometer located at 10 meters from the studied river, on the other river bank which is supposed to be not influenced by mining activities.

At each measurement location, pH, Eh, electrical conductivity and dissolved O_2 content were measured *in situ* with calibrated field probes. Water samples were filtrated at 0.45 µm. Laboratory characterization of filtrated surface water samples includes ICP-OES and ionic chromatography for major ion determination, ICP-MS for trace elements, liquid scintillation counting (according to Schonhofer *et al.* 2009 method) for dissolved ^{226}Ra, ^{228}Ra and ^{210}Po (daughter product of ^{226}Ra decay) activity measurements, and acid titration for alkalinity measurement. ^{226}Ra and ^{228}Ra activities associated with suspended particles larger than 0.45 µm were measured onto filters by gamma spectrometry using well-type detector. As the amount of sampled water into the hyporheic zone was too low (< 500 mL), pore water characterization did not include dissolved Ra determination and suspended matter analyses.

Sediment sampling was performed with a 3-cm wide hand corer into the former settling pond below 2 meters of surface water while it was performed with a shovel into the current settling pond and the river (at the same locations as the small piezometers). Sediment characterization includes sieve analysis, XRD for identifying the major mineralogical content, gamma spectrometry for quantifying ^{226}Ra and ^{228}Ra activities, X-Ray fluorescence spectroscopy with wavelength dispersive system for measuring the major oxide content, ICP-MS for trace elements, Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) and total sulfur content measurements by IR spectrometry after combustion, and moisture content measurement by gravimetric method.

Results and discussion

According to the concentrations of dissolved conservative elements measured in water samples (*i.e.* Br and Cl contents reported in fig. 1), two main end-members can be distinguished: (1) the geochemical background of non-impacted sub-surface waters on the one hand; and (2) the currently operated settling pond water to the other hand. Waters from the former settling pond and the shallow water table tend to pool with the background signature (*i.e.* subsurface waters upstream from the studied site). This observation confirms that the piezometer selected for characterizing the water table geochemistry is not impacted by mining activities. This also shows that the water of the former settling pond has been renewed since its closure in 2002 and does not correspond anymore to mine wastewater.

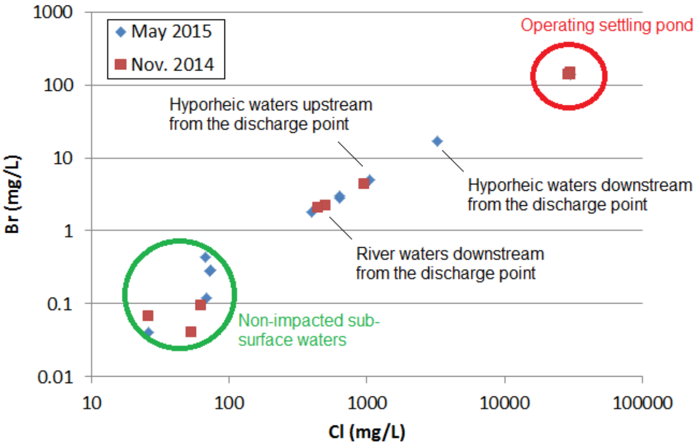

Figure 1 *Dissolved Br and Cl content measured in water samples in Nov. 2014 and May 2015*

All the other water samples appear to be a mix between these two end-members, especially the river waters downstream from the studied mining site and the hyporheic zone waters (both upstream and downstream from the direct discharge of the currently operated settling pond into the river). A significant redox contrast was found in May 2015 between the hyporheic zone (Eh~110 mV; O_2<2 mg/L) and the river (Eh~320 mV; O_2~9 mg/L). Additionally, the electrical specific conductivity was much higher into the hyporheic zone (up to 4400 µS/cm) than into the river water (550 µS/cm) upstream from the wastewater discharge. These observations together with the signature given by Br^- and Cl^- ratios show that groundwater within the hyporheic zone of the studied river is impacted by diffuse and direct wastewater releases from the operating settling pond. Dissolved barium was also detected into pore waters of the hyporheic zone both upstream and downstream from the wastewater discharge of the closest studied mine.

A preliminary reactive geochemical model built with JCHESS® (van der Lee 1998) tends to suggest that mixing of surface waters with wastewaters according to the mixing ratios given by these end-members tend to favor witherite ($BaCO_3$) precipitation (fig. 2) within the riverbed. Additional investigations are planned to demonstrate the occurrence of this process into riverbed sediments and to identify its consequences on Ra behavior through the hyporheic zone by analyzing Ra in pore waters.

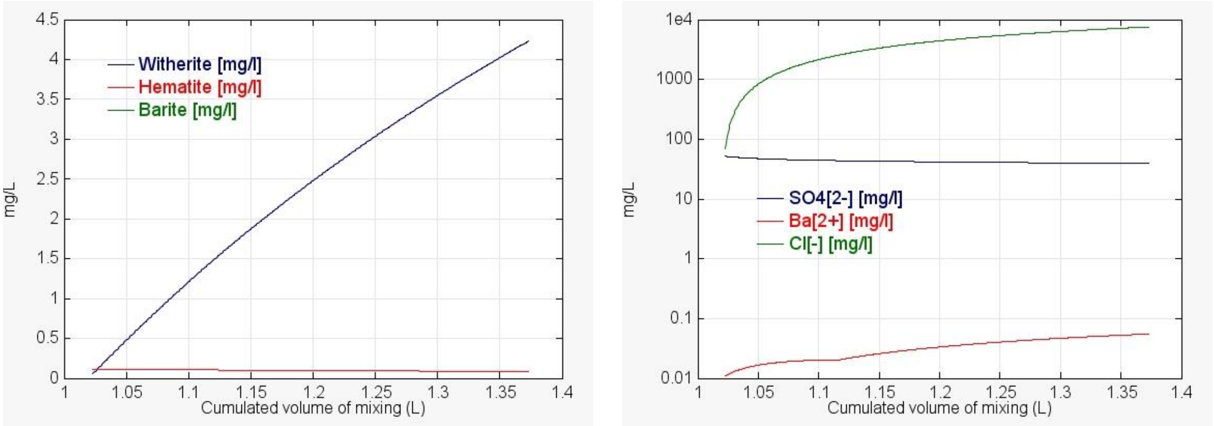

Figure 2 *Simulated precipitation/dissolution of minerals (left part) and dissolved concentrations (right part) that could occur into the hyporheic zone of the studied site due to water mixing (1L of surface water with 0.4 L of settling pond water)*

Regarding the former settling pond, its bottom sediments were found to be composed of mineral phases similar to that of the operating pond (barite, chlorite, illite, amorphous phases, feldspars and quartz). However a higher organic matter content was detected into the former settling pond sediments (14% of TOC). Ongoing investigations are performed to understand radium activity profiles detected into several sediment cores from this former pond. The objective of these additional works is to check the sustainable trapping of Ra into $BaSO_4$ in case of lake sediments where sulfate-reducing conditions could occur with depth due to organic matter degradation. In May 2015, low dissolved ^{226}Ra (~0.03 Bq/L) and ^{228}Ra (<0.01 Bq/L) activities were detected into the surface waters of this pond while high activities were measured into bottom sediments (up to 9000 Bq/kg of ^{226}Ra and 300 Bq/kg of ^{228}Ra). This observation tends to show that since the renewal of the water column into this pond (closed in 2002) natural attenuation has been favorable to the disposal of contaminated bottom sediments by limiting significantly the impact of Ra on surface water quality. However, we found a relevant total ^{210}Po activity into these surface waters (0.50 ± 0.05 Bq/L in May 2015). ^{210}Po is a short-lived (138.4 d half-life) decay product of ^{226}Ra that usually displays a complex biochemical cycling in subsurface environments due to its preferential removal by biota and rapid regeneration because of re-mineralization from sinking biogenic debris (Kim *et al.* 2011). Additional works are thus needed for confirming first that natural attenuation processes governing the fate of ^{210}Po grandparent (i.e. ^{226}Ra) will be sustainable in the long run (i.e. over several half-lives of ^{226}Ra) and second, quantifying the processes involved in the release of its progeny ^{210}Po toward surface waters.

Conclusion

This study reports preliminary results of water and sediment characterization aiming at understanding the fate of Ra through aqueous interfaces usually encountered in the vicinity of mining sites. In the hyporheic zone of a river, where groundwater tends to mix with surface waters, geochemistry of pore waters shows that diffuse and direct wastewater releases from an operating settling pond impacts water quality within the riverbed. A geochemical model built with JCHESS® suggests that mixing of surface waters with wastewaters favors witherite ($BaCO_3$) precipitation within the riverbed. Additional investigations are planned to assess the consequences of this suspected attenuation process on Ra behavior through the hyporheic zone. Moreover further investigations are performed for studying the fate of Ra trapped into $BaSO_4$ within lake sediments where sulfate-reducing conditions could occur with depth due to organic matter degradation and where ^{210}Po (^{226}Ra decay product) is detected into surface waters.

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CHAPTER 12

Extracting Value from Mine Waters

Reducing life-cycle costs of passive mine water treatment by recovery of metals from treatment wastes

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Abstract

In compost bioreactor systems, a commonly deployed technology at passive mine water treatment sites, metals accumulate in the treatment system substrate. Ultimately, this substrate becomes exhausted and requires disposal. An assessment was undertaken using a case study site in northern England, investigating how metal recovery might be used to reduce the whole life-cycle cost of treatment. The large-scale system at Force Crag mine harnesses bacterial sulphate reduction, primarily to remove zinc within a compost substrate.

Calculations of the rate of accumulation of zinc within the treatment system suggest that the value of zinc (as a pure metal) may amount to approximately €7600 after 10 years of operation, at current market prices. More significantly, the compost would be classified under UK legislation as hazardous waste because of the elevated zinc concentration. The cost of disposal of the 840 m^3 of compost in the treatment system would consequently be in excess of €0.8M. Such a high waste disposal cost would have a major influence on whole life-cycle cost of the treatment system, irrespective of exactly how long the system operates before the substrate becomes exhausted. The cost of removal of the zinc from the treatment substrate by washing has been calculated at approximately €155,000. This would reduce the volume, and therefore cost, of disposal by more than 10 times. Furthermore, it may be possible to re-use the decontaminated compost substrate, although this is an area of further investigation.

Data presented in this paper suggest that recovery of metals from treatment system substrates might offer substantial passive treatment system life-cycle cost reductions. At Force Crag, it is estimated that discounted life-cycle costs can be reduced from €1.63M to €1.12M over 10 years. Allowances for substrate decontamination processes should therefore be considered by treatment system operators from project inception, in order that these savings can be realised.

Key words: Passive treatment, metal recovery, life-cycle costs

Introduction

Passive mine water treatment has been widely adopted as a low-cost and low-impact means of tackling polluting discharges from abandoned mines (Younger, 2000). Bioreactors, harnessing microbial sulphate reduction in an organic substrate, offer advantages over other systems for installation at metal mine sites, as they simultaneously remove a range of metals and generate alkalinity (ITRC, 2013; Neculita et al., 2007; Rose, 2006). Inevitably, however, metals will accumulate within the substrates of bioreactors and eventually need to be disposed of. The costs associated with these materials can be high, particularly if they are classified as hazardous wastes (Gusek et al., 2006). Indeed, testing of a waste compost substrate from a system treating a zinciferous discharge at an abandoned metal mine for just 2 years was determined as hazardous waste under UK regulations due to its zinc content (unpublished data, Newcastle University 2013). The cost implications associated with disposal of these metalliferous, organic materials has been determined as € 495 - € 2170/t (Atkins, 2014). For context, the costs of disposing of hydrous ferric oxide wastes from aerobic treatment systems operating at coal mine sites is € 98 - € 160/t (Sapsford et al., 2015).

It has been suggested that metals might be recoverable from passive bioreactor wastes (Gray et al., 2012; Gusek et al., 2006; Gusek and Clarke-Whistler, 2005) and preliminary experimentation has been conducted to explore this (Bailey et al., 2015). Data suggest that metals are recoverable by particle size separation and leaching with dilute sulphuric acid (Bailey et al., 2015). These approaches are used by mining and contaminated land remediation systems (CL:AIRE, 2007; Wills, 2006; Tichy et al., 1996). By processing passive bioreactor wastes to recover metals, the costs associated with waste disposal might be substantially reduced, and an income stream may be generated.

This paper explores how recovery of metals from passive bioreactor wastes may be used to offset the life-cycle costs of mine water treatment. Financial and geochemical information have been collected from the Force Crag site in Northern England, UK, which has been operational since April 2014. The system at Force Crag Mine treats 6L/s of water draining from an abandoned Pb-Zn mine complex using two parallel Vertical Flow Pond (VFP) compost bioreactors of equal size, followed by a small polishing wetland (Figure 1). The total substrate volume of the system is 840m^3, consisting of a mix of 45% wood chip, 45% municipal waste compost and 10% digested sewage sludge. Further details of the treatment system can be found in Jarvis et al. (2015).

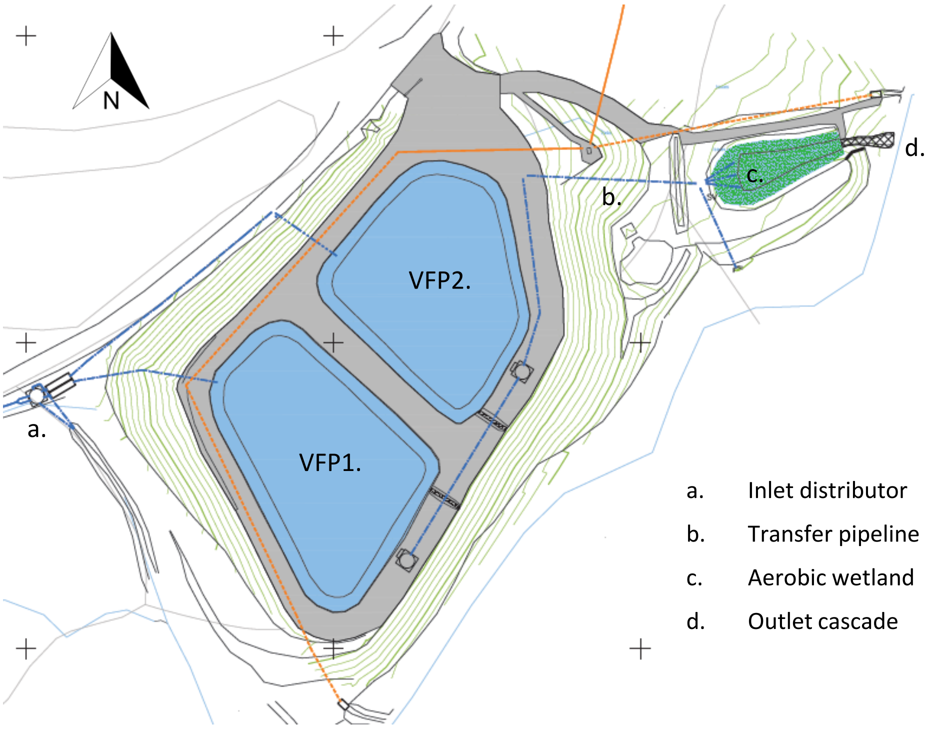

Figure 1 Force Crag mine water treatment system general arrangement, drawing courtesy of the Coal Authority. 50m grid intervals for approximate scale

Methods

Performance data for the Force Crag treatment system were collected between April 2014 and March 2015 to determine the removal of zinc within the compost substrate. Sampling was typically conducted on a weekly basis. Flow rates were measured using sharp crested v-notch weirs and bucket and stopwatch methods at locations where weirs were unavailable. Metals analysis was conducted at Newcastle University, UK, using ICP-OES.

Life-cycle cost assessments were undertaken using actual outturn figures for construction, and operational cost items based upon estimates from operational costings for more than 50 pre-existing passive treatment systems operating in the UK. Waste disposal costs were determined by obtaining quotes from 3 specialist waste carriers, with the lowest cost option of combined disposal and haulage used in forecasts. Additional financial information was obtained to determine the costs of substrate de-contamination by consultation with industrial specialists (Acumen Waste Ltd.). For this a detailed costed proposal was developed, assuming procurement of a bespoke washing rig receiving reasonable use against investment, by frequent deployment across a portfolio of treatment sites. The soil washing process was designed to separate coarse, uncontaminated substrate fractions from a metal rich fine grained fraction with a <63µm particle size, using a combination of acid leaching/neutralization and particle size separation. Costs for active treatment (as a comparator to passive treatment costs) was obtained from a detailed costed proposal for a High Density Sludge lime based system developed by Helix Projects Ltd (Schade, 2015). This active treatment approach was chosen because it is proven technology, which has previously been determined as more than 50% lower cost than alternative technologies such as biochemical sulphide precipitation and ion exchange (Younger et al., 2005). It should be noted that although latter two techniques claim to offer the ability to recover metals directly from mine waters for recycling, at the Wheal Jane study site, the quantities recoverable were not considered economically viable (Younger et al., 2005). All financial assessments have been discounted at 3.5% according to HM Treasury (2011).

Zinc removal and accumulation rate

The Force Crag treatment system was monitored in detail from commissioning in April 2014 until the end of March 2015. Data indicate that treatment performance was high: on average 95% to 99% removal of zinc (see Figure 2). Given the loading and system size, this equates to a volumetric removal rate for zinc of 1.90g/m^3/d. When considered together, these metrics situate the system within the upper-middle of a ranking of the known systems of this kind globally (Table 1).

On the basis of projections, the Force Crag treatment system will have accumulated 21,520mg/kg of zinc within its substrate after 10 years, if current performance is maintained. However, it has been found that accumulation of metals within treatment system substrates can inhibit the sulphate reduction process and thus treatment performance (Utgikar et al., 2002). Data presented by Rutkowski (2013) implies that sustained performance can result in very high zinc concentrations within substrates of compost based treatment systems (22,940mg/kg calculated based upon performance data for the Standard Mine bioreactor, Colorado – refer to Table 1, Figure 3).

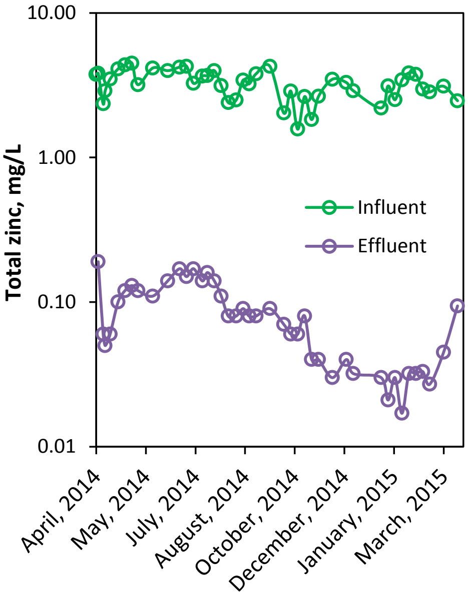

Figure 3 Zinc removal by the Force Crag mine water treatment system between April 2014 and March 2015.

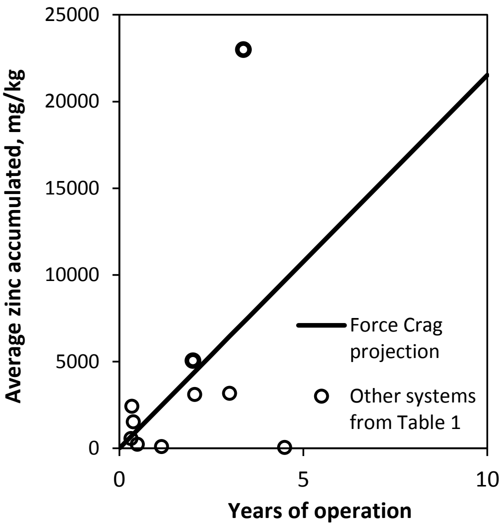

Figure 2 Zinc accumulation rate at Force Crag assuming current removal rates are maintained and, zinc content of substrate at sites in Table 1 (calculated from available data).

After 3.4 years of operation, the passive bioreactor at Standard Mine was decommissioned, yet its performance had shown no noticeable decline by this time (Rutkowski, 2013). Zinc concentrations in the Standard Mine system are estimated to be greater than forecast for Force Crag after 10 years of operation (21,520mg/kg), based upon calculations made by these authors. This implies that, after 10 years, the Force Crag system may still have not accumulated a quantity of zinc which might adversely affect its performance. Although, it is known that other factors limit the lifetime of substrates in these systems, such as plugging of substrates (Rose, 2006), depletion of substrate carbon sources required by sulphate reducing bacteria (Cheong et al., 2012; Logan et al., 2005). On the basis of these factors and examples from elsewhere, a nominal substrate lifetime of 10 years has been attributed to the Force Crag system by its operators.

Table 1 Comparative mean zinc removal rates and efficiencies from a range of bioreactor systems harnessing bacterial sulphate reduction

System name/ description, Reference	**Location**	**Influent zinc**	**Study period**	**Efficiency and removal rate (zinc)**	
		mg/L	*d*	*%*	*g/m³/d*
Nenthead, field based pilot bioreactor(Jarvis et al., 2014)	Cumbria, UK	2.2	730	68	0.9
Luttrell system, single cell bioreactor (ITRC, 2013; Hiibel et al., 2008)	Montana, USA	205	1095	99	1.45
West Fork Unit, settling / anaerobic ponds active lead mine (Gusek et al., 1998)	Missouri, USA	0.36	180	80	0.63
Burleigh Mine, up-flow bioreactor (USEPA, 2002)	Colorado, USA	57	1460	56	3.40
Burleigh Mine, down-flow bioreactor (USEPA, 2002)	Colorado, USA	57	1460	65	3.93
Cadillac Molybdenite bioreactor / oxidation pond & ALD (Kuyucak, 2006)	Quebec, Canada	1.35	420	99	0.11
Cwm Rheidol field based pilot bioreactor. Unpublished data, Newcastle University	Wales, UK	12.75	750	63	2.07
Palmerton pilot unit, smelter drainage bioreactors (Dvorak et al., 1992)	Pennsylvania, USA	317	126	100	9.58
Dalsung Tungsten Mine pilot bioreactor (Cheong et al., 1998)	South Korea	11.4	118	84	2.40
Standard Mine superfund site, Biochemical reactor (Rutkowski, 2013; Reisman et al., 2008)	Colorado, USA	24.7	1230	100	11.20
Haile Mine bioreactors (2no.) / wetland (ITRC, 2013)	S. Carolina, USA	1.8	1642.5	95	0.02
Lady Leith bioreactor and wetland (ITRC, 2013)	Montana, USA	0.75	3 visits in 2007	72	0.54
Active coal mine site, pilot bioreactor (Trumm and Ball, 2014)	New Zealand	6.3	141	100	5.40
Galkeno adit, United Keno Hill Mines wetland http://technology.infomine.com	Yukon, Canada	25		72	0.64
Force Crag bioreactors (this study).	Cumbria, UK	3.26	365	95-99	1.90

Life cycle costs

Passive treatment systems, while typically entailing relatively low initial outlay costs, have been shown to form wastes which are costly to dispose of. It has been suggested that active bio-chemical approaches, where chemicals and/or power are required in the treatment process, are preferable due to their ability to recover metals, rather than generate wastes (Johnson et al., 2006). At Force Crag, however, just 5.8t of zinc would be recoverable from mine water over 10 years, worth a modest € 7600 at current prices (LME, 2015). Considering the cost differential between a relatively low-cost active treatment system and a passive system over 10 years is € 1.8M, the financial case for passive treatment remains strong for sites such as this.

Regardless of the low-cost nature of passive treatment compared to active, waste disposal costs are still expected to be substantial, amounting to € 0.85M every 10 years at Force Crag, at current prices. De-contamination of substrates so that they can be re-used either in the treatment system or elsewhere, with disposal of a low-volume of contaminated material would therefore be preferable. Typical costs for a soil washing system (using acid leach and particle size separation as determined by Bailey et al. (2015)) have been determined as € 56/t, equating to € 58,810 for 1055t substrate at Force Crag. Additional costs which are associated with plant mobilization (estimated at € 9910) and disposal of residue (€ 85,030 - assumed to be 10% of initial substrate mass, as hazardous waste) brings the total cost to € 0.16M, at current prices. The costs in Table 2 have been discounted at 3.5% to determine the 10 year life-cycle cost, including substrate washing and replacement at the end of this period. Over 10 years, the life-cycle costs of treatment are reduced from € 1.63M to € 1.12M, substantially outweighing the 10 year cost of active treatment by HDS of € 3.41M.

Table 2 Construction and operational costs of active and passive and passive with waste reduction by soil washing at the Force Crag site

	Active treatment by HDS	Passive bioreactor treatment	Passive bioreactor with waste reduction
Capital construction	€ 1,922,000	€ 873,300	€ 873,300
Operation (labour/power/maintenance)	*€ 134,370	*€ 12,400	*€ 12,400
Substrate washing	n/a	n/a	**€ 68,720
Sludge disposal	*€ 13,240	**€ 850,330	**€ 85,030
Substrate replenishment	n/a	**€ 36,200	**€ 36,200
Chemical reagent cost	*€ 25,360	n/a	n/a
10 year 3.5% DCF life cycle cost	€ 3,410,900	€ 1,630,500	€ 1,119,400

(*annual cost; **one off cost at 10yr)

In this financial forecast, provision is given to dispose of a metal rich filter cake, derived from the substrate washing process. Recovery of metals would, however, be a reasonable proposition, given that they would be in a concentrated form. At Force Crag, it has been estimated that substrates would contain 2.19% w/w zinc after 10 years. Metal recovery tests from a similar substrate to that used at Force Crag found that >95% recovery of zinc was achievable within 100 hours using 0.5M sulphuric acid (Bailey et al., 2015). Accordingly, if metals were concentrated into a filter cake ~10% of the mass of the starting substrate, it may be reasonable to expect a zinc content of >20% w/w. At these levels, the filter cake would be far more amenable to re-cycling than the waste substrate, provided that facilities are available to receive the material.

Conclusions

Data obtained from the Force Crag compost bioreactor treatment system show high performance, achieving 95-99% zinc removal across the system. Projections suggest that at current rates of removal, 21,520mg/kg of zinc will have accumulated after 10 years, although it is known that there are a number of mechanisms constraining system longevity. Inevitably, substrate disposal and replacement will be required; however costs can be high due to hazardous waste classification of these metal rich materials.

Analysis conducted in this case study shows that despite high waste disposal costs, passive treatment still offers value for money compared to active HDS treatment over a 10 year period. Nevertheless, substrate washing to concentrate metals into a filter cake could offer substantial life-cycle cost savings of € 0.51M on a € 1.63M project. Furthermore, additional savings may be achieved if the filter cake could be re-cycled to recover metals. Provision for substrate washing at passive treatment sites should be made accordingly, in order that operators are able to achieve these life-cycle cost savings.

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Metal Recovery from Mine Waters: Feasibility and Options - An Example Assessment from the Colorado Mineral Belt, USA

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Abstract

The high concentration of metals in some mine waters and increasing stringent environmental regulations has led land owners, mining companies, technology companies and even government agencies to consider the potential for metal recovery from impacted water. The Colorado Mineral Belt in the central USA presents examples where research and testing has been carried out to characterize metal loading and potential metal recovery from mine waters and mine waste.

Key words: Mine water, metal recovery

Introduction

This paper provides a review of the limitations that exist for metal recovery from mine water and focusses on case studies from the Colorado Mineral Belt. The Colorado Mineral Belt is a northeast-trending zone that extends from southwestern Colorado, USA, to the north-central part of the state. The Belt hosts numerous precious and base metal deposits within several different mining districts. Many of these deposits were exploited in the late 19th to mid-20th century and have left potentially substantial environmental liabilities in terms of soil, sediment, water, and ecological impacts. In the last four decades, considerable efforts have been put into developing remediation strategies to mitigate environmental impacts at some of these sites. These efforts are costly and, as a consequence, a number of mining sites have not been remediated and still pose an environmental risk. Mine water is currently being treated at several locations where high tracemetal concentrations are a concern. The same contaminant sources potentially represent an opportunity for metal production and an opportunity to mitigate environmental liability.

Mine Water Chemistry

Examples of some of the mining districts are listed in Table 1 along with the anticipated composition of their associated waters. Mine water chemistry is highly dependent on many factors such as ore deposit geology (e.g., mineralogy, element enrichments, host rock type/alteration, spatial zoning), mining methods, and climate.

Mine waters are typically described by $Ca\text{-}Mg\text{-}SO_4 \pm Al \pm Fe \pm HCO_3$ with a broad range in pH and metal content. In many cases, these waters contain metals at concentrations that could potentially impact the environment and downstream drinking water supplies.

Colorado geology reflects a series of mountain ranges and basins that are dominated by the Rocky mountains. These host many of the metal bearing mineral deposits and were formed during the Antler orogeny. A major focus of this is the Colorado Mineral Belt (CMB) that extends from the La Plata Mountains north of Cortez, in Southwestern Colorado to the centre of Colorado near Boulder (Figure 1). This area was a major source of metals in the late nineteenth and early twentieth century from which more than 780 t of gold and more than 1000 t of silver were extracted (Dorset, 2011).

The CMB belt is a northeast-striking zone hosted in a Proterozoic shear zone system with a suite of Laramide-aged plutons and related ore deposits (Tweto and Sims, 1963; McCoy, 2001). The belt lies within a geologically active zone that was initiated at the time of crustal accretion in central Colorado at least 1.6 billion years ago until the present.

Table 1. *Examples of deposit types and anticipated composition of their associated waters, Colorado Mineral Belt, USA (Plumlee et al., 1995, 1999)*

Mining District	Mineral Deposit Type	pH Range	Mine Water Composition Range (in mg/L)
Summitville; Red Mountain Pass; Red Mountain	Quartz alunite epithermal	1.5 to 3	Fe, Al, Mn = 100s to 1,000s; Cu, Zn = 10s to 100s; As, Cr, Ni, Pb, Co, U, Th = 0.1s to 10s
Cripple Creek-Victor; Eldora; Magnolia	Alkalic Au-Ag-Te veins	> 7	Zn = 0.01s ; U = 0.001s to 0.01s
Central City; Silverton; Creede; Bonanza	Polymetallic veins	Variable	Widely variable depending upon the base-metal sulfide, pyrite and carbonate content of the veins, the type and amount of wallrock alteration, and the location of the mine relative to spatially variable mineralization zones
Leadville; Breckenridge; Rico	Polymetallic vein/replacement	Variable	Widely variable. Vein ores in igneous intrusions produce highly acidic mine water with high levels of Fe, Al, Cu, Zn, Pb. Replacement ores in carbonate rocks produce acidic, Fe-, Pb-, Cu-, and Zn-rich water to near-neutral water that contains high Zn.

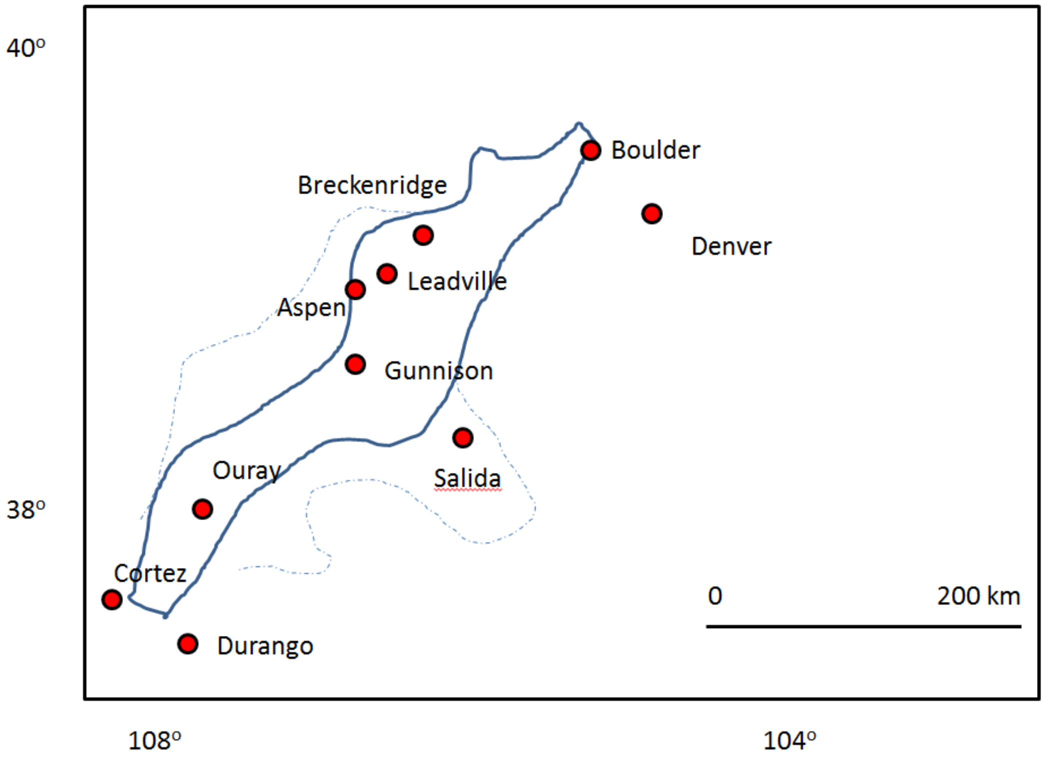

Figure 1: *Schematic of Colorado Mineral Belt (from Tweto and Sims, 1963). Area in solid is the main part of the CMB.*

Host rocks vary from Precambrian age through to Palaeozoic and Mesozoic. Igneous rocks were intruded about 60 to 70 million years ago during the Laramide orogeny. Some mineral deposits are spatial associated with these as well as with younger magmatic bodies of approximately 20-25 Ma in age (Cunningham et al 1994).

Options for Metal Recovery

Some options that exist for metal recovery include:

- Metal precipitation using biogenic produced hydrogen sulfide, such as in the SART, Paques or BioteQ systems;
- Copper cementation using copper reduction on iron metal;
- Direct electrowinning of metals from acid rock drainage (ARD);
- Ion exchange recovery directly from ARD;
- Direct solvent extraction and electrowinning (metals are extracted using conventional hydroxyoxime extractants, stripped using a spent electrolyte solution, and then electrowon in conventional cells);
- Solvent impregnate metal recovery as salts (such as in the Umatilla process) followed by stripping with spent electrolyte and electrowinning to produce copper metal; and
- Hybrid of ion exchange and solvent extraction with a two-stage recovery involving chelation using ion exchange resin and conventional solvent extraction and electrowinning to complete metal recovery (primarily copper).

Mine water treatment options typically employed to mitigate environmental clean-up tend to precipitate or remove metals as one or two products that generally cannot be economically refined to recover value. However, options do exist for selective removal of certain metals, particularly copper, zinc, silver, and uranium, based on existing metallurgical recovery processes. The most commonly applied of these are copper cementation, electro-winning and biological reduction of sulfate or sulfur to produce a metal sulfide concentrate. Initial testwork on mine waters from the San Juan mountains has shown potential for direct metal removal and application of solvent extraction, particularly for metals such as Cu, Zn and Cd, into a potentially economic precipitate.

Conclusions

Metal recovery from mine water could be a source of revenue to offset water treatment costs and at some locations may represent an economic project in its own right. A caveat exists, however, that even if the “ore potential” can be proven, and that the technology will recover economic amounts of metal, there may still be little incentive to “re-mine” many old mining districts. The is because new mining ventures may be held responsible for past mining legacies as well as any new disturbance, and the mere mention of metal value from these old districts might result in legal action from property owners or bankruptcy trustees who could lay claim to any recovered value.

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Long-term minimization of mine water treatment costs through passive treatment and production of a saleable iron oxide sludge

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Abstract

Passive technologies are generally the preferred post-closure treatment technology because of the potential for lower long-term costs than conventional chemical technologies. Passive systems produce solids and their management is often the primary long-term treatment liability. If the solids have valuable characteristics, their recovery and sale can produce income that offsets costs and decreases the long-term treatment liability. The Marchand passive system was constructed in 2006 to treat a high flow of alkaline Fe-contaminated mine water. The system has effectively decreased Fe from 70 mg/L to 1 mg/L, on average. The system accumulates approximately 420 ton/yr iron solids which accounts for about 7% of the system's volume. In 2012, 725 mton-solid of Fe sludge was removed and recovered in an on-site dewatering system. The cost to recovery the iron solids was $158/mton-solid. The dewatered sludge is being relocated and processed to a screened 60% solids product at an additional cost of $164/mton-solid. The processed solids are being sold as crude pigment. Other uses that value the purity and adsorption capacity of the iron oxides are being investigated. The presentation will describe these research projects.

Key words: passive treatment, iron oxide, sludge management

Introduction

Mine water treatment responsibilities often extend beyond mine closure and can represent a major economic liability. Passive technologies are generally the preferred post-closure treatment technology because of the potential for lower installation and long-term costs than conventional chemical technologies. Like all treatment technologies, passive systems produce solids and their management can be a significant long-term treatment liability. If the solids have valuable characteristics, their recovery and sale can produce income that offsets costs and decreases the long-term treatment liability.

The Marchand treatment system in Pennsylvania (USA) is a good example of the opportunity provided by passive treatment and solids recovery. For decades Sewickley Creek and the Youghiogheny River were polluted by Fe-contaminated flow from the abandoned Marchand Mine. In 2005 the Sewickley Creek Watershed Association (SCWA) obtained funding from the Pennsylvania Department of Environmental Protection to install passive treatment at the site. An aerobic system was installed that precipitates iron oxide sludge in settling ponds and polishes the water with a constructed wetland (Hedin 2008). The system has effectively retained Fe and contributed to the restoration of Sewickley Creek and the Youghiogheny River. The need to manage iron solids produced by the system was recognized during the design and features were included to facilitate sludge recovery and to assure that purity of the iron solids. In 2012 sludge was removed from three of the ponds. The solids were captured and are currently being processed for sale as iron oxide. This paper will describe the system's performance, sludge recovery efforts, realized and potential markets for the iron oxide product.

Methods

Water samples were collected from the influent/effluent of ponds and wetland and analyzed in the field for pH, alkalinity and temperature, and by a laboratory for Fe, Mn, Al, sulfate, acidity, and total suspended solids. All metal concentrations are total values, except on some occasions when a filtered (0.22 um) sample was collected for determination of dissolved Fe.

Solid samples were collected by hand from ponds or dewatering sludge. Moisture content was determined from the difference in weight of the fresh sample and one dried at 105°C for at least 4 hours. The resulting solid sample was stored in a sealed plastic bag to prevent rehydration. Samples of the solids were analyzed by Activation Laboratories LTD (Ancaster, Ontario, CAN) by the "4E-Exploration" package. Concentrations of 72 elements were determined by either instrumental neutron activation or ICP analysis of an acid extract of the solids (www.actlab.com).

Marchand Treatment System

The Marchand treatment system was installed in 2006 to treat a large discharge from an abandoned flooded underground coal mine. The system consists of six ponds arranged in series and a large constructed wetland (Hedin 2008). The ponds were constructed in native compacted soils that were covered with a geotextile fabric and 15 cm of aggregate to protect the purity of the iron sludge produced during recovery operations. Each pond was constructed with a ramp and sump in one corner to facilitate the placement and operation of a tractor-powered sludge pump. The wetland was constructed with native soils and planted with native wetland vegetation. The wetland does contain any features to protect the quality of the iron solids or to facilitate their removal.

Table 1 shows the average flow rate and chemistry for the system between 2006 and 2016. The influent mine water has an average flow rate of 7,088 L/min and contains 70 mg/L Fe. As water flows through the system Fe is oxidized and precipitated as iron oxide. The system lowers Fe concentrations to an average 1 mg/L (Figure 1). The final effluent has ranged as high as 6 mg/L (Figure 2) with higher concentrations typically observed in winter months when the wetland vegetation is reduced. The frequency of higher Fe discharge has increased in the last three years. This is attributed to the accumulation of Fe sludge (and decrease in retention time) and preferential flow paths that have developed in the wetland due to plant growth and animal activity.

***Table 1**. Average characteristics of the Marchand treatment system, Nov 2006 – Apr 2016.*

	Flow	**pH**	**Alk**	**Fe^{tot}**	**Fe^{dis}**	**Mn**	**Al**	**SO_4**
	L/min	s.u.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Influent	7,088	6.30	334	71.6	63.3	1.2	< 0.5	1,141
P6 Eff*	na	7.10	231	12.5	1.3	1.1	< 0.5	1,122
Effluent	na	7.75	217	1.1	0.1	0.5	< 0.5	1,163

* effluent from last (sixth) pond.

The system treats flow from an abandoned mine and the final discharge is not subject to regulated effluent criteria. If the system had a discharge permit, the final effluent would need to be have pH 6-9 with a maximum of 7 mg/L Fe and a monthly average less than 3 mg/L Fe. The system would satisfy these limits.

Table 2 shows the elemental composition of solids collected from the treatment ponds. The solids are approximately 95% iron oxide and are a mixture of amorphous ferric oxyhydroxides ($Fe(OH)_3$ and geothite ($FeOOH$). The major secondary elements are Si, Ca and C which likely represent the precipitation of quartz (SiO_2) and calcite ($CaCO_3$) and algal growth.

***Table 2.** Content of major elements in Marchand iron solids. Values are dry weight basis.*

Al	**C**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**P**	**S**	**Si**
%	%	%	%	%	%	%	%	%	%	%
0.2	0.7	0.6	52.6	< 0.1	0.1	< 0.1	0.1	< 0.1	0.2	0.9

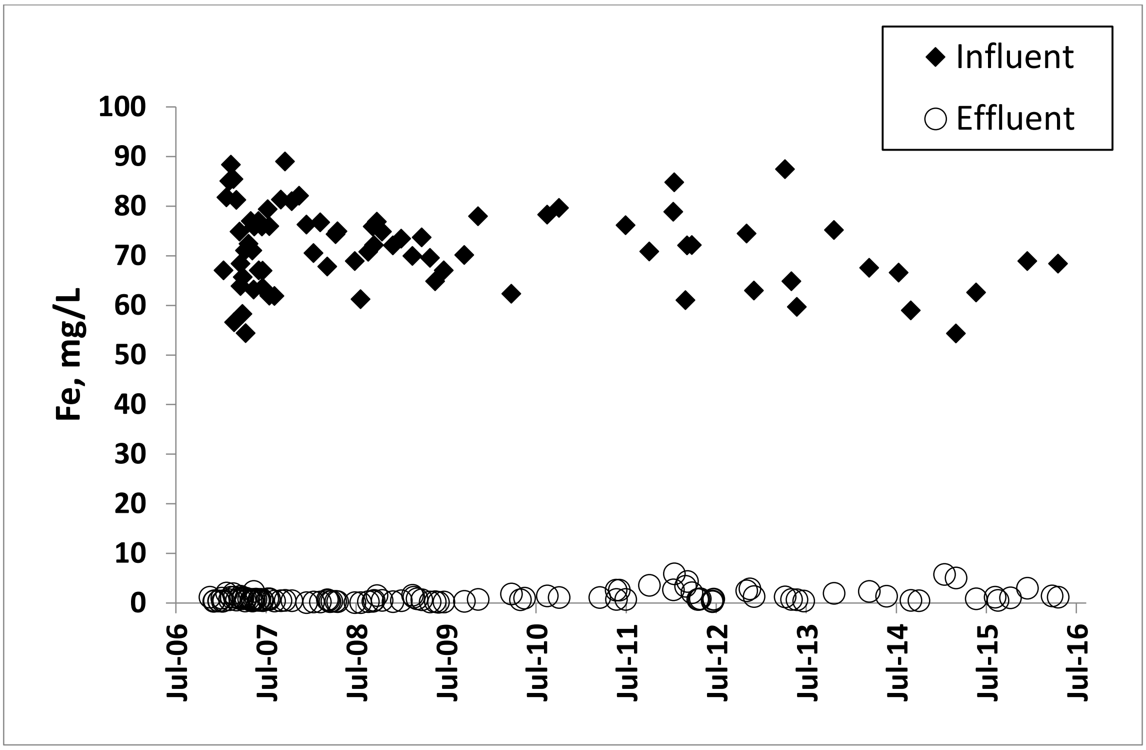

Figure 1 *Influent and effluent concentrations of Fe for the Marchand passive treatment system;*

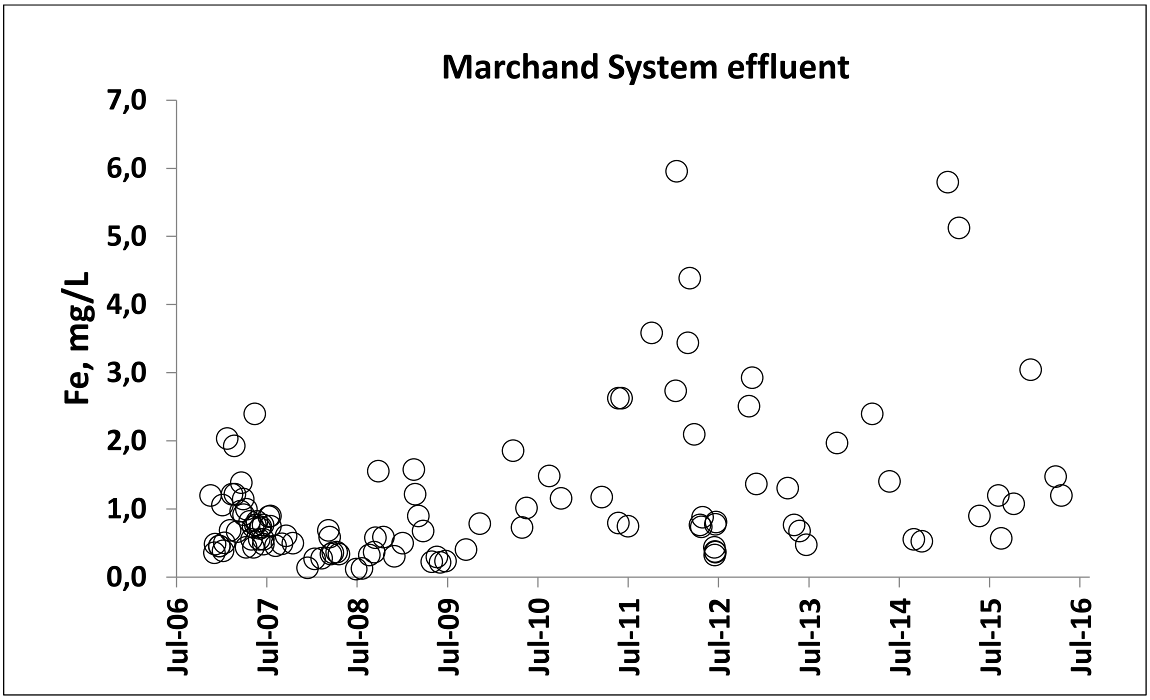

Figure 2 *Effluent concentrations of the Marchand passive treatment system.*

A common concern about the solids recovered from mine water treatment systems is the content of hazardous metals. Table 3 shows concentrations of hazardous metals identified in US EPA regulations. The significance of these metal concentrations will vary depending on the use of the iron oxide. In the case of iron oxides included in agricultural practices, the US EPA Part 503 Biosolids Rule provides metal limits (Table 3). The Marchand solids do not exceed any of the Part 503 limits.

Table 3. *Content of hazardous metals in Marchand iron solids. Restriction limits for US EPA Part 503 Biosolids Rule are also shown. Values are dry weight basis.*

	As ppm	**Cd** ppm	**Co** ppm	**Cr** ppm	**Cu** ppm	**Mo** ppm	**Ni** ppm	**Pb** ppm	**Se** ppm	**Zn** ppm	**Hg** ppb
Marchand	23	2.0	4	14	10	< 2	9	11	< 3	23	< 1
Part 503 limits	41	39	na	1,500	1,500	57	420	420	36	2,800	57

The ponds account for 59 mg/L (82%) of the system's total Fe removal. At 7,088 L/min, the ponds are removing 220 mtons of Fe/year and precipitating 419 mton/yr of iron oxide solids. Samples of the in-place sludge indicate a solids content of approximately 20% and a wet density of 1.2 kg/L. Averaged over all the ponds, iron sludge accumulates at a rate of approximately 8 cm/yr (depth). The ponds, which are 1.2 m deep, are losing approximately 7% of their volume each year due to iron sludge accumulation.

Recovery of Iron Oxide Sludge

In 2012 iron sludge was removed from the first three ponds of the Marchand system. For each pond's cleanout the process involved: 1) bypassing mine water around the pond; 2) removal of clear water overlying the settled sludge; and 3) slurrying and pumping of sludge out of the pond. At the Marchand site sludge was pumped into Tencate geotubes (http://www.tencate.com) which dewatered the sludge to 25-30% solids. The geotubes were cut open and the solids were stacked. Over time the sludge dewatered further to 40-45% solids. At other sites where sludge has been recovered from treatment systems it was pumped into specially constructed sludge basins which, because they are reusable, are less expensive than the geotube approach.

Table 4 shows the costs of installation and operation of the Marchand system. The costs are adjusted to current (2016) dollars using the US Bureau of Reclamation Cost Index for earthen dam construction. The system cost $1,212,770 to install in 2005/06. (This cost includes engineering, permitting, and project management by the owner.) Since 2006 system operation has required: 1) routine inspections and sampling, 2) repairs/upgrades, and 3) sludge removal. Routine monthly inspections are $5,000/yr. Upgrades had involved repairs to berms, cleanout of pipes clogged with iron sludge and debris, and the replacement of pipes with open troughs. As of 2016 all the pipes which were prone to plugging have been replaced with large open troughs that are easy to maintain.

Sludge removal costs are divided into pumping and capture/dewatering. All costs are expressed as dollars per mton of solid. The 2012 sludge pumping effort recovered approximately 725 mtons solid. The unit cost for sludge pumping was $59/mton and the unit cost for sludge capture and dewatering was $99/mton (both 2016 dollars). Based on experiences at other sites, the dewatering costs could be significantly lowered with the use of reusable sludge basin.

Sludge that has been dewatered to at least 45% solids is suitable for trucking to a customer or processing plant. Few customers are currently willing to accept a 45% solids unscreened product. IOR operates a processing facility where iron oxide is dried to 60-70% solids and screened to < 1 cm. This product is usable by customers. The cost to truck the sludge to the plant is $54/mton and the cost to process the material is $110/mton. The total cost to produce a 60-70% dry screened product from the Marchand iron sludge is $322/mton.

Table 4. *Costs for the installation and operation of the Marchand passive treatment system.*

	Realized Cost	**Cost in 2016**
Installation	$1,212,770 (2004)	$1,702,042
Capital Improvements		
Berm repairs	$15,000 (2010)	$16,515
New trough installation	$33,759 (2012)	$33,863
New trough installation	$22,000 (2016)	$22,000
Total Capital Costs		$1,774,420
Periodic Major Maintenance		
Sludge removal	$42,702 (2012)	$42,833
Sludge capture/dewatering	$72,073 (2012)	$72,294
Total Sludge Management	$114,445 (2012)	$115,127
Routine Operation and Maintenance	$5,000/yr	$5,000

Sales and Markets

Since 2000 Iron Oxide Recovery has sold 4,120 mtons of iron oxide. 92% of the sales has been as crude pigment. The remaining 8% has been for non-pigmentary applications. Approximately 600 mtons of the production was iron oxide recovered from ponds at the Marchand site prior to the construction of the treatment system. The remaining production was from five passive treatment systems and three sites where iron oxide had precipitated naturally from coal mine drainage.

Realized and potential markets for iron oxide recovered from mine drainage systems are discussed below

Pigment Iron oxides have pigmentary characteristics that that have been recognized and utilized for thousands of years. Two pigments are available from mine drainage solids. The raw iron oxide (goethite) is considered a yellow pigment while a calcined product (hematite) is considered a red pigment. These two pigments are used to produce the earth tone color palette. Iron oxide pigments are produced by mining natural deposits and synthetically by chemical processes. The market for iron oxide pigments is large (Tanner 2016). In 2014 the US consumed approximately 220,000 mtons of finished iron oxide pigments at an average value of $1,270/mton. Natural iron oxides are produced domestically and imported. Approximately 2,000 mtons of natural iron oxides were imported in 2104 at an average value of $520/mton. The Marchand iron oxide is generally considered a natural iron oxide. However, its purity and pigmentary strength are comparable to synthetics.

Hoover Color Corporation (Hiwassee, Virginia, USA) is a primary customer of IOR. HCC processes the IOR product to a 95% solids, calcined, milled red pigment that is used for blending and marketed specifically as EnvironOxide^{TM} (http://www.hoovercolor.com/products/pigments/type/environoxide/). The pigment's characteristics are particularly suited for wood stains and most of the dark wood stains produced in the USA contain iron oxide from mine drainage.

The pigment market is very competitive. Asian synthetic iron oxides are available in the USA for about $800/mton. Finished synthetic iron oxide pigments cost $1,500-2,000/mton.

Control of Soluble Phosphorus The release of phosphorus (P) from land-applied manure is a common water quality problem. Iron oxide decreases the mobility of P through sorption and the formation of ferric phosphate. IOR has recently cooperated in research into the use of mine drainage solids to lessen the solubility of P in land-applied manures (Sibrell et al 2015). Amendments of 6-10 g/L of iron oxide (solid) to dairy and swine manure decreases soluble P by at least 50% in both laboratory and field trials. This use of mine drainage solids may be restricted by environmental policies that define mine drainage solids as industrial wastes and prohibit their use in agricultural activities. Analysis of the mine drainage solids for hazardous metal content is necessary before this use can be considered (e.g., Table 3).

Control of Hydrogen Sulfide Iron oxide is useful for the control of hydrogen sulfide (H_2S) through its ability to inhibit activity by sulfate reducing bacteria and through its reaction with H_2S. H_2S production in manure storage facilities can create hazardous air quality conditions. Recent research at Pennsylvania State University found that Marchand iron oxide completely suppressed H_2S production in gypsum-amended dairy manure. Iron oxide is used to remove H_2S from natural gas. Sulfurtrap^R is an iron oxide based H_2S scavenger used in a fixed bed technology (http://www.chemicalproductsokc.com/h2s-scavenger).

In H_2S applications the Fe^{3+} content of the iron oxide is of primary importance. Iron oxides produced from mine water have a very high Fe content (Table 2) and application into this market will probably be driven by price competition with synthetic iron oxides.

Control of Selenium Release by Mine Spoils Selenite and selenate both sorb to iron oxides. As a result, Se is only a problem in the eastern USA coal fields where there an absence of Fe in the drainage. A recent experiment by Donavan and Ziemkiewicz (2014) showed that amending Se-rich coal refuse with iron oxide obtained from mine drainage significantly decreased the release of Se in drainage.

Treatment and Stabilization of Hazardous Metals Iron oxides readily adsorb hazardous metals and lessen their solubility in water and environmental mobility in soil environments. Iron oxides are especially good sorbants of arsenate (Daus et al.2004). Lanxess Corporation sells an iron oxide media for the treatment of As-contaminated waters (http://bayferrox.com/en/products-applications-bfx/industries/water-treatment/).

Iron oxides can stabilize hazardous metals in soils. Liu et al (2014) amended metal-contaminated soils with mine drainage iron oxide solids and found significant decreases in the availability of Cd, Cu, and Zn. Iron oxide is component in TRAPPS amendment system which is used to decrease the mobility of Pb in contaminated soils (http://www.slateruklimited.co.uk/trapps_firing_range.html). Iron oxides recovered from mine drainage perform as well as commercial grade iron oxides and provide a significant cost advantage because it is feasible to use a 60% solids screened product.

Stimulation of Plankton Growth Fertilization of Fe-deficient oceans with iron oxide has been proposed as a method for stimulating plankton growth and sequestering carbon in deep ocean sediments. Fertilization efforts to date have mainly utilized ferrous sulfate which is rapidly oxidized to iron oxide after addition to the marine waters. The direct use of iron oxide should be feasible (Hedin and Hedin 2014). This application values Fe content. Ferrous sulfate is available for $100/mton which, at 20% Fe, is equivalent to $500/mton-Fe. The processed Marchand IO, at $322/mton, is equivalent to $610/mton-Fe.

Conclusions

Passive systems can effectively treat Fe-contaminated coal mine drainage. The long-term effectiveness of the systems depends on management of the iron sludge that is produced. The Marchand passive system has operated for 10 years and has gone through one sludge recovery effort. Costs were carefully monitored. The cost to recover and dewater iron sludge on site was $$158/mton-solid. This cost can be decreased with more efficient dewatering processes. The cost to process the dewatered sludge to a screened 60% solids product was $164/mton-solid. The total cost to produce a marketable product was $322/mton-solid. The iron oxide product is currently being sold to a pigment company who processes it into finished earth-tone pigments. Other applications of iron product that have been researched or tested on a limited scale are: control of soluble P in animal manures; control of H_2S production in manures storage facilities; removal of H_2S from natural gas; and treatment/stabilization of metal contaminated waters and soils.

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An overview of the use of Ion Exchange to extract wealth from mine waters

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Abstract

This paper provides an overview of the potential for recovery of value from contaminated mine waters and waste streams. It discusses various metal ions commonly found in acid mine drainage and other mine waters (mainly Co, Ni, Zn, and U) and evaluates at what concentration they become attractive to investigate for recovery using ion-exchange technology. Waste streams are often treated to achieve compliance with environmental legislation before discharge, but recovery of valuable materials from acid discharge waters can result in economic benefits as well; in certain cases, the recovery of such metals can actually cover the cost of capital and operation and provide an additional revenue stream to the mine. The economics depend on the nature of the valuable metals, their concentrations, and volumes required for treatment.

Ion exchange is well established in mining and metallurgical processing as a primary purification technology, treating process streams in which the levels of valuable metals are relatively high. To recover these same metals from surface runoff, tailings, contaminated ground water or mine decant waters; they must be present at a certain level before it becomes worthwhile to fully investigate options for their recovery. We reviewed a number of valuable metals that are likely to be found in mine waters and, based on the capital and running costs, determined the capital payback period for varying contamination levels. Technical issues were discussed and their effect on the economics explored.

Using the model developed, it is possible to show early on in a feasibility assessment whether there is economic benefit to the processing of waste water of a given composition from a mining operation. The specific case studies that informed the model are discussed.

Key words: Mine water, ion exchange, metal recovery, modeling, economics

Introduction

Appropriateness of ion exchange

Ion exchange (IX) is a well-established technology in the hydrometallurgical field as both a competing and complementary technology to solvent extraction. The advantage of IX over other methods such as solvent extraction or even precipitation is that ion exchange can still be viable when feed concentrations have dipped below the economic threshold of the other technologies. It is interesting to note that in some cases the lower the total concentrations of metals in an aqueous stream, the more efficiently an IX resin can perform (Liberti, L. 1983).

The concentration at which a valuable metal is present in a feed water is the largest factor to consider with IX, but economy of scale, and global metal pricing must also be considered. Another aspect that must be taken into account when considering IX for any application is the competing ions in solution that may take up valuable capacity on the resin, such as iron, that will elute with the metal of value and lower the purity of the final product, and elements that may poison the resin, reducing the active sites available for exchange. These are all explored below with the aim of creating a basis for deliberation and initial economic viability for any potential value recovery from metal-containing mine or waste waters.

Composition of typical mine waters

Any given mine water can be broken down into the following constituents: value containing elements, hazardous elements, low value elements that will co-load, IX poisons, and elements of little concern with regards to the IX process. Generally we can consider first base metals (copper, cobalt, manganese, iron and nickel), lanthanides, precious group metals (PGMs), and sometimes uranium and vanadium to fall into the category of elements with economic value.

Because the source of mine waters can be so varied, and the composition of them so reliant on where in the process this waste has been produced or collected from, it has been difficult to give a rule of thumb for all potential applications. Elements that are most commonly found in mine waters that will negatively affect the performance of the resin include Fe3+, Hg2+, Pb2+ and Th4+. Especially when it comes to using an iminodiacetic resin (for base metal recovery), these elements if found at significant levels can be detrimental to a business case.

Organic load must also be taken into account, particularly when considering surface water for treatment. A pretreatment step is fairly simple to implement, but without it the resin may prematurely fail. For the most efficient ion exchanger plant, the IX media must be protected from suspended solids, organics, and oil and grease, which can coat the surface of the resin beads or create channeling and pressure drop issues. Generally, however, IX is robust and even when fouled, steps can be taken to restore the capacity.

Strong oxidizing agents are however more problematic, as they can de-crosslink the resin (an irreversible process), weakening it and causing it to lose capacity. Activated carbon pretreatment is sometimes effective in reducing the oxidation potential and damage to the resin.

This technology can be theoretically suitable to metal extraction from the majority of effluent streams, bleads, as well as mine and decant waters. Recovery of valuable materials from acid discharge waters can result in some economic benefits; in certain cases the recovery of these metals can actually cover the cost of operation and capital expenditure. The economics depend on concentration and flow rate and various impurities. These are discussed and an economic model is presented. Three case studies are discussed and used as a basis for these models.

Discussion

Metal Concentration

The first influencing factor on the economics to consider is the concentration at which a particular metal is present in a possible feed source. When the concentration of metals in a stream is very low, efficiency of removal by an IX resin is relatively high because at that point it is film diffusion rather than particle diffusion that limits the kinetics. Metal leakage is very low, and the operating capacity of the resin increases.

Based on modeling done (proprietary) for existing applications in the metallurgical field, a series of data was generated for base metal recovery by varying the feed conditions to a fixed bed ion exchange set up, graphed in Figure 1. The resin types and operating capacities were modified according to the targeted metal, and the co-contaminants were based on specific case studies.

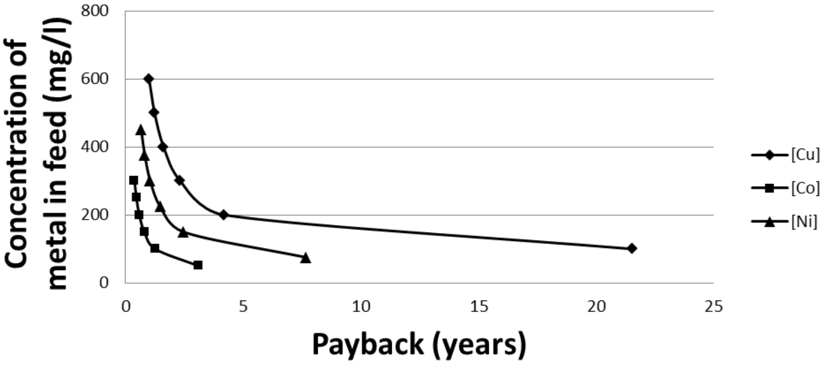

Figure 1 *Base metals- Payback as a function of the level of various metals present in mine waters (at a flowrate of 10ML/day) based on metal prices of: Co=\$22/kg, Ni=8.7\$/kg and Cu=\$4.5/kg (February 2016)*

It is important to note that where the concentrations are high, the rough guideline is that for levels above 1g/l, it may become more economical to investigate another technology, such as solvent extraction for recovery.

Two more examples are graphed below for Uranium and Vanadium (Fig 2 and 3). The chemical reagents, ion exchange resin, and calculated operating capacity have been modified for each example. The vanadium graph has been based on a case study with the aim of remediating vanadium leakage from a calcine dump. The vanadium is leached naturally by rain water and later by return of barren solution from the recovery plant.

Viability of this has been demonstrated at scale at Wapadskloof (4Ml/day heap leach & IX vanadium recovery plant) operational from 2006 until 2010 (Grobler, C. 2015)

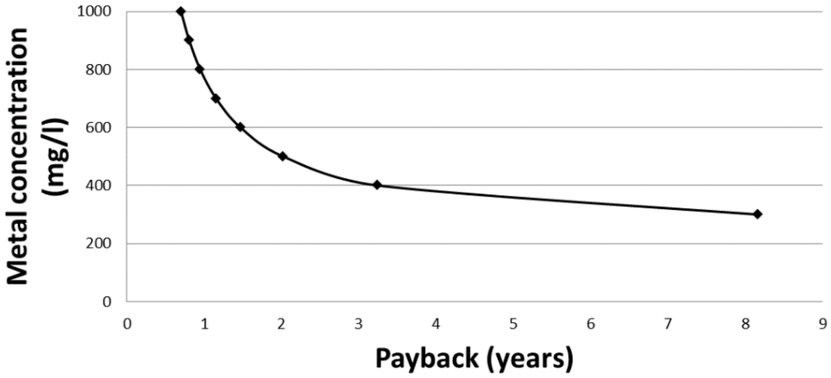

***Figure 2** Vanadium- Payback as a function of the level of various metals present in mine waters (at a flowrate of 4ML/day) at Wapadskloof based on metal prices of: V=$12/kg (April 2016)*

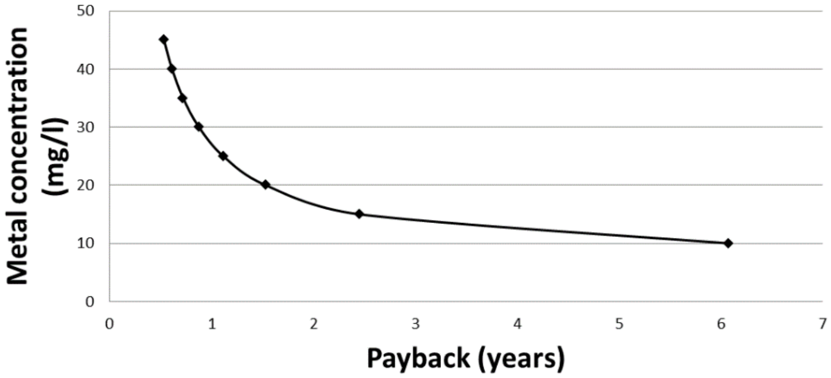

***Figure 3** Uranium- Payback as a function of the level of various metals present in mine waters (at a flowrate of 10ML/day) based on metal prices of: U=$60/kg (April 2016)*

The model used for the payback on uranium has been based on a number of different applications rather than a specific case study. Site specific issues will affect the payback period but the graph serves to illustrate where the recovery may be economic.

Uranium and vanadium are both considered to be serious environmental contaminants and the economics can sometimes be offset by the reduction in environmental impact. Although often viewed as a complication, they can both be recovered with relative ease using IX.

Flowrate / economy of scale

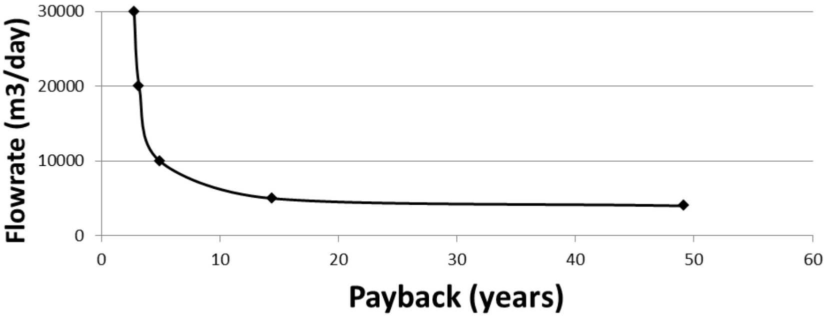

Figure 4 *Example of payback period as a function of flowrate for Chibuluma Mines PLC*

In Figure 4, a case study is represented (Hardwick, E. 2008). This particular example was modeled based on pilot work done at Chibuluma Mines PLC. The details of the case study, and some of the assumptions used for calculations are shown in Table 1, have been updated to 2016 figures. Assumptions on the costs of reagents are not detailed here. For operations smaller than 1Ml per day it is recommended that another model is produced to calculate payback. There are some cost-saving measures such as the utilization of GRP vessels that should be taken into account with small flowrates that have not been worked into this particular model.

Table 1 *Chibuluma Mines PLC, 2008. Full scale (10ML/day) calculations based on pilot scale testwork based on updated metal prices of: Co=$22/kg, Ni=8.7$/kg and Cu=$4.5/kg (February 2016)*

Metal Recovered (kg/Day)	
Co	264
Cu	3 215
Operating Costs as Percentage of Turnover	51%
Capital expenditure	$4 425 000
Plant Payback (Years)	4.9

Competing ions/ poisons

Competing ions and poisons are very specific to the type of resin used. The resin choice is often made on how suitable it is for the recovery of a specific element, but it is possible for water to contain trace amounts of other metals that have an even higher affinity to the resin functional group, thus taking up active sites and reducing the capacity of the resin for the element of value.

Iron, especially in the ferric form, is commonly found in metallurgical streams. Most common IX resins have a high selectivity for trivalent iron. The iron may displace the desired element and poison the resin over time. Aminophosphonic resins may lose useful capacity over a period of months and therefore become uneconomic. It is possible to use a resin with a lower selectivity for iron upfront of these resins to protect them. Alternatively iron may be removed by precipitation by raising the pH above 3 and filtration.

Radioactive elements when present may make the recovered metal unsaleable. An example is thorium in the recovery of rare earths (Hubicki, Z.). Thorium may be removed by precipitation or selective elution. Uranium can be recovered separately on a strong base anion resin (Botha, M. 2009). Radium may be removed using a strong acid cation resin (Clifford, D. n.d.), whereas according to Chemviron Carbon "Radon can be removed from water by adsorption on activated carbon but after the adsorption, a radioactive decay process follows, in which radon is transformed into lead 210, a radioactive material." (Ormshaw, D. 2012).

Metal price fluctuation

The concentration at which a metal becomes economically viable for recovery is heavily dependent on the sales price of the product produced. Metal prices have varied greatly in the past, and their movements can be unpredictable. Below is a study done on the effects of LME shift on the economic tipping point of these types of applications, focusing on copper, cobalt and nickel as examples. It should also be borne in mind that the quoted LME prices are going to be higher than those obtained as a selling price. The form of the metal product (such as carbonate) is likely to affect the price. In cases where the recovered product can be returned to process, the full value may be obtained.

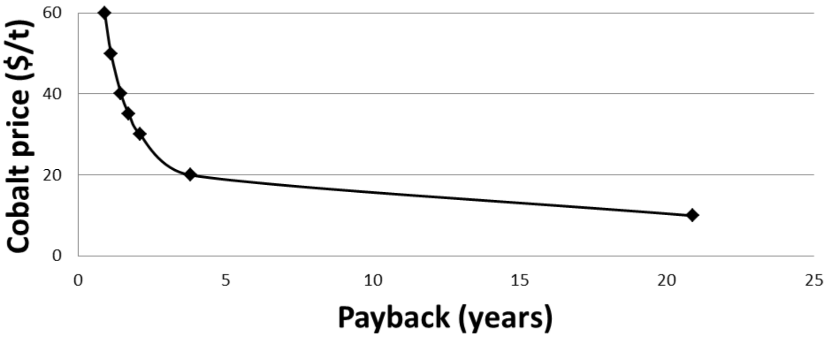

Figure 5 *Example of payback period as a function of metal pricing (Co) where concentration of Cobalt in the feed is 50ppm, Flowrate 10Ml/day [Zambian cobalt refinery]*

Figure 5 shows the effect of London metal exchange (LME) pricing on the economics of a prospective project, specifically for the case of cobalt. The assumption is that it is possible to extract 80% of the cobalt, with a conservative 20% allowance for downtime, and a product sale of typically 65-70% of LME.

Similar graphs can be created for other metals of interest, bearing in mind that the recovery percentage will be determined by the factors discussed, as well as the selectivity of the resin for the particular element, and operational factors.

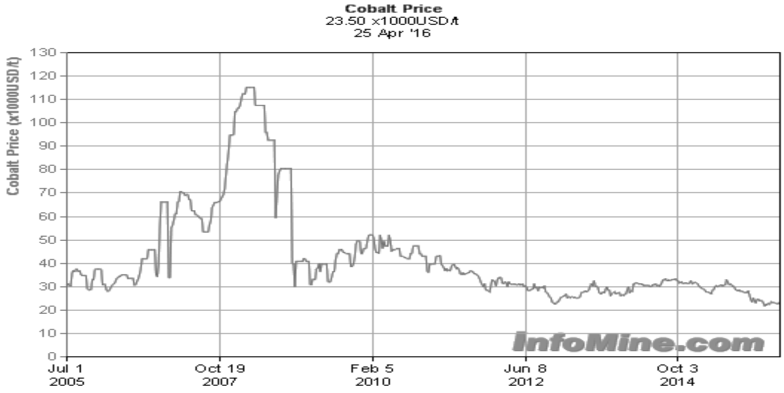

Figure 6 *Cobalt metal pricing fluctuation over 2005-2015*
Courtesy of infomine.com (Infomine Inc., 2016)

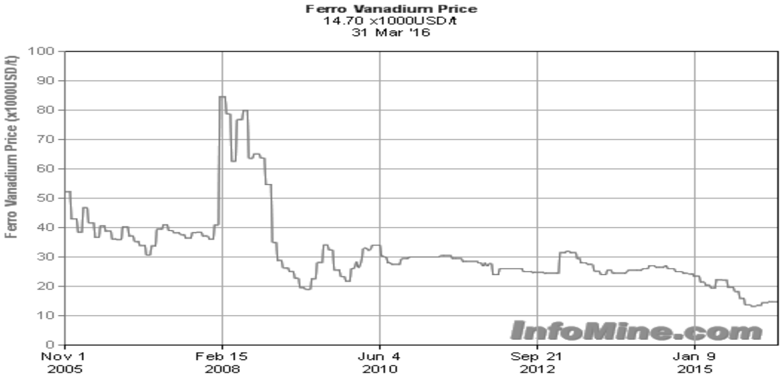

Figure 7 *Vanadium metal pricing fluctuation over 2005-2015*
Courtesy of infomine.com (Infomine Inc., 2016)

Metal prices over the last 10 years show a strong downward trend (Fig 6 and 7); however even at their lowest point metal recovery can be economic at sufficient flow and concentration.

Conclusions

Very often waste streams from mines are considered as problems rather than opportunities. In some cases it is clear that such opportunities are worthy of further attention. In addition to the advantages to the environment there is also an economic return. When looking at trends, particularly over periods longer than 5 years, the metal prices are invariably downturned. Because of this depression in metal pricing, there have been operations that have become less economical, even for relatively high concentration streams. The recovery of metals in waste steams can improve the overall yield of a metallurgical processing plant, and return it to economic viability. Ion exchange can be economic where other technologies cannot be, and it is worth considering a stream for treatment even at reasonably low concentrations of desirable metal.

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Membrane Electrolysis – A promising Technology for Mine Water Treatment, Radionuclide Separation, and Extraction of valuable Metals

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Abstract

Membrane electrolysis processes can be appealing alternatives to other mine water treatment processes, especially for the selective separation and recovery of pollutants. The RODOSAN® process was developed for the simultaneous separation of sulfate and heavy metals and generation of buffering capacity. The process has been tested on a pilot scale and currently allows for sulfate separation at efficiencies of 40% to 60% with quantitative elimination of heavy metals. Sulfate is converted to ammonium sulfate, which can be used as a fertilizer. The regeneration processes have been optimized to allow more highly mineralized water to be treated in industrial membrane electrolysis cells without any process disruptions. Separation of radionuclides and valuable chemical elements from mine water, deep geothermal water and formation water is also possible using this process platform.

Key words: membrane electrolysis, sulfate removal, heavy metals, radionuclides, pilot tests

Introduction

Acidic, sulfur-rich, heavy metal-loaded mine water, or acid mine drainage (AMD), is a problem in lignite, bituminous coal, and sulfide ore mining operations around the world. If such water is allowed to flow into receiving streams without prior treatment, it can render them unsuitable as drinking or process water resources. Particularly in regions with low water availability, this can lead to massive water supply problems. Such large-scale problems are already known to exist e.g. in Chile, Peru, and South Africa. The semiarid and arid copper mining regions of Chile, for example, consume approx. 30 m^3/s water for ore processing with the greater part being contaminated, which significantly impacts the water quality in the receiving streams (COCHILCO 2015).

The water quality of numerous streams in the watershed area of the Elbe river is also strongly affected by continuously high salt loading. Mineral weathering (pyrite oxidation) also occur over wide areas, resulting in highly loaded groundwater that is unfit for use as drinking or process water. The situation is particularly worse in some regions of Central and Eastern Germany, where centuries of extensive mining have left their mark and where mining operations are still expected to continue to a lesser extent over the next few decades. In part high inflows of primarily sulfate-rich water from the Lausitz and Central German lignite fields, the former ore mining regions e.g. of the Erzgebirge, and numerous others into the receiving streams are related to this, and even problems with sulfate concentration in drinking water in the german capital of Berlin can be traced back to it.

For some time now, this manifest water contamination has been resulting in demands for technical measures for limiting sulfate emissions. For water impacted by ore and bituminous coal mining operations, separation of heavy metal ions, naturally occurring radionuclides, and arsenic is being brought into focus. Conditioning of formation water and geothermal fluids in connection with the so called borehole mining is also gaining attention. These fluids often contain recoverable metals. Different approaches for developing membrane electrolysis methods for treatment of this water are reported below.

State of the Art and Current Research and Development

In Germany and in numerous other countries, the state of the art in treatment of mine water from coal and ore mining operations remains treatment by neutralization with lime and iron/aluminum precipitation. Sulfate normally cannot be separated to any significant extent because the solubility product for gypsum is usually not exceeded. Hardening inevitably occurs. Numerous other methods and approaches have been developed for treating mine water, but only a few are being used under specific application conditions. Hence, they will not be discussed further here. Besides lime precipitation, precipitation with barium salts, as schwertmannite, or with aluminates has been proposed (e.g., Wallhalla and SAVMIN process, Smit 1999). Apart from in part high process costs, the treatment and disposal of the sludge must be addressed. German BMBF has made considerable expenditures to drive the development of microbiological processes (passive and active processes). High-performance sulfate reduction according to the GEOS Freiberg process (www.geos.de) and autotrophic sulfate reduction according to the DGFZ process (F. Bilek et al. 2008) are in so fare at the most advanced stage of development. These processes have not yet been implemented industrially in Germany. Passive processes in the form of constructed wetlands are being implemented in practice to some extent (Eden Project, GB). However, they have the disadvantages of low space-time yields, poor controllability, and hence they are not compliant with the need to treat larger water volumes that are typical for domestic mining and remediation operations.

Membrane processes such as reverse osmosis, nanofiltration, and electrodialysis have also been suggested. Water of drinking water quality can be generated at the diluate side, but, depending on plant capacity, larger volumes of concentrate may arise and must be disposed of unless discharge to rivers of sufficient capacity is possible. The costs (excluding costs of disposal) are as high as or higher than for electrolysis at the current stage of development. Over the last few years Vattenfall Europe Mining has been working with BTU Cottbus on the development of elaborate downstream precipitation processes for generating recoverable/disposable products from such a concentrate fraction, but this has proven to be difficult.

With considerable funding from BMBF, a process for electrochemical treatment of this water was developed and optimized. Tests were then performed on a pilot scale with multiple process variations and different mine water sources mainly on behalf of LMBV mbH. A number of process disturbances arose, especially in the treatment of water with lime and gypsum supersaturation, but have by now been solved.

Working Principle of the Electrochemical Sulfate Separation Process (RODOSAN® Process)

In the Rodosan® process, raw water is feed into the cathode chamber of a membrane electrolysis cell. When a sufficiently high cell potential is applied, (sulfate) anions migrate through specially selected anion exchange membranes into the anode chamber, where they are concentrated and then converted to ammonium sulfate either directly or in a subsequent stage with aqueous ammonia. While oxygen is formed at the anode (peroxydisulfate formation is also possible), pure hydrogen is formed at the cathode and can be utilized as a secondary energy source. As a result, the sulfate becomes depleted in the cathode chamber, the pH-value increases, and hydrolyzable cations are precipitated. Depletion of aluminum, iron, and manganese to trace amounts occurs. Feed-in of CO_2 into the cathode chamber is a proven method for further sulfate removal (gypsum splitting). So hydrogen carbonate partially substitutes sulfate in this process. Figure 1 illustrates the working principle.

With this process, also wastewater with elevated chloride concentrations can be treated to produce chlorine, chlorate, etc.

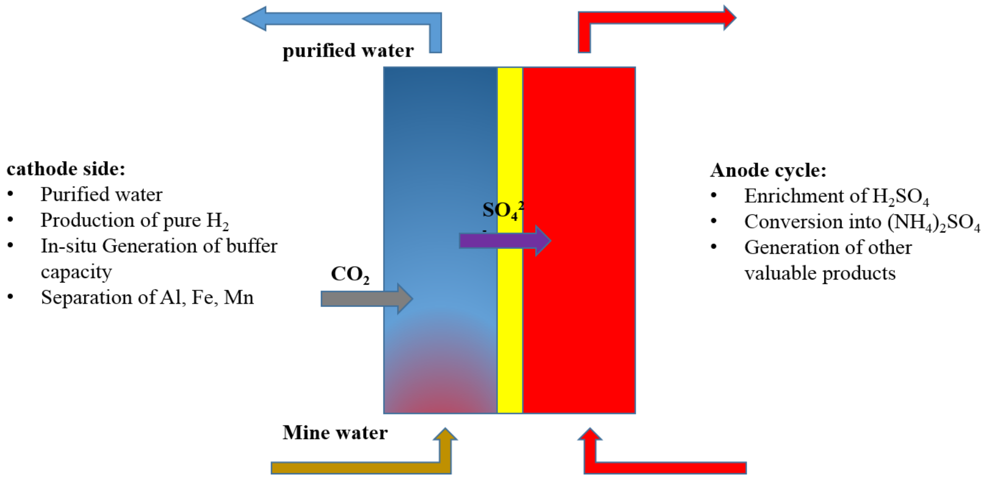

Figure 1 *Schematic diagram illustrating the working principle of the Rodosan® process.*

Figures 2 and 3 below show the membrane electrolyzers and the location of one of the pilot plant, respectively

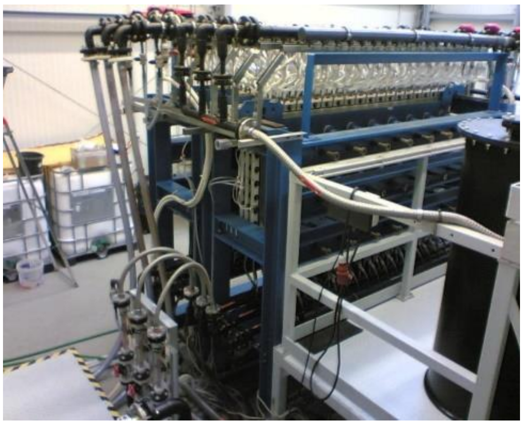

Figure 2 *Uhde®-type electrolyzer*

Figure 3 *Plant location*

The test facility capacity ranges from 2 m^3/h to 6 m^3/h, depending on the specific treatment objective and the starting hydrochemical parameters. Experience from around 20,000 hours of operation has been accumulated thus far.

Applications and Results

In the pilot tests performed up to now, several different water types with differing hydrochemistries from the Lausitz and Central German lignite fields were used. A considerably number of other water types was investigated on the laboratory scale.

The decommissioned open pit at Sedlitz (Lake Sedlitz) is in the Lausitz lignite field; the Lake Bockwitz is south of Leipzig. Its water has been neutralized with soda. In the Tzschelln mine water treatment plant (GWRA Tzschelln), the sump water from the Nochten strip mine is treated by lime neutralization. The parameters given in Table 1 apply to the plant process. Remarkable is the very high calcium content of the Tzschelln water after lime neutralization, which initially caused significant problems regarding process control.

Table 1 *Hydrochemical data for treated water from strip mining operations.*

Parameter	Lake Sedlitz	Lake Bockwitz	GWRA Tzschelln
pH	3.15	5.8	7.6
K_b7.0 (mmol/L)	1.6	0.5	-1.4
Cl^- (mg/L)	35.7	22	16
SO_4^{2-} (mg/L)	890	1060	1880
Al^{3+} (mg/L)	2.3	0.3	0.02
Fe_{total} (mg/L)	10.3	0.22	0.03
Mn^{2+} (mg/L)	1.9	0.9	2
Ca^{2+} (mg/L)	166	263	630

Figure 4 shows the mean sulfate removal ("dSO4") values and the volume-specific energy consumption ("Espez-V") values for electrochemical treatment of the water sources listed in Table 1.

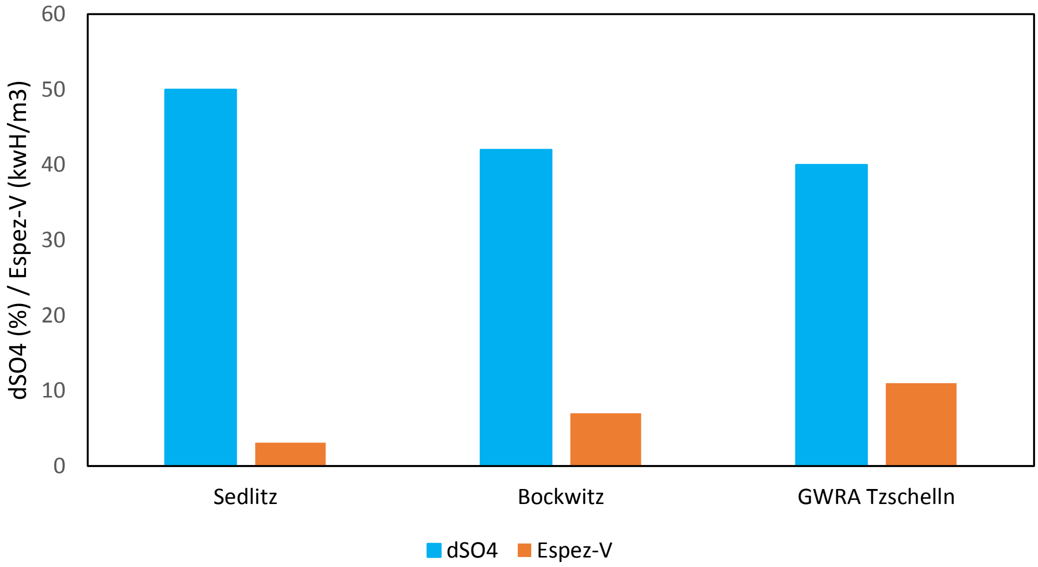

Figure 4 *Sulfate separation and specific energy consumption*

Sulfate separation efficiencies of between 40% (GWRA Tzschelln) and > 50% (RL Sedlitz) and specific energy consumption values of between 3.1 kWh/m^3 and 11.3 kWh/m^3 were obtained in continuous operation. Sulfate separation is hence a relatively energy-intensive process. Aluminum, iron, and manganese are removed down to trace amounts. At the same time buffering capacity (3–10 mol/m^3) is generated during treatment.

In a further test series with water from GWRA Tzschelln, regeneration processes were optimized for the cells ("opt. regeneration") and a modified internal cell design ("opt. cell") was tested. This enabled stable process control with sufficient technical availability and led to a considerable decrease in the specific energy consumption (Figure 5) of nearly 40% (given as E relative), extending the applicability of the process to include treatment of more highly mineralized water.

With industrial use of the process, economically relevant amounts of coproducts are generated, as shown in Table 2. The values are based on a plant throughput of 0.5 m^3/s for the given water sources.

Table 2 *Coproducts generated in the treatment of 0.5 m³/s of each of the mine water sources and electrical power consumption values*

Parameter	RL Sedlitz	RL Bockwitz	GWRA Tzschelln
dSO_4 (%)	50	42	42
$(NH_4)_2SO_4$ (t/year)	7,800	9,600	15,300
H_2 (millions of m3/year)	1.7	6.0	8.5
P_{el} (MW)	5.4	12.5	14.0

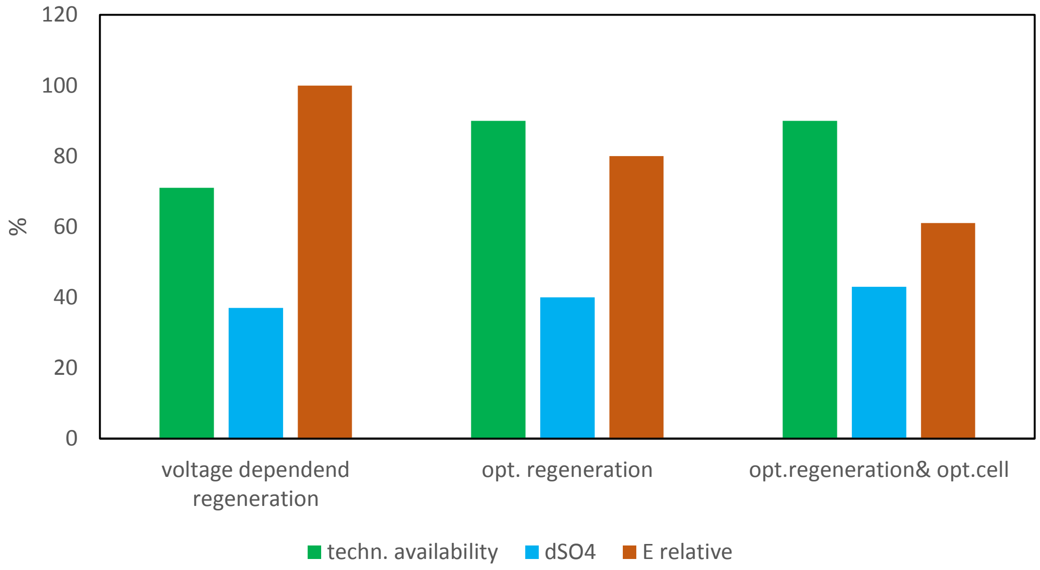

Figure 5 *Performance improvements resulting from optimization of the regeneration process and the cell*

The generated ammonium sulfate solution can be used as a fertilizer (if necessary, after further concentration). Tests are currently underway to determine its suitability as a fertilizer. Hydrogen is available as a secondary energy source. Because the plants can be operated flexibly, they could find use as buffer elements in energy supply networks.

With membrane electrolysis, heavy metals and radionuclides can also be removed efficiently from water. In the case of hydrolyzable cations ((Al), Fe, Mn), this occurs when the pH is raised in the cathode chamber. In laboratory tests with highly acidic mine water, it was shown that uranium and thorium could also be effectively removed (Table 3).

Table 3 *Separation of uranium and thorium during membrane electrolysis of acid mine drainage*

Parameter	Inlet	Outlet
UO_2^{2+} (mg/L)	12.4	0.28
Th^{4+} (mg/L)	0.21	< 0.005

Thorium is precipitated hydrolytically in the form of highly insoluble thorium hydroxide. In the case of uranium, overlapping of the coprecipitation of uranium and any iron present and precipitation as UO_2 following reduction of the uranyl cation in the cathode reaction occurs. Electrochemical kinetic investigations were performed to confirm this.

A modified version of the process was developed for separation of toxic heavy metals and radionuclides from highly saline waters such as are (co)extracted in geothermal plants at great depths or during natural gas extraction. Heavy metals contribute decisively to scaling; elimination of radioactive Pb-210-

containing scales is especially cumbersome. Treatment (conditioning) of the geothermal brines or formation water is a promising method for avoiding these problems, particularly in the case of Pb-210.

The process variant developed for this purpose differs from the previously described process primarily through the fact that precipitation occurs in a purely galvanic process. Further changes in the chemistry of the hydrochemical system are undesired and are avoided through appropriate membrane selection (e.g., cation exchange membranes instead of the normally used anion exchange membranes) and careful adjustment of mass transfer between anode- and cathode compartment.

The test equipment shown in Figure 6 was developed for practical testing on a small pilot plant scale under in situ conditions (approx. 100 °C and 10 bar).

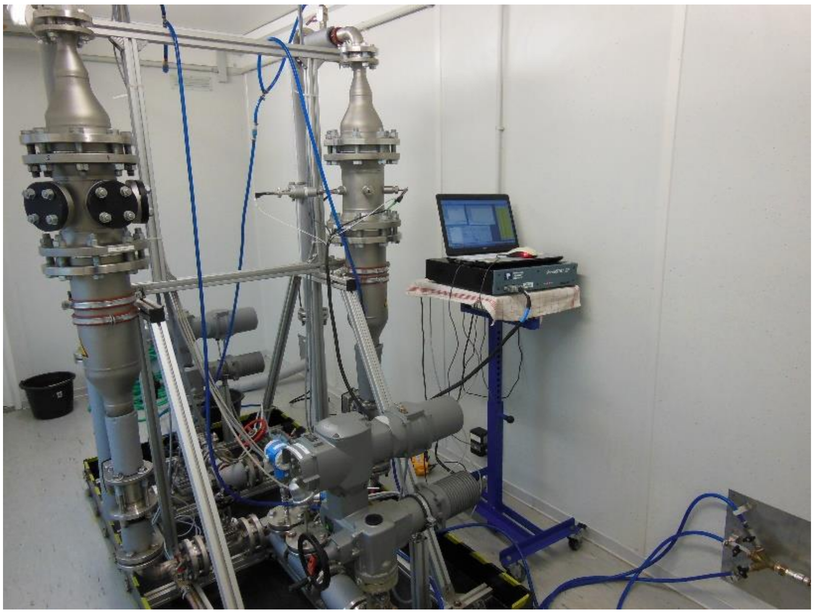

Figure 6 *Test bench for in situ precipitation from geothermal brine*

The test results obtained up to now show that both Pb-210 and other heavy metals can be separated with high efficiencies (Figure 7). Very short residence times are sufficient for precipitation of Pb-210.

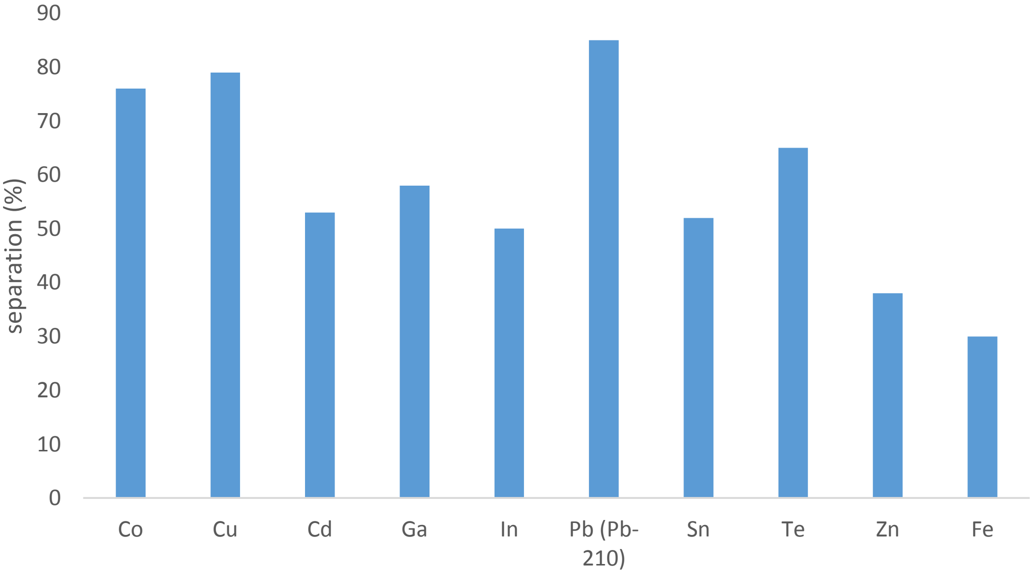

Figure 7 *Separation of heavy metals from geothermal brine – borehole GSB1*

The dominating factors for successful precipitation appear to be the residence time and the cathode material. Especially in the case of precipitation of Ga (and Tl), the cathode material may have to be chosen extremely carefully. Current efforts are being directed at optimizing the process on a pilot plant scale.

Conclusions

Electrochemical membrane processes are a promising technological route for environmentally sensitive treatment of mine waters or for conditioning of geothermal brines and formation water. They allow for at least nearly waste free operation and are capable to process greater water volumes due to the modular system design. Nevertheless energy consumption and costs of equipment should be reduced further to enable broader practical use. This are the main topics of current R&D.

Acknowledgements

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Experimental determination of process parameters for mine water treatment and permissible utilization of the iron-rich residues

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Abstract

Addressing the objective of designing and sizing the technological steps of a mine water treatment plant to be built, the procedures and major results of determining relevant process parameters from experimental process simulation are described in this work. This approach includes generation of expectations from thermodynamic modeling, pre-experiments for designing and sizing of experimental setups, estimation of upscaling factors and task-specific reactor experiments along the process chain of mine water oxidation, neutralization, flocculation, sedimentation, dewatering and re-use of residues. By testing different types and doses of coagulants, coagulation aids, and orders of dosing, a new treatment sequence was found to provide the best iron elimination result. Based on the process parameters, the technical components of the treatment plant and the volume / mass of residues were sized and a permissible alternative for re-use of the iron hydroxide loaded residues (EHR) proposed.

Because emplacement of such alkalinity loaded residues within mining dumps appears licensable and is already practiced at a lignite mine nearby, a series of reactor experiments was performed to investigate the interaction and fate of EHR embedded within tertiary overburden sands for scenarios of simulated groundwater recharge and rerise. The results show that the carbonate alkalinity in EHR effectively buffered acidity stored or generated by pyrite weathering in the overburden sands, thereby thwarting acid dissolution of EHR. The output of acidity, sulfate, Fe^{2+}, and heavy metal ions from test reactors was lower than from EHR-free control reactors, and lowest when mixing EHR with the overburden substrate. The overall results neither indicate chemical dissolution of EHR nor suggest favorite conditions for microbial iron reduction.

Key words: Process simulation, mine water treatment, residue utilization, groundwater recharge / rerise

Introduction

Mine waters usually require treatment to comply with regulatory threshold values for discharge into public streams. For the expansion of an open-cast lignite mine, a new mine water treatment plant had to be planned. The task was to design and size the technological treatment steps to fulfil the official thresholds for discharge quality: pH 6.5–8.5, dissolved oxygen (DO) >5 mg/L, total suspended solids (TSS) <30 mg/L, total iron (Fe-tot) <1.5 mg/L, dissolved iron (Fe-diss) <0.2 mg/L. This contribution demonstrates a feasible approach of determining critical parameters from experimental bench-scale and mesoscale process simulation to select ideal additives and arrange and size the treatment steps. A second objective was to propose alternatives for permissible utilization of treatment residues loaded with iron oxy-hydroxides (termed EHR). Based on authorized practice at an operating treatment plant, lab experiments were designed to investigate interactions and fate of EHR buried together with tertiary overburden sands in deep mine dumps for the scenarios of groundwater recharge and rerise.

Methods

To address the first objective, a step-wise process simulation workflow was developed including

- Comparison of actual mine water quality data with forecast values,
- Characterization of relevant mine waters, selection of a *typical* and a *worst-case* test water;
- Pretests and bench-scale simulation experiments for single treatment steps (oxidation, neutralization, flocculation, sedimentation);
- Combination of treatment steps in a mesoscale experiment, collection of EHR for dewatering;
- Refinement of critical treatment steps, estimation of an upscaling factor;

- Gross design and sizing of treatment process technology.

This contribution can only illustrate selected steps of this workflow to meet space limitations.

Based on the proposed licensable utilization of EHR, samples of tertiary overburden sand, deposited EHR, and deep groundwater were collected from the Schleenhain lignite mine to study the second objective. Soil physical and chemical properties and reactivity of test substrates were determined to size the load of substrates and arrangement of layers in the experimental reactors, operated according to intermittent-flow batch reactors by setups shown in Figure 1. This means one pore volume of test substrate was exchanged with test water at a flow rate of up to 1 m/d, followed by a 24 h rest to enable equilibrium with the hydraulically less active pore space. By applying eleven of such exchange-and-rest cycles during the experiment, and assuming a porewater flow rate of 0.2 m/d as an upper bound through a 30 m thick mine dump, the experiments would mimic fundamental chemical reactions over a period of at least 5 years. The simulation of slower microbial reactions was neglected for this test phase because organic carbon contents of the test substrates were very low. The collected reactor effluents were analyzed for pH, redox potential, acidity, alkalinity, inorganic (DIC) and organic carbon (DOC), sulfate, iron, and other ionic components. Total alkalinity and sulfur were balanced considering input, output, and change of reactor pools.

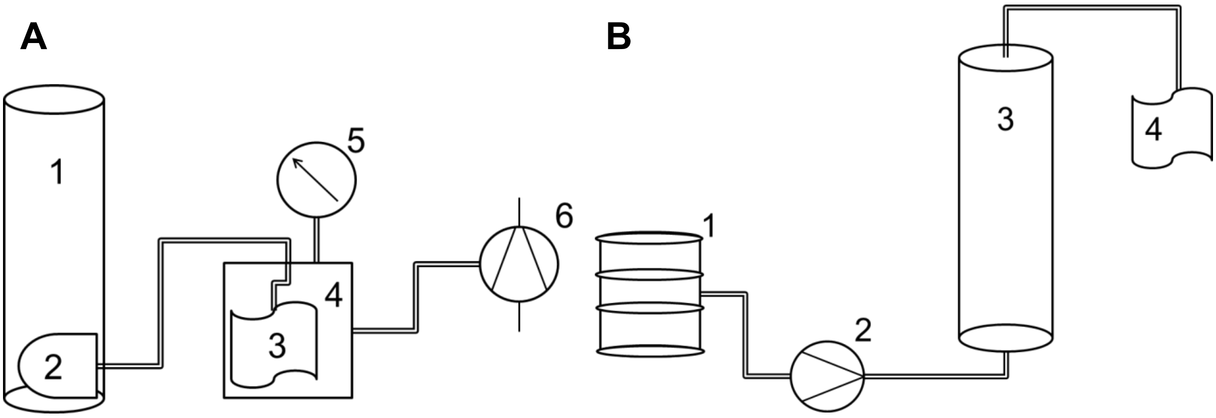

Figure 1 Sketch of experimental setups for simulation of (A) groundwater recharge: Open-top column filled with test substrate (1), vacuum porewater sampler (2) connected with Tedlar bag (3) stored in a pressure vessel (4) at which a vacuum pump (6) can induce low-pressure of 0.1 bar checkable by a gauge (5); and (B) groundwater rerise: Groundwater stored in a stainless steel vessel (1) is transferred by peristaltic pump (2) into a column filled with test substrate (3), and the effluent is captured in a Tedlar bag (4).

Only standardized and accredited analytical methods were applied, and all results were documented in lab reports. Open-source PhreeqC code with implemented database was used for thermodynamic process simulation.

Results of Treatment Process Simulation

Neutralization potential. In-situ acidity, alkalinity, and their change when reaching air equilibrium after complete oxidation and CO_2 exchange, were calculated with PhreeqC by stepwise precipitation of thermodynamically supersaturated mineral phases. Contrary to some other mining areas, intrinsic alkalinity of all test waters exceeded the acidity generated by hydrolysis of oxidized Fe(II) and Mn(II). Hence, a neutralizing step was unnecessary. Calcite precipitation was predicted to stabilize pH_{eq} of 7.8–8.0, while gypsum remained undersaturated. Batch titration experiments confirmed these results.

Oxidation kinetics and lime supply. Without technical aeration, the Fe(II) oxidation rate revealed $1 \cdot 10^{-6}$ M/h. Aeration with a gas flow of 17 L/h increased this linear rate to $1.8 \cdot 10^{-4}$ M/h. However, a 50 g/m^3 supply of slaked quicklime (CaO) led the Fe^{2+} concentration exponentially decrease below the target value within 30 min, mainly due to increased pH (Fig. 2). Assuming initially anoxic mine water with 10 to 50 mg/L Fe(II) and volumetric flow of 120 m^3/min, an air demand of 0.019–0.096 m^3 per 1 m^3 of raw water was calculated. To meet this demand, we proposed an appropriate number of spiral aerators to be arranged in the front part of the water processing channel. To determine the optimum quicklime demand for pH adjustment, the applicable dose range was first estimated by PhreeqC. Then, a series of individual batch experiments was performed with supply of 0, 6.1, 30.7, and 92 g/m^3 of slaked quicklime to the test water, which was aerated for 0, 5, 10, 20, 30, 60, and 90 min by a gas flow of 12 L/(L•h). After each time, the corresponding batch water was analyzed with respect to pH, O_2, Fe^{2+}, Ca^{2+}, and TIC. According to the results (not shown here), a quicklime dose of roughly 60 g/m^3 would ensure compliance with the official Fe-diss threshold value within 30 min. One of the test waters showed that this dose can even be reduced if the mine water contains sufficient particles with catalytically active surfaces.

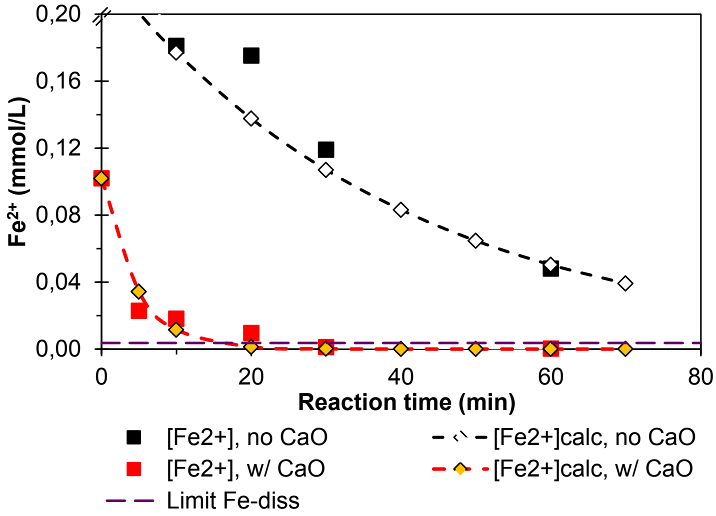

Figure 2 *Oxidation kinetics of Fe^{2+} in the absence and presence of slaked quicklime (CaO) for test water #2. Squares show analyzed data, curves are calculated from a kinetic rate law according to Singer & Stumm (1970).*

Coagulation and sedimentation. The aim of this treatment step was to select the most effective coagulation aid among three high-molecular anionic products that differed with respect to charge density. Initial volumes of test water were oxidized in the presence or absence of slaked quicklime. After splitting the pre-treated waters into forty 1 L glass cylinders, various doses of coagulation aid were added. Coagulation effectivity was determined by comparing the settling rates and the supernatant Fe-tot concentrations as a function of settling time. The combination of 60 g/m^3 quicklime with 0.06–0.12 g/m^3 coagulation aid with low charge density led to the most efficient removal of Fe-tot and the lowest TSS values of the treated test water. However, all test batches exceeded the Fe-tot threshold value of 1.5 mg/L. By the initial supply of coagulant, the mass of settleable solids increased by a factor of 2 to 3, due to enhanced settling of both Fe oxy-hydroxides and calcium carbonate.

Mesoscale process simulation. The aim of this experiment was twofold: (i) combine the single treatment steps into a mesoscale process to demonstrate the applicability, and (ii) gain enough EHR substrate for dewatering tests and analysis. The experiment was conducted in a 1 m^3 reactor for two test waters according to a detailed treatment plan: (i) filling the reactor, (ii) aeration for 40 min by gas lance, concurrent supply of 60 g/m^3 of slaked quicklime, (iii) short-stirred dosing of 0.06 g/m^3 coagulation aid, (iv) water quality monitoring over a 4 h settling period, (v) separation of settled residue, (vi) dewatering tests and analysis of EHR constituents. While the TSS concentration fell below the threshold value within 4 h of settling time, the Fe-tot concentration came close but missed the threshold value of 1.5 mg/L (Fig. 3).

Optimized iron precipitation. To further improve the efficiency of Fe precipitation, additional approaches were tested in batch experiments with 1 L glass cylinders:

- Supply of varied doses of additional coagulants prior to the supply of slaked quicklime, including a highly cationic organic product and a weakly cationic polyaluminum chloride (PAC). For the latter, an adjusted pH ~5.5 was tested in addition to the primordial pH condition. Fe-tot concentrations after 2 h of settling time did not go below the threshold value (Fig. 4).

- Test of a novel dosing sequence by split supply of slaked quicklime, with a dose of 12 g/m^3 into the oxidation step, and a dose of 48 g/m^3 into the flocculation zone *after* the supply of coagulation aid. The aim was to co-precipitate colloidal Fe(III) through initiated precipitation of calcite. Fe-tot concentration fell below 1 mg/L, thus fulfilling the official threshold value of 1.5 mg/L (Fig. 4). However, the TSS concentration exceeded the 30 mg/L threshold value by 60 %, due to delayed settling of calcite particles. This shortcoming can be compensated by a turbidity dependent dose rate control.

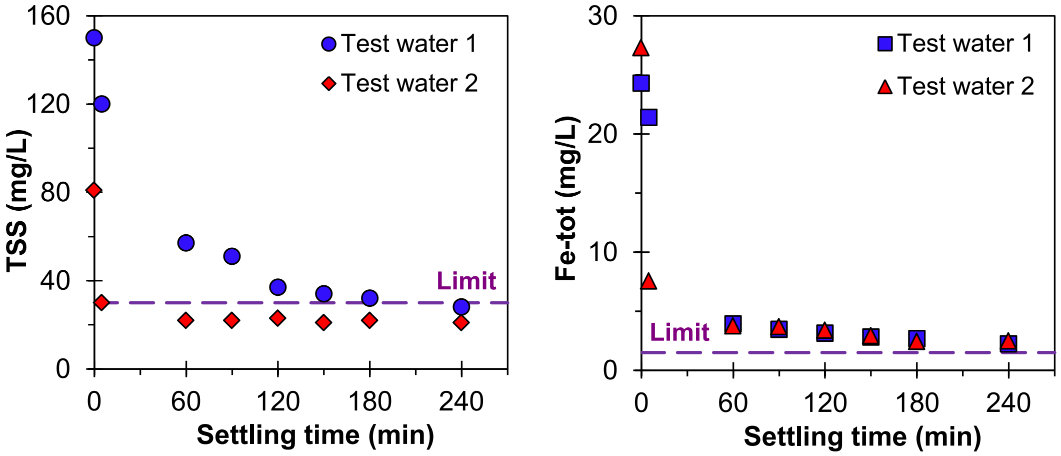

Figure 3 *Concentration of total suspended solids (left) and total iron (right) of the two treated test waters as a function of settling time. Coagulation aid was intermixed within the first 3 min of time scale.*

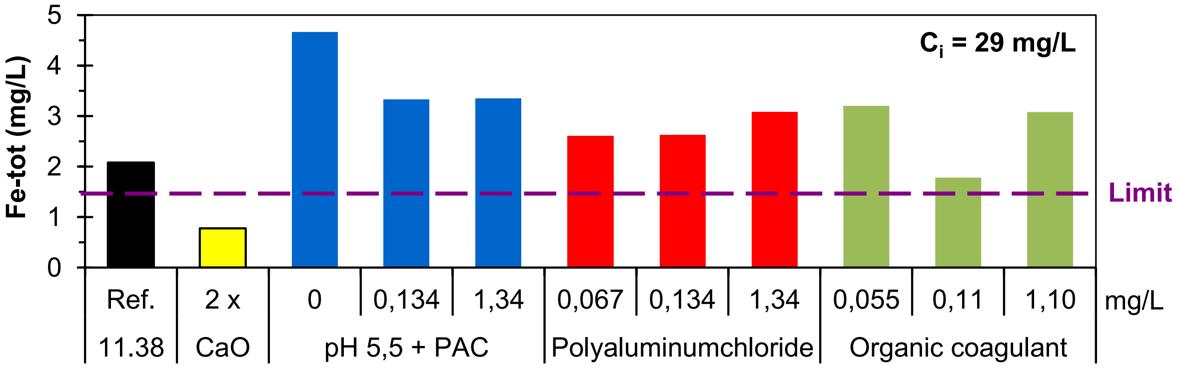

Figure 4 *Remnant Fe-tot concentration from initially 29 mg/L after 2 h of settling by testing varied final concentrations of coagulants (PAC = polyaluminum chloride and organic product) at primordial pH or adjusted to pH 5.5, as well as split supply of quicklime (CaO) relative to a reference batch with previous treatment.*

Scaling factor. The aim was to determine a downscaling factor based on Fe-tot concentration between a running treatment plant (Schleenhain, combined effluent water) and a 1 L static batch experiment that mimicked the treatment process. Carried out on four sampling dates in October 2014, an average downscaling factor of 3.0 ± 1.1 was obtained. Taking into account experimental and analytical uncertainties, this factor corresponded to an upscaling factor of 0.3–0.5 from bench scale results to full scale plant operation.

Dewatering. Applying the standardized capillary suction time (CST) method on the EHR residues collected from mesoscale process simulation, values of <3 kg s/(g dw) indicated good ability for dewatering (Bahrs et al. 1994). Gravitational thickening of these residues was simulated in a plexiglass cylinder by applying constant overpressure of +285 ± 15 hPa. Within 48 h, ~40 % of initial volume got lost. To keep the residues suitable for pumping, solids content shall not exceed 10 M%. Hence, a yield of 200 to 360 m^3/d of thickened residue would be expected for the anticipated full-scale throughput of 120 m^3/min (Table 1). Extended dewatering was simulated by centrifugation at 4,400 *g*. While it would further increase the solids content and lower the load of EHR residue, filter pressing technology would be very costly. Based on the solids content of naturally dehydrated EHR deposited in diked cells of the Schleehain mine, the size and loading capacity of prospective disposal areas within active dump sites were estimated for the planned treatment plant.

Table 1 *Process parameters obtained from mesoscale process simulation to size full-scale mass flow parameters. CST (capillary suction time) is a standardized method to quantify the ability for dewatering.*

Experimental process step	***Parameter, unit***	***Test water*** 1	**2**	***Mass flow estimate for full-scale throughput of 120 m³/min***	**Test water** 1	**2**
Sedimentation (4 h)	Solids content, g/kg	65	22	Settleable solids, L/m³	1,49	3,44
	CST, kg s (g dw)$^{-1}$	0,62	2,24	Residue flow rate, m³/d	257	594
Gravitational thickening (5 d)	Loss of volume, %	41	50	Estimated loss of volume, %	40	40
	Solids content, g/kg	137	48	Thickened residue yield, m³/d	154	357
Dewatering simulated, 4400**g*	Solids content, g/kg	380	193	Dewatered residue yield, m³/d	50	78
				Dewatered solids yield, t/d	21,8	16,4

Gross design of treatment process. Taking all results together, a four-routed treatment plant was sized for anticipated throughput of 120 m³/min. The engineered concept included one inlet structure, serial oxidation reactors, two-step flocculation reactors, four settling tanks, two quicklime slaking reactors, two make-up reactors for flocculation aid (FA), and one thickener (Fig. 5). A second thickener shall be considered for technical redundancy.

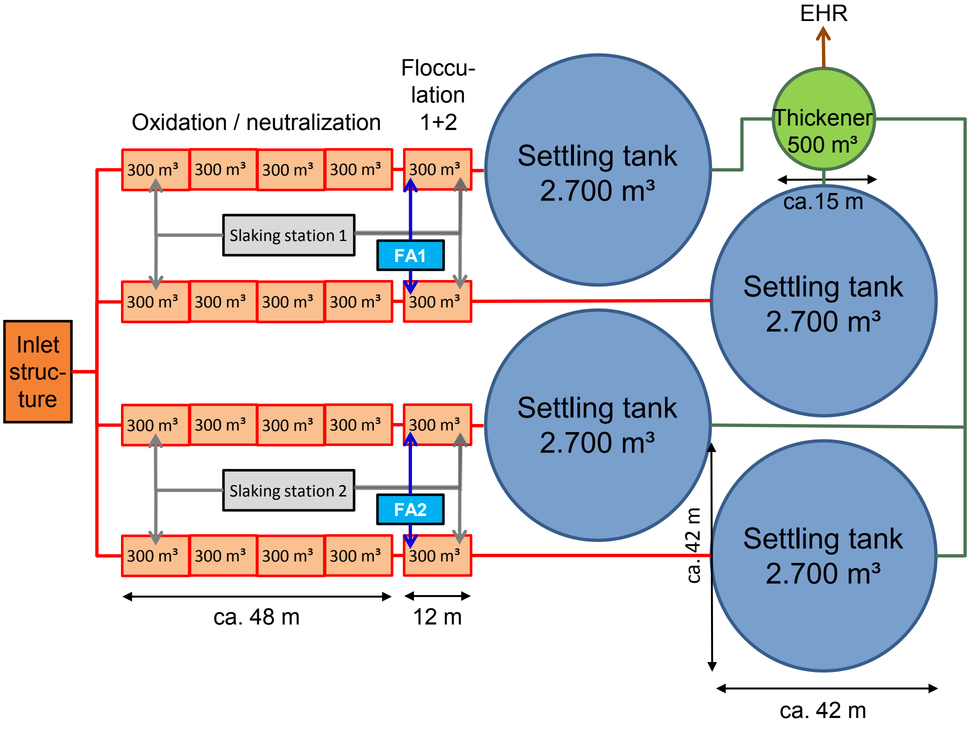

Figure 5 *Gross-sized process flow scheme of planned mine water treatment plant (see text).*

Results on Handling Treatment Residues

Permissible utilization. Precipitated residues are an undesired, but technically inevitable by-product of mine water treatment, to be handled as "waste" according to the EU conformable Closed Substance Cycle Waste Management Act. This means that re-use or recycling is to be favored over backfilling or dumping. Because the EHR contains acid buffering capacity (mainly Ca/Mg carbonates), and heavy metal and arsenic contents are expected to comply with the LAGA Z0 indicator values, non-risky emplacement within mining dumps appears licensable. The mine operator was authorized the disposal of mine water residues within active dump sites of the operating Schleenhain lignite mine in 2009. Thickened EHR suspension is pumped from the treatment plant into diked cells later on buried by continued dumping of overburden (Jolas et al. 2013).

Process simulation on effects and fate of buried EHR. The main research question was whether EHR is safe to be embedded within excavated tertiary sands that liberate acidity due to pyrite oxidation. The processes of groundwater recharge and rerise were simulated with columns containing settled residues sandwiched between excavated tertiary sands. Reactors devoid of residues served as a control. All test substrates and deep groundwater were collected from the field site and major properties characterized before and after running the experiments. Synthetic rain water was used to mimic recharge conditions. Figure 1 shows a sketch of the experimental setup.

Key properties of test substrates. The overburden test substrates (medium sands) collected from two aquifers (GWL3 and GWL4) differed considerably with respect to intrinsic acidity. Acidity of GWL3-sand was almost ten times higher than that of GWL4-sand, consistent with a five times higher sulfide content. Of similar size were total porosity (0.45 and 0.40) and DARCY hydraulic conductivity ($1.2 \cdot 10^{-5}$ and $4.8 \cdot 10^{-5}$). The settled EHR collected from a dump cell had by 90 % particles <2 µm, bulk dry density of 0.15 g/cm^3, total porosity of 0.95, DARCY K_f of $2.5 \cdot 10^{-8}$, and alkalinity of 6.1 mol/kg dw. Other properties are reported in Ulrich et al. (2015). Various pre-experiments were carried out to determine hydraulically active porosity, Van-Genuchten parameters, and acid-base reactivity in order to size the reactors and the load ratio of test substrates. The aim was to achieve breakthrough of acidity or alkalinity in the effluent within the experimental runtime. The resulting concept of load size and layer arrangement of the experimental reactors is described elsewhere (Jolas et al. 2013, Ulrich et al. 2015).

Simulation of groundwater recharge. This scenario was simulated by infiltrating synthetic rainwater from the uncovered top of four reactors (R). R3 contained a 7 cm thick layer of EHR on top of a 20 cm GWL3-sand layer. Despite a 3.2-fold surplus of alkalinity relative to the substrate's acidity in the reactor, breakthrough of alkalinity did not occur. However, the concentrations of acidity, dissolved iron and sulfate in the effluent were lower and declined more rapidly than in the reference reactor R2 devoid of EHR (Fig. 6). Detailed mass balance proved that this output was not only driven by hydraulic elution, but also by pyrite oxidation progressing in the tertiary sand substrate. Capping this substrate by EHR abated pyrite oxidation and the transport of acidity, dissolved iron and sulfate into deeper aquifers. Over the course of the experiment, only 16 % of the EHR alkalinity got consumed, probably due to shortcut flow through cracks that formed whilst progressive dewatering. Reactor R5 contained a 10 cm thick layer of EHR mixed with GWL4-sand overlain by 37 cm of pure GWL4-sand. Due to a 1.25-fold surplus of acidity in the reactor, breakthrough occurred after two pore volumes exchanged. Nevertheless, effluent acidity, dissolved iron and sulfate concentrations were lower and redox potential was higher than in the reference reactor R6 devoid of EHR (Fig. 6). The EHR alkalinity was fully consumed, showing that mixing of the substrates enhanced the chemical reactivity.

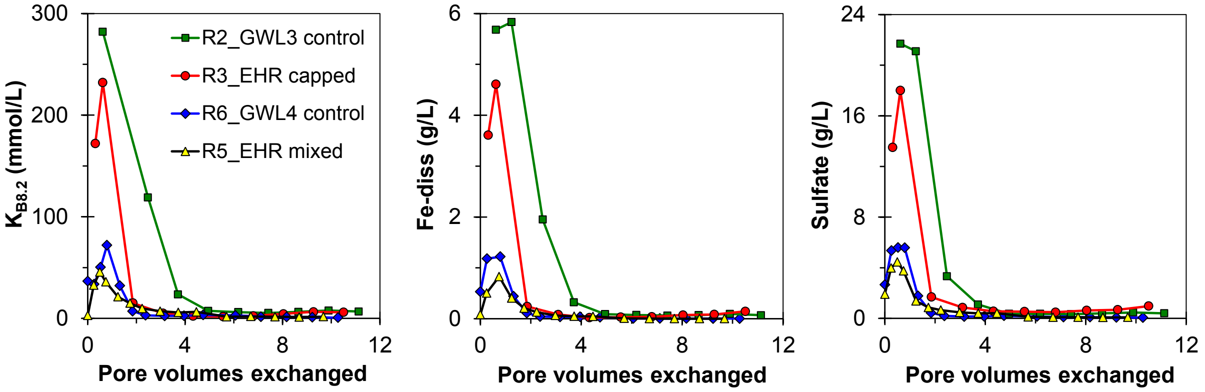

Figure 6 *Course of acidity, Fe-diss, and sulfate concentration as a function of pore volumes exchanged in reactor R2 (control w/ GWL3-sand), R3 (GWL3-sand w/ EHR on top), R5 (GWL4-sand on top of mixed EHR), and R6 (control w/ GWL4-sand) with simulated groundwater recharge.*

Simulation of groundwater rerise. This scenario was simulated by infiltrating original groundwater from bottom to top of three closed reactors. R7 and R8 contained EHR layers sandwiched between a GWL4-sand layer on top and a bottom GWL3-sand layer (50 cm thick in each reactor). While R7 carried a compact layer of EHR 12 cm thick, the same amount of EHR was mixed with GWL4-sand to a 23 cm thick layer in R8. Both reactors contained a 2-fold surplus of alkalinity relative to the substrate's acidity in the reactor. The reference R9 contained 50 cm of GWL4-sand on top of 50 cm of GWL3-sand. Within seven pore volumes exchanged, the effluent pH slightly increased from pH 2 to pH 4. Thereafter, the effluent pH converged to pH 6.0 of infiltrated groundwater (Fig. 7). The effluent of R7 reached the same pH value already with five pore volumes exchanged, and the effluent of R8 even exceeded this pH value after two pore volumes exchanged due to breakthrough of alkalinity. Correspondingly, the redox potential fell from 700 to 200 mV, eventually approaching the infiltrated groundwater value of 300 mV. The export of dissolved iron (Fig. 7), sulfate, and acidity (not shown) from reactors containing EHR was lower than from the reference reactor. Detailed mass balance showed that intrinsic alkalinity of EHR retained substantial amounts of the acidity stored, and generated over the course of the experiment. At least 15 % of the EHR alkalinity was consumed. About twice this proportion of EHR alkalinity was consumed in R8, containing the same amount of EHR but mixed with tertiary sand. This result demonstrates that mixing alkaline EHR with acid overburden substrate will increase its buffering efficacy.

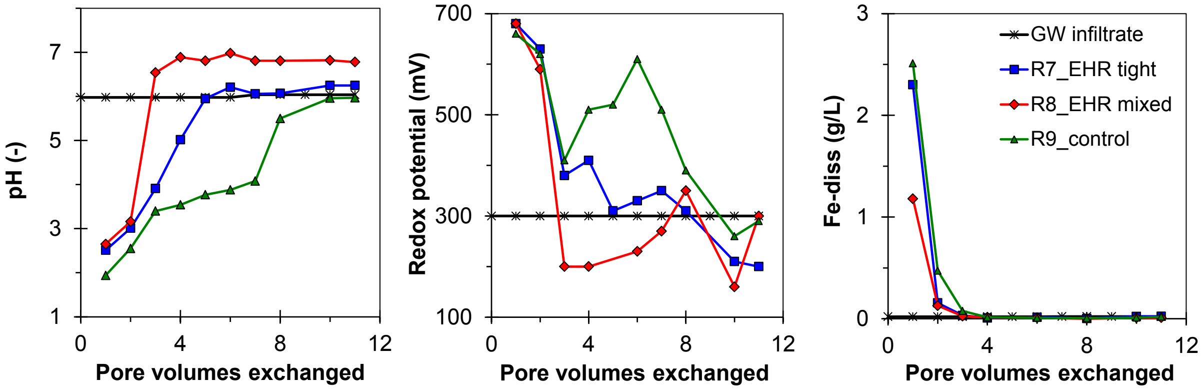

Figure 7 *Course of pH, redox potential, and Fe-diss concentration as a function of pore volumes exchanged in reactor R7 (tight EHR layer), R8 (mixed EHR layer) and R9 (control) with simulated groundwater rerise.*

By depicting the experimental results in a stability field diagram of iron as a function of pH and redox potential (Fig. 8), one can see that upon initial elution of accumulated Fe^{2+}, the presence of EHR under simulated groundwater rerise will quickly shift the environmental conditions towards the thermodynamically favored solid Fe hydroxide phase which is known as sparingly soluble. The results demonstrate that carbonate alkalinity in EHR acts as a buffer against acidity stored or generated by overburden substrates containing oxidizable sulfides. This prevents low pH conditions favoring acid dissolution of Fe hydroxides. In addition, redox potential did not fall below 200 mV, hence reductive EHR dissolution would not be expected. The low organic carbon contents of the test substrates (<0.1 M% in tertiary sand, 1.0 M% in EHR, and 3 mg/L DOC in groundwater) appear unfavorable for enhanced microbial Fe(III) reduction. Eventually, buried EHR would equilibrate with conditions typical for deep aquifers (pH ~6, E_H ~300 mV, low microbial activity). Nevertheless, more research focusing microbial effects on EHR and site-specific determination of biogeochemical process parameters is needed to predict the long-term fate and stability of EHR buried within tertiary overburden.

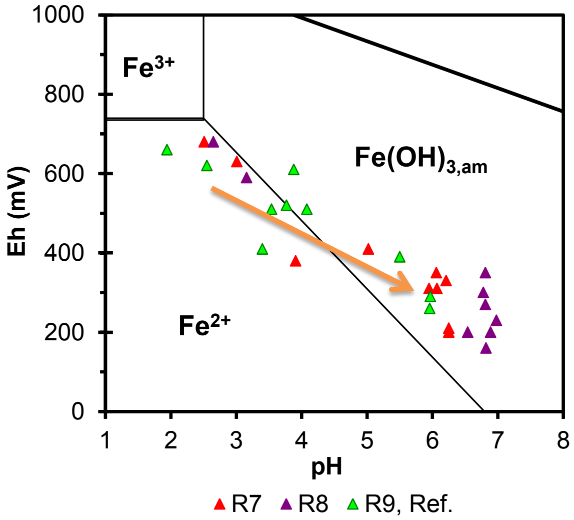

Figure 8 *Fe-O-H stability diagram (45 mM Fe-tot, 10 °C) depicting effluent data from three reactors with simulated groundwater rerise; arrow indicates shifting within the experimental runtime.*

Conclusions

Process parameters determined from task-specific simulation experiments are decisive for many purposes of environmental engineering. This contribution exemplifies their value for different objectives, (i) design and gross-sizing of process technology for mine water treatment in order to meet official threshold values for discharge, and (ii) prediction of effects and fate of iron-rich treatment residues buried together with tertiary overburden substrates that liberate acidity upon groundwater recharge and rerise. Concerning the first task, this work demonstrated that Fe precipitation from mine water could be enhanced by modifying the treatment sequence. Adding slaked quicklime as a coagulant after the supply of coagulation aid accelerated the agglomeration and settling of colloidal iron oxy-hydroxide particles.

Concerning the second task, the simulation experiments showed that alkalinity loaded EHR from mine water treatment is suited for storage in deep mine dumps. Because alkaline EHR successfully neutralized acidity from tertiary overburden, acid dissolution of Fe oxy-hydroxides did not occur. Reductive EHR dissolution requires low redox potential <200 mV, which was not observed in the simulation experiments due to low organic carbon contents and thus microbial activity. However, further research is needed to study long-term microbial effects on EHR stability at dumping sites with higher organic carbon content. Burial of alkaline EHR from mine water treatment in deep dumps of active lignite mines can be considered a remedy against acid loading to groundwater and surface waters, thereby saving prospective costs for water conditioning of remaining pit lakes.

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Recovery of copper from Chilean mine waste waters

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Abstract

Two copper-containing waste-water streams from a Chilean mine site were identified as potential sources of revenue: Source 1 is raffinate from a copper solvent-extraction circuit; Source 2 originates from a reservoir receiving acid mine drainage as a result of natural snow melt. The streams are currently treated with lime to increase the pH for process and environmental purposes; any dissolved copper is precipitated, which renders it unrecoverable via the mine's conventional sulphide flotation process. These streams contain 80 to 240 mg/L dissolved copper that can be profitably recovered. An options analysis identified four potential technologies that may be applicable: BioteQ (biological or chemical precipitation of copper as the sulfide, which could then be processed through a nearby concentrator or smelter), EMEW (direct electrowinning of copper to produce high-purity saleable copper metal in the form of cylindrical tubes or metal powder), ELSA (a proprietary technology that produces a 95% copper sludge by cementation with iron), and ion exchange (a well-known technology that is widely applied in a variety of waste-water applications, particularly for the removal or recovery of low concentrations of valuable or toxic metals). This paper describes the ion-exchange concept and provides a preliminary process design, financial estimate, and economic feasibility assessment for the application of ion exchange to the recovery of copper from these two waste-water sources. Advantages of ion exchange compared with the other process options are discussed.

Key words: copper, acid mine drainage, mine waste water, ion exchange, economics

Introduction

Los Bronces, an Anglo American-owned mine located 65 km northeast of Santiago, Chile, at an altitude of 3500 m, processes copper sulphide ores. High-grade sulphides are subjected to comminution and then upgraded through a flotation circuit, following which concentrate is trucked to a nearby smelter for further processing. Low-grade run-of-mine material is accumulated in the valleys of the natural topography, where it is dumped-leached using drip irrigation with sulphuric acid. The resulting copper-containing pregnant leach solution (PLS) is treated for copper recovery by solvent extraction (SX). SX produces two streams: a purified concentrated rich electrolyte, from which copper is recovered by electrowinning (EW), and a copper-barren raffinate, a portion of which is limed for neutralisation. Sludge from the neutralisation process reports to tailings and clarified water is re-used for process purposes. The raffinate (~600 m^3/h) still contains an average of 240 mg/L Cu prior to lime neutralisation, representing some 1220 t/a Cu.

A second waste source of copper is the mildly acidic water that is pumped from the mine pits, combines with snow melt and clarifier overflow from the raffinate neutralisation plant, and accumulates in a reservoir. This source has an average flowrate of 2000 m^3/h (with seasonal fluctuations) and contains 80–180 mg/L Cu (up to 3060 t/a Cu). On eventual closure of the mine, this source will continue to generate acid mine drainage and acidic copper-containing liquors from snow melt off the leach dumps and has the potential to become an environmental liability if not treated.

These two waste-water sources represent a combined loss of some 4200 t/a Cu, with an estimated annual value of USD 21M, assuming a price of USD 5000/t for London Metal Exchange (LME) Grade A cathode. Recovery of the metal value from these wastes not only provides additional revenue to the mine, but would reduce the volume of neutralisation sludge generated by 7000 dry t/a during the operational phase and limit long-term environmental impact and closure liabilities.

Various technologies were evaluated for application to these two waste waters. The objectives were to recover copper as a saleable product and minimize the amount of copper reporting as metal sludge to the tailings dam. The technologies considered included lime neutralisation, reverse osmosis, conventional SX–EW, sulphide precipitation, ELSA cementation, ion exchange (IX), and the EMEW process. This paper outlines the basis of the IX process, discusses reasons for its preference as the waste-treatment methodology of choice, and provides a preliminary business case for application to the recovery of copper from these two sources. Comparison with the alternative technologies is also provided.

Waste-Water Compositions

Table 1 presents the composition and physical characteristics of the two streams identified for potential copper recovery at Los Bronces.

***Table 1** Composition of Los Bronces copper-containing waste streams (data from 2012).*

Species	Source 1: SX raffinate	Source 2: Mine water reservoir
	Concentration (mg/L)	Concentration (mg/L)
Al	1610	64.9
Ba	—	0.15
Ca	440	590
Cd	—	0.05
Cl	75	—
Co	8	0.55
Cu	240	80–180
Fe	260	65
K	10	34
Mg	1170	270
Mn	320	23
Na	30	69
Ni	4	0.4
P	30	<0.02
Zn	110	7.0
SO_4^{2-}	22 200	3380
NO_3^-	—	20.3
pH	1.6	3.4
TSS	40	110
Eh (mV)	600	—
Flowrate (m^3/h)	580 ± 200	1940 ± 210
Temperature (°C)	12–20 (avg. 17)	12–20 (avg. 17)

Application of Ion Exchange to the Recovery of Copper

IX is widely used in waste-water treatment, both for recovery of valuable metals and for removal of hazardous species before discharge. A resin with iminodiacetic acid functionality (Fig. 1) was selected for this application. These resins reject Ca and Mg strongly and are selective for copper over base-metal cations other than Fe(III): Fe(III) > Cu >> Ni > Zn ~ Co ~ Cd > Fe(II) > Mn > Ca > Mg > Na. Selectivity for copper arises from the chelating mechanism by which loading occurs. Copper loads at ~pH 3, at which pH most Fe(III) has been removed from solution by precipitation. Fe(III) loading is kinetically much slower than that of Cu(II) so discrimination against iron is possible when the residual amounts in solution are small. These resins are capable of removing Cu to <0.05 mg/L from both low ionic strength streams and strong electrolytes (Jurrius et al. 2014). Elution is carried out using 100 g/L H_2SO_4 and the resin is returned to the loading cycle in the H^+ form. The product stream is a high-purity electrolyte containing ~50 g/L Cu that is suitable for subsequent processing for metal recovery by electrowinning or crystallisation.

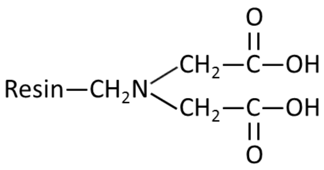

Figure 1 *Iminodiacetic-acid resin functionality in the hydrogen form.*

Process Description for Ion-Exchange Treatment of Los Bronces Waste Waters

A conventional fixed-bed ion-exchange (FBIX) configuration is proposed, using three columns in a lead–lag–elution configuration, as shown in Fig. 2. The operating conditions are given in Table 2.

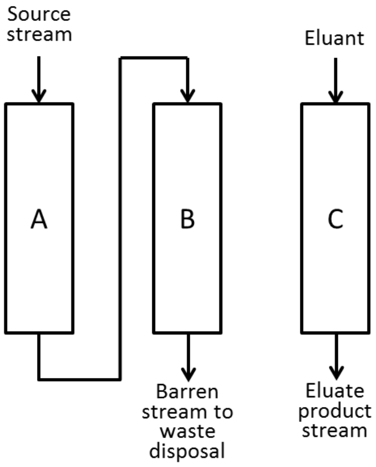

Figure 2 *Lead–lag–elution fixed-bed ion-exchange configuration.*

Feed solution is fed to Column A (lead column) and this outlet is fed to Column B (lag column). Lead Column A will reach capacity first when the resin becomes completely loaded with copper; lag Column B scavenges any residual copper that exits from Column A. Column A is then be taken off-line for elution. The feed is then directed to Column B, which now becomes the lead column, and eluted Column C becomes the lag column. The columns continue to rotate in this manner: there are always two columns on loading and one on elution.

Table 2 *Process design specifications for copper removal from Los Bronces mining waste waters by cation exchange using an iminodiacetic-acid resin.*

Parameter	Source 1	Source 2	Comment
Cu in feed (mg/L)	240	130	Can handle wide variability in feed [Cu]
Cu in barren (mg/L)	<10	<10	Can achieve <1 mg/L Cu if required
Cu in eluate product (g/L)	20–50	20–50	Eluate [Cu] can be tailored to suit selected downstream product-recovery operation
Cu recovery (%)	>95	>95	Can be readily increased to >99% as required with small impact on capital cost
Eluant	100 g/L H_2SO_4		
Feed flowrate (m^3/h)	600	2000	
Product flowrate (m^3/h)	2–10	7–17	Depending on [Cu] in product stream
Plant footprint (m^2)	50–60	170–180	Estimated for 2.5 m diameter columns

Source 1 requires pH-adjustment from pH 1.6 to pH 3, which will also remove ~260 mg/L Fe present in the stream. Source 2 (pH 3.4) can be treated as received. Source 1 originates from an SX circuit so it may be contaminated by small amounts of organic phase, which is well known as a resin foulant. Installation of an upfront organic-removal system may be required, which will have the added benefit of returning recovered organic to the SX circuit and thereby lowering operating costs of that unit operation. A clarified feed solution (total suspended solids (TSS) <10 mg/L) is required for FBIX:

both sources can contain up to 100 mg/L TSS, so upfront clarification of the streams is required, in addition to making provision for regular removal of solids from the top of the resin bed by backwashing after elution.

The eluate product is a concentrated $CuSO_4$ solution, containing 40–50 g/L Cu in acidic media. It may contain small quantities (<5 mg/L) of Co, Ni, and Zn, as well as trace amounts of Ca and Mg. The electrolyte will, however, be of quality suitable to be fed to an electrowinning circuit for the production of LME Grade A cathode. The flowrates of the product streams are less than 20 m^3/h (and may be as low as 2 m^3/h) because of the high upgrading that can be achieved by IX. This makes the downstream capital requirements very small. This stream can be treated in several ways, and the composition (copper concentration and acidity) of the eluate can be readily adjusted to suit the requirements of the downstream operation. Options for product recovery include the following:

(i) Electrowinning: The preferred option at sites where adequate tankhouse capacity exists is to send the eluate directly to an existing conventional electrowinning process for copper recovery as cathode.
(ii) Crystallisation: Where an existing crystalliser exists with spare capacity, then crystallisation of a $CuSO_4{\cdot}5H_2O$ product represents a cost-effective option to treat the product stream.
(iii) EMEW: The eluate can be fed to a small compact EMEW circuit from which high-grade copper cathode can be produced. The size of unit required will be considerably smaller than for direct EMEW processing of the source streams. Furthermore, much higher recovery and current efficiency will be achieved because of the significantly higher copper concentration and elimination of Fe(III) from the electrolyte.
(iv) Sulphide precipitation: Copper can be precipitated as a saleable sulphide. This method of product recovery is least desirable because it requires both precipitation and smelting steps, and a relatively low-grade copper product is obtained.

Source 1 also offers the possibility of recovering cobalt and nickel using a two-step elution process, should their value warrant this: cobalt and nickel are less strongly bound on the resin so can be eluted first using dilute H_2SO_4 (~50 g/L), followed by copper elution using strong H_2SO_4 (80–120 g/L). As required, cobalt and nickel can be further separated and concentrated by IX, although, for this application, it would be preferable to precipitate a mixed hydroxide product for toll refining.

With respect to other streams generated in the IX process, the initial and final portions of the eluate stream will contain low concentrations of copper, but will still be high in acid so can be recycled to the leach circuit where the acid can be used and there is further opportunity to recover any contained copper: only the high-grade portion of the eluate proceeds forward as the product liquor. The barren stream exiting the IX loading cycle will have similar composition to the feed, except that copper concentrations will be reduced to 0.1–10 mg/L and most iron will have been removed in the upfront pH adjustment step for Source 1. Copper is be replaced by the hydrogen ion equivalent. The barren stream is suitable for discharge following liming to remove trace residual base metals.

Business Case for the Recovery of Copper from Mine Waste Waters by Ion Exchange

Table 3 lists the financial estimates for this process, based on the use of Lewatit TP 207 resin (Lanxess) and the operating conditions given in Table 2.

A typical standard IX column has a volume of 12 m^3 and diameter of 2.5 m. Using a lead–lag FBIX configuration and assuming a loading flowrate 10 BV/h, Source 1 will require five columns (2 × lead–lag plus one for elution), while Source 2 will require 16 columns (the elution cycle is very short compared with that of the loading cycle, so an addition elution column is not necessary). The columns will be piped in a manifold arrangement, such that any column can be in any position, allowing for optimum usage of the resin. If space constraints dictate, the column diameter can be increased up to 5 m, enabling fewer columns and a lower footprint to be achieved. This will have the advantage of lowering the capital cost. For these applications, increasing the column diameter from 2.5 m to 3.0 m reduces the capital cost by approximately 30% for both sources. There is no particular advantage or disadvantage of using larger diameter columns: the maximum size is usually limited by transport of the constructed columns to the site. The diameter:height ratio is typically designed at 1:2. The total resin volumes required for Sources 1 and 2 are 60 m^3 and 190 m^3, respectively.

Table 3 *Preliminary financial assessment of ion-exchange options for copper removal.*

Parameter	Source 1	Source 2	Comment
Cu in product (g/L)	40	40	Can be tailored to suit downstream operation
Cu recovery (%)	95	95	Can be increased to > 99.5% as required
Cu production (t/a)	930	2330	Depends on recovery targeted
Revenue (MUSD/a)*	5.19	9.4	Assumes that product recovery is by EW, producing LME Grade A copper quality
Operating cost (USD/t Cu)**	1,730	1,230	
Operating profit before deductions (USD/t Cu)	2,970	3,460	Dependent on Cu price
Capital cost (MUSD)***	5.3	13.0	Includes first-fill resin; can be reduced by using larger diameter columns
Payback period (month)	19	22	Depends on [Cu] in feed and flowrate

* Based on an LME copper price of USD 5000/t and a conservative 94% LME value paid for a cathode product.
** Based on labour, reagent, utility, and maintenance costs.
*** Excludes upstream organic- and TSS-removal steps that may be required and pumping and pipeline costs.

Capital costs are estimated from typical 2016 global equipment and materials costs, and based on construction of columns and tanks in rubber-lined mild steel with polypropylene piping. The plants can also be constructed in stainless steel, but capital costs will be higher. A basic programmable logic controller for automatic process control is included. This preliminary costing employs estimates of the costs of civils, plant housing, utilities, engineering design, and project management based on accepted percentages of main mechanical equipment (columns, tanks, pumps) costs for similar engineering projects. Capital costs exclude pipeline and pumping costs (to transport the feed from the raffinate pond or reservoir to the plant) and any provision for removal of entrained organic or TSS, should these prove to be necessary. Calculations are based on an estimate of 95% plant availability, which is readily attained for a plant of this nature. The downstream product-recovery process is excluded, as the selection of this unit operation will be site-specific.

Operating expenses are based on Chilean reagent, utilities, and labour costs (April 2016). One supervisor (USD/a 100,000) and six operators on shift rotation (USD/a 55,000 ea.) are required to operate the plant. Maintenance is estimated at 3% of capital equipment cost. The reagent costs and consumptions are given in Table 4. The lime requirement includes both pre-neutralisation of the feed ahead of the IX circuit (Source 1) and neutralisation of the barren stream for disposal. (Note: this lime requirement is currently required to neutralise iron and acid for direct disposal, so does not represent an additional cost to the existing circuit.) Resin replacement, based on a lifetime of five years, comprises 25–30% of the total operating costs.

Table 4 *Estimated reagent consumption and costs.*

Reagent	Cost (USD/t)	Consumption (t/t Cu)	
		Source 1	Source 2
Lime (85% CaO)	150	3.3	0.1
Sulphuric acid (98%)	80	1.6	1.6

In terms of sustainability, although both of these streams can be recycled for process purposes during the operational phase of the mine, Source 2 in particular (and likely run-off from other areas, including the leach dumps) will become a waste stream post-closure that will require treatment. Installing a copper-recovery process during the operational phase can generate ongoing revenue; post-closure, it would be fully paid off and can potentially continue to generate revenue while addressing ongoing environmental issues. A process that can provide flexibility in terms of flowrate throughput and wide variations in copper concentration is required.

Summary of the Applicability of Ion Exchange to Copper-Containing Mine Waste Waters

IX is a simple concept and the process is easy to operate and readily automated. It is possible to achieve very low Cu in the barren solution (< 0.1 mg/L), enabling this stream to meet legal discharge limits. The process is capable of handling fairly wide variations of copper concentration, flowrate, and temperature, provided the design criteria are appropriately specified. A relatively inexpensive iminodiacetic-acid resin can be used for this application and a product stream containing up to 50 g/L Cu is produced. The technology is very well known for copper removal, with more than 1000 applications to industrial and process wastes globally, so limited piloting is necessary, which allows for rapid implementation. Use of an FBIX configuration requires a small plant footprint.

Other factors that need to be considered with respect to the implementation of this technology include the potential needs to clarify source feeds to ensure TSS <20 mg/L (preferably <10 mg/L) and remove organic contamination from Source 1 to avoid poisoning of resin (<10 mg/L entrained organic). Copper ions in the waste water are exchanged for another ion that reports to the discharge (H^+ in this case). The product stream requires subsequent treatment by electrowinning, crystallisation, or precipitation/cementation to yield a saleable copper product. The preferred option will be dictated by the availability of existing tankhouse or crystallisation capacity already available on a site to limit capital expenditure requirements.

The project economics and payback period are strongly dependent on the prevailing copper price, but, even under the current conditions of commodity price pressure, the project has advantages in terms of sustainability and reducing longer-term mine closure liabilities.

Alternative Copper-Recovery Technologies

Several competing technologies for copper recovery from these wastes were also considered. Their advantages and limitations with respect to these two applications are outlined below.

Lime neutralisation: Lime (CaO) and limestone ($CaCO_3$) are commonly and widely used for treatment of acidic wastes. This approach is easy to engineer, simple to operate, can precipitate toxic metals, and is cost-effective for treating high volumes of waste waters. Metal species are precipitated as a hydroxide metal sludge, which is toxic if heavy metals are involved, requires storage, and presents long-term liabilities post-decommissioning. Stringent water quality requirements are not met. It is uneconomic to recover metal values from the sludge and copper losses would be high.

Reverse osmosis: This purification technique is used mainly in desalination applications. Because the water is processed through a semi-permeable membrane, high concentrations of dissolved metals and sulphates in waste waters cannot be handled. The brine waste produced will require separate treatment. Although strict water-quality criteria for discharge can be met for many applications that contain low concentrations of metal contaminants, this process is costly (both in terms of capital and operating costs), energy-intensive, and uneconomical for selectively recovering dissolved metals, especially when taking into account that further downstream processing would be required.

Solvent extraction–electrowinning: Although SX–EW is widely employed for primary recovery of copper (Schlesinger et al. 2011), it is generally considered to only be cost effective for feed concentrations above about 1 g/L Cu (Sole 2008). The SX process is equilibrium-driven, so has low extraction efficiency at low metal concentrations and low pH: raffinate concentrations can seldom be reduced below 100 mg/L Cu. The large organic inventory and electrical requirements of ~2 MWh/t Cu for electrowinning make this process capital- and energy-intensive.

Sulphide precipitation – BioteQ process: BioteQ's ChemSulphide® process involves the chemically assisted precipitation of copper as the sulphide (BioteQ 2016). The waste stream is fed into a precipitation reactor where the metal species reacts with NaSH. The precipitation slurry overflows to a clarifier, which provides the primary liquid–solid separation. A portion of the underflow is returned as seed material to the precipitation reactor; the remaining underflow is filtered and a copper sulphide cake is discharged. The process exchanges sodium (from NaSH) for copper, thereby increasing the sodium content of the discharge liquor. A biological option is also available, in which an upfront biological reactor generates H_2S gas from the metabolic reduction of elemental sulphur by anaerobic bacteria, which is used instead of NaSH as the precipitation agent.

The BioSulphide® system is more complex and capital-intensive than the ChemSulphide system and produces a product that is lower in copper content. Given the extreme monthly variations in ambient conditions at Los Bronces, the chemical option was considered to be more reliable and easier to control. The process is flexible with regard to flowrate and concentration fluctuations and gives selective and high recovery of copper over other base metals present. A disadvantage of the process is that the sulphide cake contains ~30% moisture, which will incur costs either for drying or for transportation of water: Chagres smelter is, however, relatively close to the Los Bronces site.

Several commercial case studies are available for zinc, cadmium, and nickel precipitation. For copper, in particular, the chemistry of the process has been proven for treatment of an acid mine drainage stream of very similar composition and flowrate at Dexing, China, which has been operating successfully since 2009 and has won a Chinese environmental award (BioteQ 2010).

Cementation – ELSAMetal process: ELSAMetal is a proprietary technology that produces a copper sludge by cementation with iron (ELSAmetal, 2016). The waste stream enters a reactor at its base, the sacrificial metal is fluidised, and the reactor is subjected to ultrasound to increase the effective surface area. The cementation product exiting at the top of the reactor contains ~95% Cu and is in the form of a powder. The process chemistry is well known and was commercially practiced for purification of copper streams by cementation with scrap iron for many decades before the advent of SX; however, it is designed for high concentrations of copper and the extent of reaction is expected to be limited for the low concentrations of this application. Downstream handling of residual iron in the cementation cake is required. Specific details of the technological innovations of this particular process are not available and there are no similar commercial operations for evaluation.

EMEW: EMEW® (Electrometals Technologies 2016a, 2016b) is an electrowinning process using a novel electrode configuration that enables efficient copper recovery from dilute solutions. The cathode comprises a stainless steel cylinder (approximately 25 mm in diameter), in the centre of which is an anode rod. Dimensionally stable anodes, made of titanium with precious-metal oxide coatings, are used. The overpotential for oxygen evolution on these materials is reduced by some 15% (Sandoval et al. 2010) when compared with conventional lead anodes, thereby lowering energy consumption. The cells are supplied in 30-cell modules. Electrolyte enters the cylinder tangentially at its base and flows in a spiral manner between the cathode and anode, exiting at the top of the cylinder. The very high flowrate of electrolyte through the cylindrical cell improves mass transfer, enabling electrodeposition to be carried out at high current density and from dilute solutions (1–20 g/L Cu). The technology claims to reduce residual copper in solution to <0.1 g/L. Copper can be deposited in powder form (for electrolytes containing <1 g/L Cu) or as cylindrical cathode tubes, weighing about 25 kg, which are periodically removed from the cells, compressed, packaged into bundles, and sold (Roux et al. 2007).

Although EMEW has been implemented at a wide range of sites for various applications, the low concentrations of the two source feeds for this application (~200 mg/L Cu) are of concern. It is likely that the current efficiencies will be low, especially because the iron content of the streams is similar to that of the copper (65–260 mg/L Fe). The technology is claimed to be suitable for feeds containing a minimum of 100 mg/L Cu, so morphology of the cathode deposit is likely to be powdery and non-adherent to the cathode blank, creating more difficult product handling. One potential advantage of EMEW technology is that it can be operated under outsourced conditions, with the operator taking a portion of revenues. This would provide a low-risk option, allowing the mine to focus on its core function of primary metal production, while still gaining some financial benefit from toll treatment of the waste streams.

Although EMEW is not particularly attractive for direct treatment of these waste waters, it does, however, represent a viable option for treatment of the IX product stream. The flowrate will be two to three orders of magnitude lower, allowing significant reduction in capital and operating costs, as well as plant footprint. Los Bronces currently has no conventional electrowinning or crystallisation capacity available (which would be the preferred product-recovery processes to treat the IX eluate), so inclusion of a small, modular EMEW circuit would provide a cost-effective means of product recovery when used in conjunction with IX.

Recommendations

The various technology options were evaluated based on technical capability, complexity, sustainability, and economic considerations. The BioTeQ ChemSulphide and combined IX–EMEW options were selected for further evaluation. Although the capital cost of the latter is some 40% higher for processing of Source 1 and 80% higher for Source 2, its annual operating costs are 50–55% lower. It should be noted, however, that some 80% of the capital cost of the combined IX–EMEW process is attributed to the EMEW component: if existing conventional tankhouse capacity is available on site, then the capital requirement for the IX component alone (Table 3) becomes extremely attractive.

The ChemSulphide process generates a filter cake containing 44–53% Cu and ~30% moisture, which requires further processing through a smelter; the IX–EMEW process generates a saleable copper cathode of LME Grade A quality. A concentrate containing 50% Cu will generally earn about 65–75% of LME copper value, while Grade A cathode earns 100% of LME value. Piloting of these options will enable more accurate operating performance and operating costs to be assessed, along with resilience of the process to changes in copper concentration, flowrate, and ambient temperature.

Conclusions

Ion exchange is demonstrated to be a straightforward, reliable, and relatively low-capital technology for the recovery of copper from mildly acidic mining waste streams, and can be profitably operated to create additional revenue for mine sites. It readily handles fluctuations in feed concentrations and flowrates, and can be optimised to consistently produce a low-volume, high-purity, high-concentration product stream from which LME Grade A copper cathode or other value-added copper chemicals can be produced.

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A sustainable approach to managing the treatment of mine waters associated with historic mining

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Abstract

The Coal Authority operates over 70 mine water treatment schemes across the UK and treats around 100 billion litres of mine water per annum to protect the water environment. Funded by the United Kingdom Department of Energy and Climate Change to manage the legacy of historic coal mining in Britain, the Authority is challenged to build new mine water treatment schemes within a flat line budget.

In 2015, the Coal Authority commenced an innovation work stream to accelerate efficiencies and generate income to off-set costs. This programme ambitiously aims to deliver the UK coal mine water treatment programme without government funding and with improved environmental benefits. These aims will be achieved through efficiencies, income generation, adopting transferable technologies, using renewable energy and introducing step-change innovation.

To achieve this aim step changes are needed in terms of design and operation of schemes, but also in terms to how the water and by products are considered. Step-change designs include the adoption of small footprint schemes with minimal chemical dosing requirements and below ground schemes. Aeration and degassing technologies are being progressed to accelerate iron deposition rates.

By products for reuse include mine water for non-drinking purposes; over 63 MW of low carbon recoverable heat and over 4,000 dry tonnes of ferrous hydroxide ochre produced each year. A Ferrous Hydroxide Product Project is underway aiming to cease disposal to landfill and deliver commercial uses for this material. Options for re-use include phosphate management in rivers, agriculture and wastewater treatment, and conversion into pigments and coagulants. Commercially viability requires innovation throughout the product development process including in desludging, dewatering and processing.

Approaching mine water as an asset and understanding the value of benefits delivered by mine water treatment is helping the Coal Authority ensure the long-term sustainability of mine water treatment in the UK.

Key words: mine water, sustainability, innovation, energy, efficiency

Introduction

The Coal Authority builds and maintains mine water treatments schemes to resolve the environmental impact of rising mine water within coal mines and, more increasingly, metal mines. It is funded by the UK Government and its coal mine operation and maintenance programme operates under a flat line budget of circa £10million per annum. With a programme to build between one and three new mine water treatment schemes per annum there is a need to find efficiencies or generate incomes to absorb the cost of managing these additional schemes.

In 2015 the Coal Authority undertook a comprehensive innovation exercise to reimagine all aspects of how it delivers its mine water treatment scheme programme with the aim of dramatically reducing its need for Government funding and delivering a more sustainable delivery model. This work was successful in identifying new ways of working and the implementation of the innovation programme delivery phase commenced in late 2015.

The innovation programme seeks to deliver whole life cost savings, generate incomes, provide more sustainable sources of energy and minimize energy use. To achieve these it requires motivated capable partners, introducing step change designs, adoption of transferable or novel technologies, commercial agility and to maximise value from its assets. This in itself is a cultural change for the Coal Authority and requiring a new vision and new delivery structure.

Although having only been launched in late 2015, the innovation programme has already been successful in initiating partnership working with water companies, local authorities and developers. It has let a design and construct and operate and maintaining contract for its portfolio of mine water treatment schemes with contractual requirements to deliver innovation and efficiencies. It has started trialling new technologies and focussing a substantial part of the Authority's research and development programme to deliver small footprint, low cost schemes. There is an active renewable energy programme and income contracts secured from managing energy demand.

Sustainable use of treated mine water

The Coal Authority treats approximately 100 billion litres of water a year, which is then discharged to watercourses. At present all of the treated water is discharged to receiving watercourses. This water has potential financial value and has a sustainability value in managing water scarcity issues. An analysis of water quality indicates there is high potential for its use in industry, agriculture and a grey water market. Changes in legislation introduced in the UK Water Bill opens up commercial opportunities as a water supplier and the Coal Authority has commenced discussions with how to sell water into this market. Separately it has engaged with talks as a private supplier to large water users.

An analysis of this water indicates that a high percentage has commercial value. Water Conductivity of untreated mine water in schemes is shown in table 1.

Table 1. *Water conductivity at UK coal mine water treatments schemes 2016*

Water quality	Conductivity (uScm^{-1} at 25^{O}C	Mine water treatments schemes	Aggregated flow (Ls^{-1})	Flow percentage (%)
Low salinity	< 1500	39	1000	34
Medium salinity	1500 – 3000	21	1100	38
High salinity	> 3000	11	850	28

Water recycling opportunities becomes more favourable with large industries due to water scarceness, droughts, quality of raw water and new technologies being able to optimise / upgrade existing process waters. Where water quality does not meet user requirements, options are being investigated to raise the water quality using membrane bio-reactors, ultra-filtration, reverse osmosis and electro deionisation. The financial model for such treatment is based on the partially treated mine water costs having been absorbed by the existing costs of managing the scheme for environmental benefit. Therefore, the profit made from such schemes goes directly to offsetting the costs of the environmental benefit schemes.

The use of this supply of water complements the Water Recycling Model of: Water Conservation, Water Re-use, Water Recycling, Process and Product Integrity and Environmental Impact. Incomes from the sale of water and sustainability of supply are being well received by water companies, industries and regulators in the early discussions.

Sustainable use of mine water heat at surface

Geothermal energy represents a major source of carbon free energy (P.Younger Geothermal Energy: Delivering on the Global potential, 2015). The Coal Authority extracts approximately 100billion litres of water per annum typically ranging from 11 to 20 ^{o}C. A trial of heat exchangers at the Dawdon Mine Water Treatment Scheme (Bailey et al.,2013) has been successful in producing space heat without maintenance issues for ochre build up or adverse reactions to the hypersaline mine water. By extracting water from the direct feed prior to aeration there have been no issues of ochre deposition within the heat exchanger.

By removing five degrees centigrade as an efficient extraction rate (Dawdon Heat Pump Report Ecolinx 2013), from the portfolio of MWTS's, at the point of water coming to surface, a potential 63 MW of heat can be harvested. This heat asset has a significant value in financial terms and in the supply of a low carbon sustainable energy source to reduce the UK's reliance on fossil fuels.

The Authority has a commercial advantage over alternative means of using ground source heat, and mine water heat extraction, in that the many of the costs are covered by the schemes operational costs. These costs include; access to mine water through boreholes, shafts and adits; pumping costs; and disposal of cooled water.

The Coal Authority has two heat schemes progressing with a combined 3.6 MW of heat potential and another nine schemes at early discussion stage.

Sustainable uses for ochre

Mine water treatment schemes in the UK produce approximately 4,500 tonnes dry solids of Ferric Hydroxide per annum. Historically, this has been disposed of to landfill. Costs of desludging and disposal of sludges has increased as schemes have matured. In 2015/2016 the desludging and disposal costs were $1.75million.

To offset these costs and provide commercial incomes the Coal Authority is engaged in a programme to find commercial markets for this material and is in discussions with foundries, coagulant manufactures and pigment manufactures (S.Bearden, 2002). Discussions with regulators are ongoing on end of waste but also the potential use of this material for sustainable environmental improvement.

In addition to the work on ferric products, areas of innovation to be explored in 2016/2017 include desludging, sludge handling, sludge drying and sludge preparation efficiencies. This work is to increase potential for economically viable products to be created or for the ochre to go in as feedstock to industry.

With many of UK water courses having high phosphate levels and with increased phosphate targets under the Water Framework Directive, the Coal Authority is working with water companies on a number of opportunities to reduce phosphate levels in watercourses and water bodies using iron rich mine water, ferric sludges and ferric products.

In 2005 the Coal Authority entered into a joint venture with a water company combining the treatment of a raw coal mine water discharge and secondary treated sewerage effluent. Data collected over the past decade indicates that there are no seasonal trends between the interactions of iron and phosphate; this is likely due to the consistent temperature of the mine water. Presence of HFO and iron flocs is key to phosphate and ferrous iron removal, with the initial interactions between iron and phosphate being essential. Using co-treatment mechanisms can help realise the new Water Framework Directive targets for phosphate without the need for the addition of chemical dosing. Further work with Water Companies is ongoing to develop niche products that target upstream or point of origin issues of phosphate, such as from agricultural sources, as well as from waste water treatment works.

Sustainable energy use

During 2015 the Coal Authority undertook a review of its mine water treatment schemes and land holdings for the use of renewable energy. This has identified a large number of schemes that will benefit from the use of renewable energy sources when this power is used on site. Changes in Government subsidies in late 2015 have reduced the profitability of feeding surplus capacity into the electrical grid such that currently electricity generation is only viable to the Authority for use rather than export. However, as technologies change and cost of infrastructure changes this might change in the future.

A rolling programme of introducing renewable energy schemes onto sites started in March 2016. Typically these will be 50kW solar schemes, such as that recently installed at Dawdon (Figure 1). Use of wind turbines, wind pumps, mini hydro, hydro and energy storage are being progressed based on an assessments of cost benefit and sustainability targets. A number of existing schemes have been identified with the opportunity for direct feed from wind turbines, existing hydro schemes and biomass power stations. Discussion with these energy providers are ongoing.

Figure 1 *Dawdon active scheme 49.92Kw scheme installed in 2016 consisting of 192 260 W panels.*

As water treated by mine water schemes has a typical flow of less than 200 L/s there is little opportunity to generate significant hydro power to offset the cost of pumping. A review of existing schemes is to be carried out to identify opportunities to source power from watercourses. The location of new schemes will consider locations sufficiently close to water bodies with a high flow as a means to provide sustainable power sources and reduce operating costs.

Realising value from mine water treatment schemes

Existing mine water treatment assets offer a number of opportunities to provide savings and generate incomes. These include leasing of land to energy generators, incomes from power use variation and letting of land for commercial incomes.

The UK's electrical network and system frequency is a continuously changing variable. When demand is greater than generation, the frequency falls, and when generation is greater than demand, the frequency rises. National Grid controls and monitors system frequency in real time using second by second metering to balance demand and generation.

The Coal Authority has recently enrolled in a contract with a Frequency Response aggregator, committing an initial 325 kW into a firm frequency response programme. Additional opportunities are being progressed. The result of this, coupled with power management will be altering pumping regimes such that existing and future pumped schemes are managed at a water level that can allow some downtime of pumps. This enables pumping to occur at times of cheaper energy tariffs and for pumps to be shut down during peak demand times to balance the power network. Careful consideration is needed to ensure that any additional drawdown or treatment capacity needed does not remove savings from energy management. This is considered under careful cost benefit analysis and whole life costs for each scheme.

Another opportunity being progressed is the siting of power generators on mine water treatment schemes to feed into the electrical grid at times of high income. The grid is coming under increasing stress as a result of decreased electricity generation capacity, with the last coal fired power station due to be out of commission by 2023,. The Government is seeking companies to provide extra STOR (Short Term Operating Reserve) capacity, in small power plants that can come on-line quickly. These are supplied under 10 or 15 year contracts. With some Coal Authority sites having land availability and access to the grid, there is an opportunity to create extra value by leasing out suitable sites to operators and generating a substantial extra annual income.

Whole life cost savings through contract management

In 2015 the Coal Authority let two NEC3 framework contracts; one for the design and construction; and the other for operational maintenance of mine water treatment schemes. Contractors were selected who would bring efficiencies and innovation to provide whole life costs savings and who would work effectively in a tripartite manner with the Coal Authority and each other. The contract manages efficiencies through a pain/gain mechanism which provides financial incentives to deliver savings.

To promote innovation, contractors can receive funding from an innovation fund set up by the Coal Authority. This fund operates independently of the pain/gain mechanism so allows risks to be taken in the trialling of new technologies or initiatives. Where innovation is successful the contractors receive financial benefit from the savings provided.

To assist the innovation process the Coal Authority is establishing an innovation hub and innovation log. The log has been populated initially with over 360 innovation and efficiency opportunities ranging from small incremental improvements to step change novel technologies. This log is under regular review to provide a dynamic tool to provide focus to innovation and for taking the most effective opportunities forward.

Catchment management approach

Mine water treatment schemes have been developed historically based solely on capturing and treating the mine water at the point of discharge or point of greatest access to provide the cheapest possible outcome. The business case for each scheme has been built on a cost benefit assessment, with the benefits appraisal identifying the benefits of cleaning the water and some benefits of the scheme itself. However, in future, schemes will be developed using a catchment management approach with a wider view of benefits.

The catchment management approach does not just look at the benefits of removing or preventing the pollution, but also on the wider benefits to stakeholders within the catchment. Where potential users of water, heat or other mine water related products or services exist then these factors will be taken into account when considering mine water treatment location and design.

A theoretical example might be that the cheapest location and treatment for a mine water discharge is near the point of discharge with easy capture and minimal pumping to a passive treatment area. This would have historically been the preferred option. However, taking a catchment management approach, the new preferred solution might mean that the level is controlled by pumping a former mine entry. This additional pumping is off-set by:

- a wind turbine that can be sited adjacent to the mine water control point;
- a treatment location adjacent to a waste water treatment works, which takes raw mine water to help coagulate raw effluent and improve sludge settlement without the need for processed chemical coagulants; and

- final mine water effluent treatment polishing provides a habitat island for migratory birds and local ecological amenity for community use.

This is but one example of multiple permutations that can be explored by involving various catchment stakeholders such as developers, water companies, wildlife trusts and community groups.

Such an approach is being delivered at one of our sites, where the scheme is adjacent to a derelict industrial site in an area of economic deprivation. By working with the developer, the local authority and interest groups, an energy efficient development is planned, using both heat and water from the pumped mine water, and energy from local wind and biomass to directly power the pumps. This is a multiple win situation:

- the Coal Authority gets power at a reduced rate and off-sets the cost of mine water treatment through sale of heat and water;
- the developer gets a unique selling point for their site to encourage sustainably focused industries to their sites;
- the local authority gets regeneration of the area with new jobs to replace the ones from old industries; and
- the planet gains from energy and water efficiency from reuse of heat and water, and low carbon energy generation.

Many more such projects are being planned, with implementation over the next few years.

Small footprint design

Mine water treatment schemes in the UK typically follow two design routes:

- Small footprint, high chemical and energy use active schemes; or
- Large footprint low chemical use passive schemes.

Designs have previously been based on PIRAMID Consortium guidelines (PIRAMID Consortium, 2003 Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters). The Coal Authority is now investigating transferable technologies and potential novel technologies of its own design, which have the potential to deliver small footprint, low cost, low chemical use passive schemes. To achieve this aim the scheme components have been split into three key functions:

- Energy use;
- Rapid deposition; and
- Polishing.

A number of technologies have been identified in all of these areas, each of which has been prioritised and trials in 2016/2017 will identify if the priority technologies will deliver significant benefits.

The controlled deposition of iron is seen an important component in improving performance and reducing costs at existing mine water treatment schemes, and in the delivery of future small footprint schemes. Rapid deposition could provide savings in chemical costs, desludging, reed bed maintenance and retention lagoon sizing. It has a high likelihood of improving performance of existing schemes and replace/improve the use of cascades. It is of interest in the Ochre Product Project in delivering continuity of supply for Ferric Hydroxide products.

A number of technologies from other industries have been assessed that will accelerate rapid deposition of iron, with trials currently being carried out on self-aspirating aerators used in the shale gas industry.

Additional novel technologies within the Research and Development programme in 2016/2017 include small footprint solutions to replace reed beds, minimise lagoon size and resist ochre build up on surfaces. These technologies will help drive down capital, maintenance and energy costs, with potential additional benefits such as ability to free up land or provide consistent materials for commercial use.

Conclusions

The Coal Authority is carrying out an ambitious programme of efficiencies and innovation based on its 2015 innovation exercise. Many of these opportunities have contributed to the creation of a cohesive vision of partnership working involving a wide number of stakeholders including water companies, regulators, land developers, industry, communities, local authorities and government agencies. Discussion with these groups under its Catchment Management Initiative have been well received, with all parties seeing substantial benefits that exceed the sum of their individual interest or contribution.

A number of technologies and initiatives are being trialled to deliver the small footprint, low whole life cost, low carbon footprint, income generation schemes which are the ultimate ambition of the innovation programme. A large number of water company opportunities have been identified which have commercial and sustainability opportunities, Engagement on these opportunities is in early stages but promising. The success of the innovation programme will be reviewed at the end of 2016/2017 to identify which areas show greatest promise and which are of lesser priority.

Acknowledgements

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Membranes and minewater – waste or revenue stream

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Abstract

Membrane technologies are capable of treating mine waste waters to produce clean permeate water for reuse and a concentrate stream that can be used for valuable metals recovery. In this paper, the authors have researched and identified 363 mines with potential to use Reverse Osmosis (RO) Nanofiltration (NF) and Ultrafiltration (UF) membrane technology. There are sixty-seven operational membrane plants and fifty-one of these have been commissioned in the last ten years. 69% of these are in gold and copper mines. In precious metal mines, waste water can be concentrated using membrane plant so additional metals can be recovered from barren liquor. Acid mine drainage (AMD) is increasingly treated and then reused or sent off site as a valuable resource for domestic and agricultural use. The membrane plant can suffer from rapid fouling and calcium sulphate (gypsum) scale. The reasons for this are explored and new techniques for preventing sulphate scale and to clean fouled membranes are introduced.

Key words: reverse osmosis membranes; ultra-filtration, waste water; mining, acid mine drainage; metal recovery; membrane cleaning; antiscalants; calcium sulphate, gypsum

1. Introduction

The mining industry is the fourth largest user of water. To extract 1 ounce of gold 33,000 litres (8382 USgalls) of water is required and for 1 kg of copper 18,000 litres (4752 USgalls). GWI 2014 (1) Mining is often carried out in remote locations with scarce water supplies. Mining companies are increasingly conscious of the environmental impact of their activities and are investing significant amounts in water infrastructure and management systems to reuse water, improve metals recovery and treat effluents before discharge. Projections by Frost & Sullivan for 2014 anticipate an estimated US$13.6 billion of expenditure in mining-related water infrastructure, almost doubling the 2011 global spend. Szyplinska 2014, stated that over 90% of mine water can be reused if treatment technologies such as reverse osmosis and microfiltration are applied. (2) The uptake of this technology has increased over recent years as improvements have been made in the operation and maintenance of membrane plants. The challenging feed waters cause rapid scaling and fouling. In this paper, the authors have identified 363 mines with potential to use RO/NF/UF membrane plants. Sixty-seven operational membrane plants in mines have been identified and referenced Fifty-one of these have been commissioned in the last ten years with 65% of the plants used in gold and copper mines. In precious metal mines, waste water can be concentrated using membrane plant so additional metal can be recovered from barren liquor. Acid mine drainage (AMD) is increasingly treated and then used as a supply to the mine for process and domestic use. The Anglo American Emalahleni project in S. Africa took the AMD water from three coal mines and converted into drinking water for 80,000 people in the surrounding communities. (3)

Membrane plant can suffer from rapid fouling and calcium sulphate (gypsum) scale. The reasons for this are explored and new techniques for preventing sulphate scale and to clean fouled membranes are introduced. Typical mine feed water quality is outside of the parameters of normal RO/NF/UF plant operation. A scaling prediction model has been developed and new sulphate antiscalants formulated that can cope with extremes of pH, soluble metals, and sulphate loading. Details of new methods for cleaning membranes including permeate backflush, use of effervescing reagents and microbubbles are described and explained. Subsequent papers will describe real case studies.

The drivers for recent rapid adoption of membrane plants are both economic and regulatory. The efficient operation of membrane plant can recover precious metal from the waste water and produce clean water that can be used for the process. Further improvements in keeping membranes clean results in environ-mentally damaging waste waters being reused. The mining companies extract value from this through increased yields, reduced environmental risk and effluent charges, increased good will and water supply to the local communities. The areas where membrane plant can be used in copper and gold mines are described and two examples are used to illustrate the potential.

2. Membrane use in mining

There are many wastewater sources generated by mining which have high concentrations of total dissolved solids (TDS), mainly consisting of sulphate, metals, carbonate and calcium at acid and alkaline pH. Sulphate is produced by the oxidation of pyritic ores simplistically represented by the equation:

$$4\ FeS_2 + 9\ O_2 + 4\ H_2O \rightarrow 8\ H^+ + 4\ SO_4^{2-} + 2\ Fe(OH)_3.$$

Calcium can also be present at elevated levels if lime is added to help neutralise acidic wastewaters. There are a whole host of other possible constituents due to the chemicals dosed in the metal extraction process for flotation, leaching, then cyanide destruction and further pH adjustment. Treating the affected water prior to disposal reduces the environmental toxicity of discharge and stored water. Membranes can remove suspended and dissolved solids producing a low volume concentrate stream typically 25% of the feed volume and a pure stream of water that can be used for process, and even drinking if correctly treated. The concentrate stream can contain enough precious metals to be classed as a pregnant liquor and be diverted to the leaching process for metal extraction. Membrane separation is used extensively around the world in industrial and municipal applications and has a consistent cost effective performance. Only recently has this technology been more commonly adopted in the mining industry.

2.1 Reverse Osmosis (RO), Nano-Filtration (NF), Ultra-Filtration (UF). Micro-Filtration (MF)

Reverse osmosis is a way to get clean water out of dirty water or salt water by forcing water under pressure through a semi-permeable membrane. RO removes all suspended solids and ca. 99% of soluble cations and anions while allowing water to pass through the membrane, as it is one of the smallest molecules with a molecular weight of 18. RO elements have ~100 amu (Dalton) molecular weight cut-off.

Nano-filtration is the same as RO except that the membrane pores are slightly larger so divalent ions are rejected but monovalent ions pass through the membrane. NF has 200-400 amu (Dalton) molecular weight cut-off.

Ultra-filtration (UF) technology uses a membrane barrier to exclude particles as small as 0.001 – 0.1 µm microns, including bacteria, viruses and colloids from fluids.

Micro-Filtration is a physical filtration process where a contaminated fluid is passed through a special pore-sized membrane of 0.1 – 10 µm to separate microorganisms and suspended particles from process liquid.

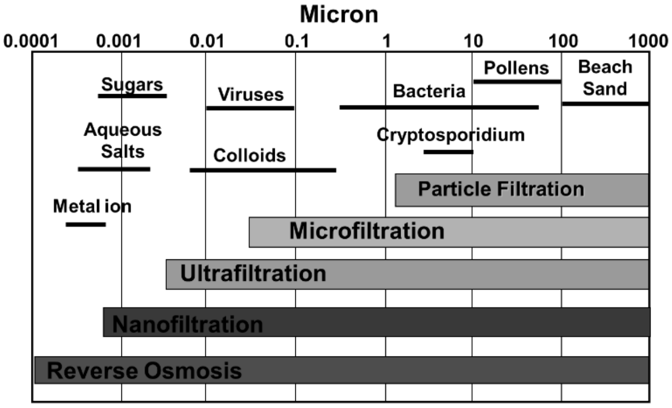


***Figure 1** Filtration spectrum of membrane processes. Courtesy of DOW Water Solutions.*

2.2 Mines with potential for membrane use

An extensive database of mining companies and their known mine locations was prepared and then researched for the applicability of membrane use. Sites with reference material for actual operational membrane plant were focused on and detailed data compiled. The geographical location of 363 possible or suitable mine sites for membrane plant were identified and positioned on the map as a black dot.

Confirmed membrane plant locations are represented by coloured balloons by geographical cluster areas in figure 2.

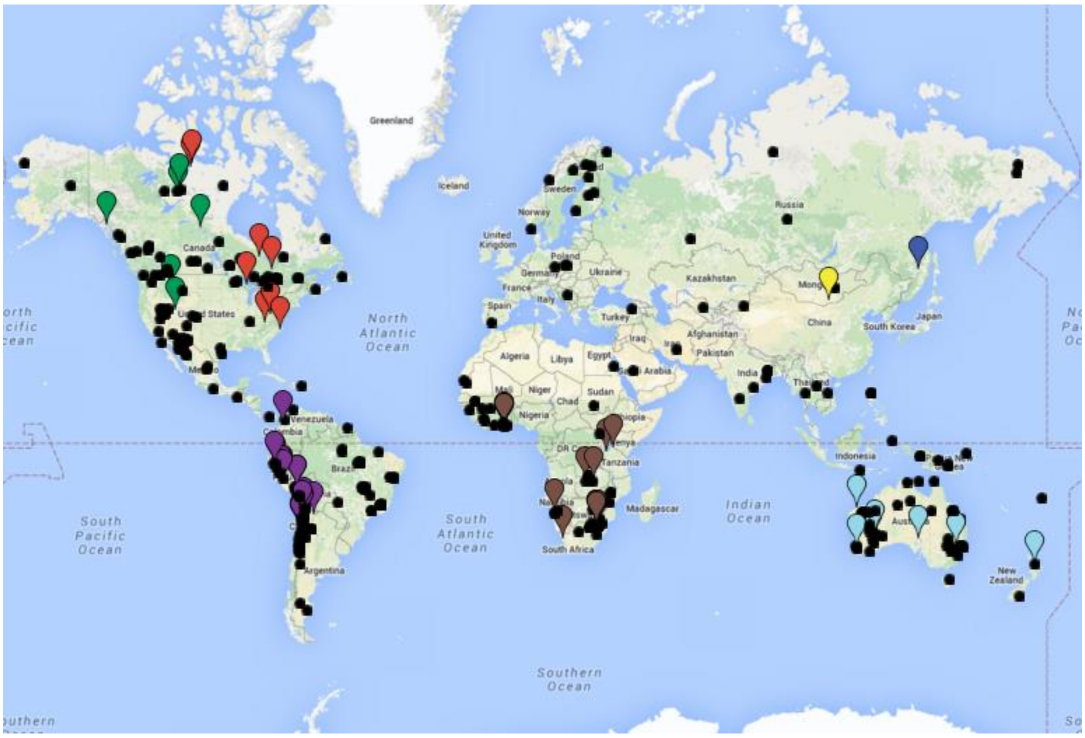


***Figure 2** Mine locations and actual membrane plant*

2.3 Mines with operational membrane plant

A total of 67 operational membrane plants were identified. Of these, Latin America had the most plants principally in Peru and Chile. The number of plants in Chile was boosted by the presence of 12 sea water RO units. These are required to produce source water that is pumped to the mines due to the lack of local ground water or surface water. Gold and copper account for 69% of the mines that have invested in RO plants. It is thought that many of the plants that are registered as present for acid mine drain (AMD) clean up may also be using the concentrate water for metal recovery. Only 15 plants were registered as being specifically designed for enhanced metal recovery. There is a lack of detailed description of plants design and operation as intellectual property and operating practices are protected.

***Table 1.** Membrane plants by geography, mine type and water use.*

Location	No. of plant
North America	15
Latin America	25
Europe	1
Australasia	7
Asia	1
Africa	18

Mines	No. of Plant
Gold	30
Copper	16
Coal	9
Diamonds	3
Iron	3
Others	6

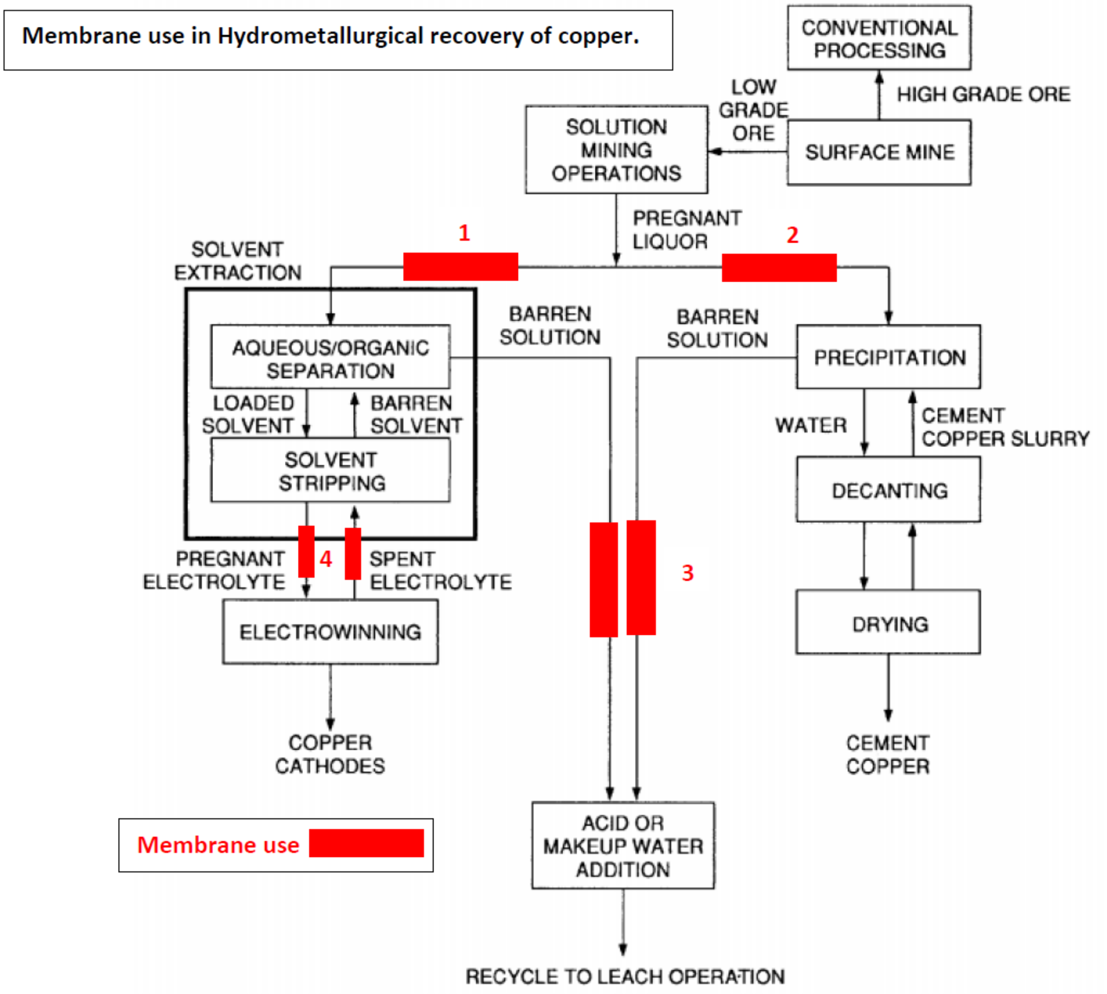
Water use	No. of Plant
AMD Clean up	22
SWRO	17
Metal Recovery	15
Drinking	8
Leachate	5

3. Enhanced Metal Recovery

Mining firms are now being forced to treat AMD wastewater in order to get licenses to mine. If the treatment can result in some metal recovery this can help negate the investment costs in treatment and even make a profit. Conventional AMD treatment and metal recovery involved adding lime or limestone to remove the acidity of wastewater, creating a hydroxide sludge and then attempting to extract individual metals. This required a substantial investment in infrastructure and had a high operational energy and chemical cost. The use of membranes allows waste water streams to be treated, fresh process water to be recovered and reused, and in certain applications precious metals can be recovered. Figures 3 and 4 show areas in the copper processing cycle and the gold heap leaching operation where membranes have been applied. A case study outline of membrane applications in a copper and gold mine is given below.

3.1 Mexicana de Cananea Copper Mine

One of the earliest large scale examples of using reverse osmosis membranes to clean up wastewater and recover metals was the Mexicana de Cananea mine, located in northern Mexico. The mine was facing closure due to insufficient water and a threat of flooding of the operational parts of the mine. 17 Million cubic meters of wastewater had accumulated in the Cananea pit which had been used as a pregnant leach reservoir since the 1980's. After successful pilot plant tests the mine decided to install a full-scale membrane plant in 1997 which was used to: remove water from the pit, recover water from the tailings thickener, increase the copper concentration in the acid leach water feed from the Cananeapitto copper extraction plant, remove excess water from the leach circuits, and produce clean water for mine process water application. Harrison Western 1997 (4)



Adapted from Source: Technical Resource Department: Extraction and Beneficiation of Ores and Minerals, Volume 4 Copper, August 1994 U.S. EPA.

Figure 3. *Membrane use in the copper processing cycle*

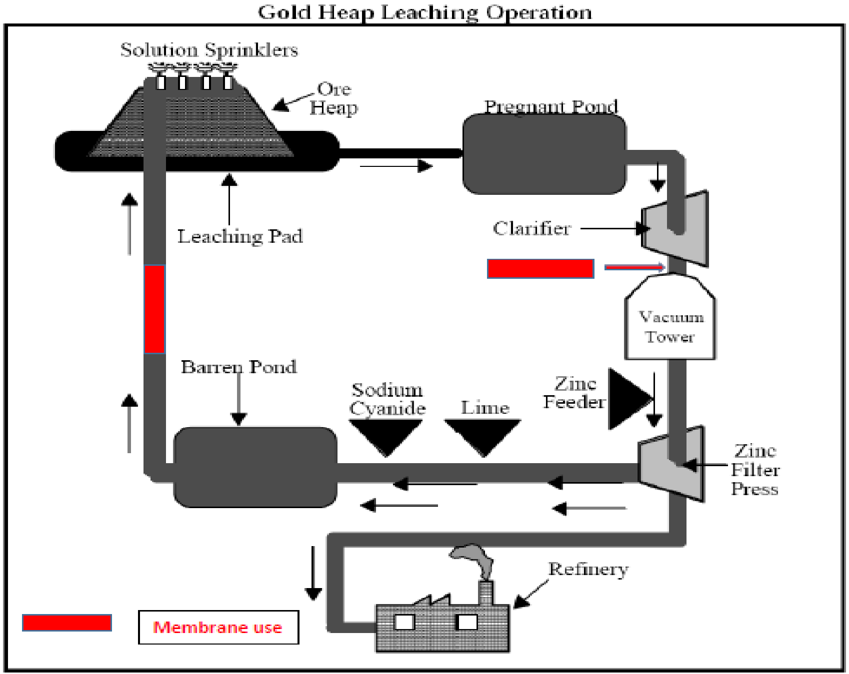
The RO plant was designed to treat a feed water flow of 900m³/hr (4000 US gpm) operating at 50% recovery and producing a 2000 US gpm concentrate stream with 1.6g/L of copper and 2,000 US gpm of clean permeate water for reuse. The objectives were to increase the feed copper concentration to the

SX/EW plant. Solvent extraction and electrowinning (SX/EW) is a two-stage metallurgy process that first extracts and upgrades copper ions from low-grade leach solutions into a solvent containing a chemical that selectively reacts with and solubilizes the copper in the solvent. The copper is extracted from the solvent with strong aqueous acid, which then deposits pure copper onto cathodes using an electrolytic procedure (electrowinning). There was an increase in the cathode copper production by more than 14% creating savings of $212K in process water cost and $27K in sulphuric acid costs and reduce the pit water level. The overall water balance of the pit indicated that its level would continue to drop by about 3.5 meters per year, which is equal to approximately 1 billion gallons per year. The typical capital cost for the membrane plant according to Hanison Western (1997) was $1.5- $2.5 USD/USgall/day. $8.5 to 14.5 million. The operating costs included; power consumption, prefiltration and pretreatment operations, antiscalant and cleaning chemicals, membrane cleaning, and membrane replacement. The typical operating costs were $1.00 - $2.00 USD/1000 gallons water recovered, giving a payback period of 1-3 years. The cost for a lime precipitation system accounting for the loss of copper would be approximately $5.00 USD/1,000 US gallons of water recovered.

3.2 Yanacocha Peru Gold Mine

Minera Yanacocha (Yanacocha) is the largest gold producer in South America and its' mining and processing operations are located at elevations ranging from 3,500 to 4,100 meters in the Andes Mountains, 48 kilometers (30 miles) north of the city of Cajamarca. The gold is extracted by blending the ore with lime and placed on the heap leach pad. Dilute cyanide solution (ranging from 30 to 50 mg/L Free cyanide) is applied through drip and spray irrigation to the heap leach surface. There are seven reverse osmosis modules at Yanacocha (250 m3/h each one) and five excess water treatment plants (two in Carachugo and three in Yanacocha), two carbon plant precious metals recovery plants, and two Merrill Crowe processing plants. During the rainy season, there is a production of excess and increasingly dilute pregnant liquor. The reverse osmosis plants are used to dewater the pregnant liquor making the Merrill-Crowe gold extraction process more viable. Additional RO plants also remove excess cyanide and metals allow the permeate water to be discharged and additional gold recovered via a carbon column. Currently, 2,750 m3/hr of barren leach solution is treated and discharged safely into the environment.

Gold Heap Leaching Operation



Source: U.S. EPA, Office of Enforcement and Compliance Assurance.

Figure 4. *Membrane use in Gold leaching operation*

4. Membrane Scaling and inhibition

Scaling is the unwanted precipitation of sparingly soluble salts onto equipment surfaces during operation due to the solubility of a salt being exceeded. In an RO or NF plant feed water gets increasingly concentrated as it passes from one membrane to the next and is at its most concentrated just as it leaves the last membrane element in the pressure vessel known as reject or concentrate water. A plant is described as operating at a certain recovery rate. That is the proportion of permeate (product) water to concentrate (reject) Table 2 illustrates the ratio of recovery rate to cycles of concentration water. As recovery rates increase so do the cycles of concentration until solubility of certain salts are exceeded and precipitation is followed by crystal growth.

Table 2. *Recovery & cycles*

Recovery Rate	Cycles of Concentration
50%	2
75%	4
80%	5
90%	10

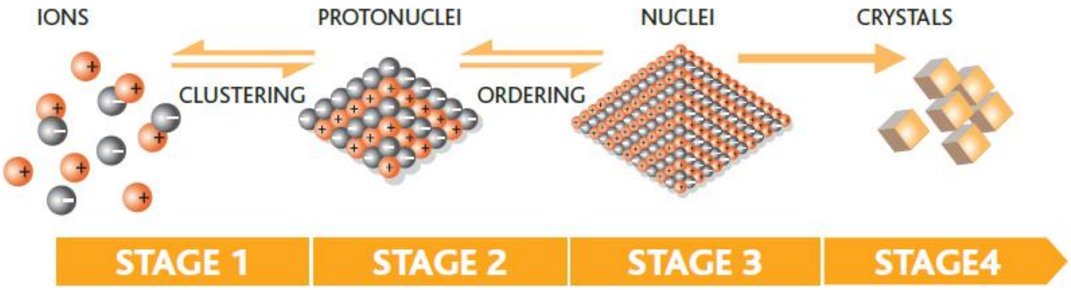


Figure 5. *Scale forming process*

Figure 5 shows how ions and cations are attracted to each other and start to form shapes when physically closer to each other when concentrated. Eventually these nuclei become more ordered until precipitation from a solution occurs and a solid is formed. Antiscalants inhibit this precipitation reaction by physically blocking the attraction at the nuclei and ordering stage and distortion of crystal growth. Scale formation in membrane systems is a well-known and documented problem. Its presence in the mining industry is particularly severe due to the chemically stressed waters that are used and the presence of soluble metals.

In a report on the NF treatment leach water at the Bingham Canyon mine Bayer (2004) stated that "The primary difficulty was gypsum (calcium sulphate) scaling in the pressure vessels and concentrate lines." In the Kennecott design report for the |Bingham Canyon water treatment plant RO system (KUCC 2002), it is reported that "gypsum saturation in the RO system is exceeded up to 700%, and silica saturation is exceeded as well." (6) Other studies Harries, 1985 and Jarusutthirak 2007 have warned against fouling due to the precipitation of calcium sulphate and severe reduction in the permeate flux.

One of the earliest studies found which was published in 1970 clearly highlighted the problems of scale formation. The report was written by Donald G. Mason of Rex Chainbelt Inc. on behalf of the Pennsylvania Department of Mines and was titled "Treatment of Acid Mine Drainage by Reverse Osmosis". Whilst advocating the process of reverse osmosis to clean up the water and produce good quality water fit to drink the report highlighted scaling and fouling issues stating that:

- Iron III in the presence of oxygen at a pH of 3.5 caused serious iron fouling of the membranes, which resulted in a rapid decrease in product water flow.
- Ten percent of modules failed after 813 hours of operation

- Module failures were always associated with chemical cleaning of the membranes using sodium hydrosulfite.

Mining water becomes acidic and laden with sulphate due to the oxidation of pyritic ores simplistically represented by the equation: $4\ FeS_2 + 9\ O_2 + 4\ H_2O \rightarrow 8\ H^+ + 4\ (SO_4)^{2-} + 2\ Fe(OH)_3$. Calcium sulphate scale is particularly problematic as its formation is complex and it is particularly difficult to take back into solution and therefore clean from a membrane surface.

4.1 Calcium Sulphate Chemistry

There are three major forms of calcium sulphate, hemihydrate – $CaSO_4(H_2O)_{0.5}$, dihydrate – $CaSO_4{*}2H_2O$, and anhydrite – $CaSO_4$. These have differing solubility isotherms as shown in figure 1. For RO waters the dihydrate form predominates. The solubility of calcium sulphate, in the dihydrate form ($CaSO_4.2H_2O$ -gypsum) is similar to calcium carbonate, which decreases with increasing temperature although this is less marked than the other species. However whilst the precipitation of calcium carbonate scale can often be minimized by reducing the pH of the feed water, calcium sulphate solubility is independent of pH until you get to very acidic conditions pH1-2.

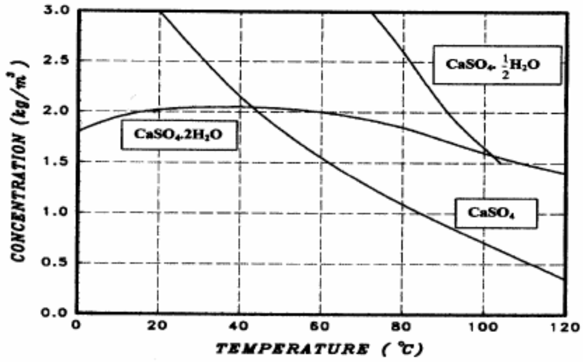


Figure 6: *Solubility of forms of calcium sulphate*

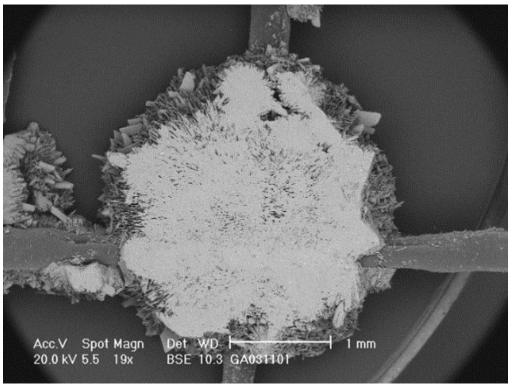


Figure 7: *Rosette formation on spacer*

It is reported in literature Gouellec et al [1] that gypsum scale forms via lateral growth of crystals directly on the membrane surface as well as the deposition of crystals onto the membrane surface. Studies in the Genesys laboratory in Madrid frequently shows crystal platelets forming in the low flow cross over points of the feed spacer – see fig. 2. This feature is further demonstrated when the spacer is removed from the membrane surface during autopsy and it becomes clear the scale is deposited within the spacer layer rather than at the underlying membrane surface. Studies by Rahardianto et al indicated a variation in scale formation due to varying surface topology of different membranes [2]. Scale formation occurs initially in needle form developing into platelets and rosettes. The scale is frequently damaging to membrane surfaces through particulate abrasion and is difficult to remove with chemicals. The development of calcium sulphate scale in the membrane can be further complicated by the potential for precipitation to occur before water concentration along the membrane surface. In these cases an amalgam of partially formed crystals can form. Ben Ahmed et al investigated the effects of different antiscaling compounds showing that phosphonate compounds inhibited the germination of scale crystals and polyacrylic compounds acted as dispersing and crystal distortion agents.(3)

4.2 Scale inhibition

Controlling scale build up is vital for the efficient operation of a membrane plant. This is done firstly by accurately predicting what scaling species are likely to exceed their saturation points and secondly applying physical or chemical treatments so the predicted saturation points can be extended safely. Reducing the recovery rate can stop the scale formation but means the plant does not operate as efficiently as it could. To determine the scaling potential, you need to compare the ion product IPc of the considered salt in the concentrate stream with the solubility product K_{sp} of that salt under conditions in the concentrate stream. (8) This requires an accurate feed water analysis including pH, conductivity and major cations and anions. The operating details of the plant such as flow rates, pressure, temperature and the recovery rate to give cycles of concentration are key to make accurate calculations. Over the last

30 years membrane manufacturers have developed design software that also includes scaling prediction software. The authors have developed their own software and adapted it for use specifically in mining applications.

4.2.1. Scaling Prediction Software

To run the programme data is input about the project, membrane manufacturer and model, water type, plant data and a water analysis for cations and anions. The software then automatically calculates the scaling indices for calcium carbonate, calcium, barium and strontium sulphate, calcium fluoride, calcium phosphate, iron, manganese, aluminium, silica and magnesium hydroxide. Variations in recovery rate, pH and temperature will result in an automatic recalculation of the % saturation point which is expressed graphically. By clicking on the treated button the most appropriate antiscalant and dose rate is chosen and the effect this has on reducing the %saturation of different scale species is expressed graphically. Changes in recovery rate, pH and temperature and water analysis will automatically result in changes in the antiscalant does rate. The untreated and treated situation can be compared. See figure 8

Recovery 80.0

Feed Water pH 8.4

Operating Temperature (°C) 20

RECOMMENDED ANTISCALANT

GENESYS LF

Dosages

For Scale Control - Feed	2.58	mg/l
For Iron Control - Feed	0.24	mg/l
Total Feed Dose	2.82	mg/l
Genesys-LF in Conc.	14.12	mg/l
Operating Time	24.0	hr/day
Set Dosing Pump To	563.91	ml/hr
Daily Requirement	17.65	kg/day
Acid not used	0.00	mg/l
Daily Acid Requirement	0.00	l/day

% Saturation:	$CaCO_3$	$CaSO_4$	$BaSO_4$	$SrSO_4$	CaF_2	$Ca_3(PO_4)_2$	Fe	SiO_2	Al	Mn	$Mg(OH)_2$
Conc. Untreated	179.97	165.61	875.15	174.06	2005.04	0.00	173.13	114.86	114.86	961.83	1.51
Conc. Treated	93.09	59.15	17.50	17.41	14.32	0.00	11.54	76.57	74.58	64.12	0.02

Figure 8. *Genesys Membrane Master 4 scaling prediction software*

4.2.2. Antiscalants

All antiscalants work at a sub-stoichiometric level by one or more closely inter-related mechanisms of threshold inhibition, crystal distortion and dispersion. Threshold inhibition – prevents the precipitation of salts once the salt has exceeded its solubility product. The chemical inhibitors retard or delay the clustering process of charged ions and protonuclei. The most effective threshold inhibitors are sodium salts of phosphonic acids, which have the added advantage of sequestering iron in a stoichiometric reaction. This is vital in membrane applications, as any soluble iron will cause rapid fouling. Crystal Distortion – chemicals affect the ordering and growth reactions of crystals causing an irregular shape and weak structure. Chemicals with effective crystal distortion properties tend to be polymers of low molecular weight 2,000-10,000. Many of these polymers show some threshold effectivity whilst others have dispersion properties. Importantly they are ineffective at preventing iron deposition and instead tend to react with iron to produce iron acrylate, which irreparably damages the membranes. Crystal Dispersion – occurs when the inhibitor chemisorbs onto the crystal surface and imparts an additional surface charge causing repulsion and ultimately dispersion. The growing crystal needs to be enveloped in a polymer of high Molecular Weight 20,000-40,000 to gain a significant surface charge. Few of the antiscalants on the market utilise polymers of a sufficiently high molecular weight to cause chemisorption on to crystal surfaces.

Formulation – Following an analysis of the chemistry, formation, dynamics and kinetics of the specific scaling species some potentially active ingredients are chosen to be combined into formulations and then tested against known standard performing antiscalants to see if an improved performance can be observed. When developing a calcium sulphate specific antiscalant the key attributes summarized in table 3 were studied.

Table 2. *Properties of calcium sulphate scale*

Species	Crystal form	Kinetics	Position	Seeding Agents
Calcium sulphate	Monoclinic prisms, needle & platelets	Slow	Last element	Colloidal calcium sulphate

Based on observations above certain assumptions regarding molecules that have differing properties can be made. Calcium sulphate is strongly crystalline developing through weak needle and platelet forms to highly stable rosettes particularly in low flow areas around the membrane feed spacer. Due to these features combinations of phosphonates and crystal distortion and dispersion agents were used to develop a formulation that was more effective than conventional antiscalants. Threshold testing – is conducted by making up standard beaker solutions of specific scaling species. The various formulations are then added at different dose rates and the solution agitated for different contact times at 25°C. The samples are filtered and the filtrate analysed for the presence of the scaling species. The % threshold inhibition can be determined as the percentage of scaling species that remained in solution. The initial results then allow further tests to be conducted with the most promising formulations. Differing operating pH, temperature and incubation times are used. Finally tests on the formulations against all common scaling species are carried out so the final formulation has a broad spectrum of activity whilst being very effective against a specific scalant. The results of threshold testing and product formulation resuted in: Genesys CAS – a calcium sulphate antiscalant blend of three different phosphonic and carboxylic acids.

5. Membrane fouling and cleaning

Fouling is the deposition on the membrane surface and feed spacer of suspended solids in the feed water. It happens in the lead elements of a membrane plant as soon as particles hit the membrane surfaces. The main sources of fouling are bacteria, clay, colloidal silica, organics and metal oxides and hydroxides. Pretreatment chemicals that are used to agglomerate suspended solids for removal by filtration media can also result in fouling of membrane surfaces. They include coagulants such as aluminum sulfate, ferric chloride and organic flocculants. Several methods or indices have been proposed to predict a colloidal fouling potential of feed waters, including turbidity, Silt Density Index (SDI) and Modified Fouling Index (MFI). The SDI is the most commonly used fouling index and acceptable levels are quoted by membrane manufacturers of 2-3. Analysis of the results of autopsies of lead membrane elements by the Genesys Membrane Products laboratory in Madrid showed that 35% had clay (alumino-silicates), 27% organic matter and 22% biofilm. These three foulants made up 84% of the deposits identified. Figure 9.

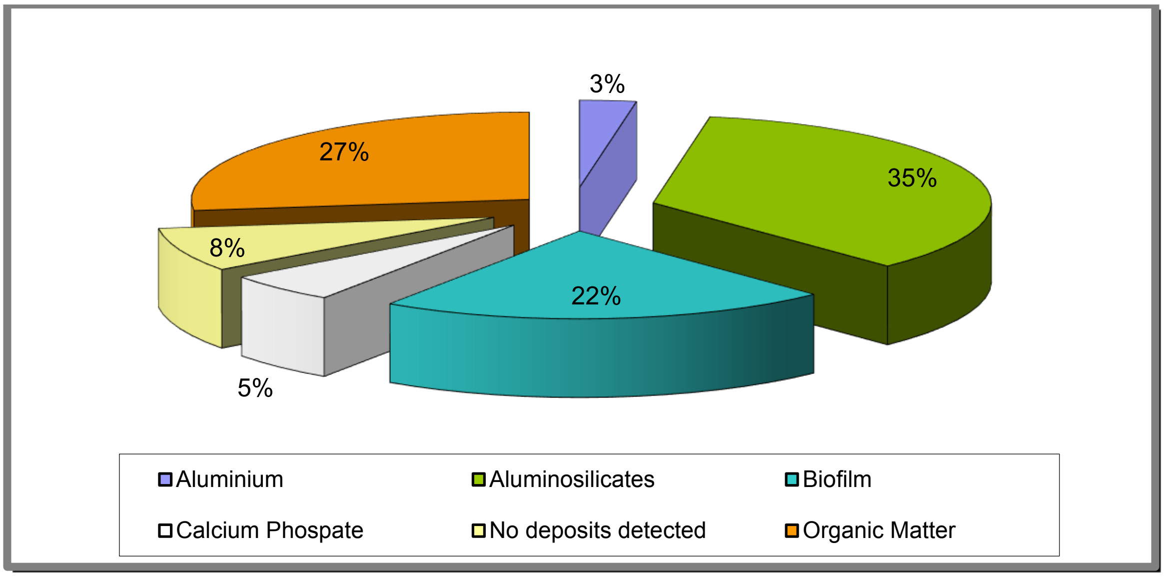


Figure 9. *The main types of foulant identified on membrane elements from the first position during autopsy (2001-2014). Source: GMP laboratories statistics*

Significantly clay, biofilm and organic fouling are notoriously difficult to remove from a membrane surface because they can become compressed into the membrane surface and pores causing plugging, and are impermeable making them resistant to chemical attack. The types of feed water in mining applications that membrane plants have to deal with contains all of these foulants combined with metals in suspension and solution. Frequently the pre-treatment systems are inadequate and the feed water variable which increases the fouling tendency in mining and is regularly reported in literature. A case study by Nieuwenhuis et al 2000 on a tubular and spiral wound RO plant use to treat AMD and ash water for boiler feed water commented on a successful operation but highlighted "The major issue that was reported with the standard cleaning in place (of the membrane plant) was that it was not completely effective in mitigating biofouling which resulted in the lower reported flux in the spiral wound RO plant" The targeted cleaning frequency was monthly but in reality each train was cleaned 2.5 times per month and the flux was only 20.1 L/m².h compared with a target of 25 L/m².h Cleaning was done with a mixture of commodity chemicals. The propensity for rapid fouling and scaling of membrane plants used in mining has lead the authors to look at more sophisticated methods for effective cleaning outlined below.

5.1. Membrane Autopsy and cleaning tests

An autopsy is a destructive test but gives invaluable information regarding the type of deposit on the membrane surface, the condition of the membrane, and how best to clean it. The excerpts below from membrane manufacturers, confirm that they agree that identification of the deposit on the membrane surface is key to optimum cleaning. "Each cleaning situation is different; therefore specific cleaning recommendations are dependent on the foulant" [2]. "The appropriate solution to use can be determined by chemical analysis of the fouling material. A detailed examination of the results of the analysis will provide additional clues as to the best method of cleaning" [4].

Different chemistries are required to remove different foulants and scalants. The preferred method of analysis is membrane autopsy which uses various scientific methods to accurately identify the individual types and amounts of foulants present. Different cleaning chemicals are tested against the membrane with characterization of flux and salt rejection (SR) used to establish the most efficient cleaning procedure. Autopsy of cartridge filters and SDI filter papers can identify likely deposits present on lead elements. A small sacrificial 2" element could also be installed to simulate operating conditions; an autopsy is performed after a suitable time to establish the fouling nature of the main system. Feed water analyses, scaling prediction software and normalized data can all be used to help give clues to the foulant.

5.2. Cleaning Chemistry

Basic cleaning chemistries are described in table 4 below and are referenced by membrane manufacturers in their cleaning guides. The selection of the appropriate cleaning chemicals has a major effect on the success and, most importantly, frequency of the CIP procedure.

***Table 4**. Traditional cleaning chemistry*

Type	Action	Typical Chemical
Acid	Solubilisation	Hydrochloric, nitric, sulphamic, citric
Non Oxidising Biocide	Biocidal	DBNPA, Isothiazolin
Caustic	Hydrolysis, Solubilisation	NaOH,
Chelant	Chelation	EDTA
Detergent	Emulsifying, dispersion, surface conditioning	STPP
Oxidant	Oxidation, disinfectant	Hypochlorite, ozone, hydrogen peroxide
Surfactant	Emulsifying, dispersion, surface conditioning	SDS

Many different chemical formulations are commercially available. The choice of which to use is often made on cost/kg of the individual product, although in reality, the cost of any effective product in terms of operational costs of a fouled system is extremely low, and pay-back will be quickly achieved. When selecting a suitable chemical it is therefore of greater importance to consider different evaluation criteria; application rates, performance of the individual products against your specific foulants (availability of documented scientific evidence) and onsite technical support. Overall evaluation of the success of a cleaning chemical should be performed over a longer period to give an indication of the change in required cleaning frequency of the RO system. Experience shows that employing a successful cleaning regime can reduce required cleaning frequency by several times per annum. Many researchers have shown that the use of speciality formulated cleaners combining different chemistries incorporating detergents, chelants and surfactants have an enhanced cleaning effect on membranes when compared to the use of commodity acids and alkalis.[1] Commodities also tend have transition metal impurities which can damage the membranes and leave them prone to subsequent catalysed oxidation reactions.

5.3 Chemical Application

Foulant identification and chemical selection are vital. Since all cleaning situations and RO systems are different, it is not possible to produce a generic cleaning procedure for all membrane plants. All of the factors below must also be considered when designing a suitable cleaning procedure:

- Temperature is vital for removal of organic foulants, generally 35-40ºC is acceptable. For removing inorganic scales, temperature of the CIP water may affect solubility and therefore removal. Lower temperatures are generally required.
- Contact time is also vital; in a highly fouled system, cleaning cycle times should be maximized to ensure efficient removal. Speciality chemicals will reduce the time required for cleaning. Sufficient time for optimum cleaning must be allowed, with additional cycles added if necessary, by emptying and refilling with the same chemical.
- pH is important for removal of both MAIN groups – organic based foulants and scales. Monitoring pH changes during the CIP will help to evaluate success.
- RO permeate should be used to prepare CIP solutions and to flush the system between application of different chemicals.
- Pressures and flow rates can be altered in line with membrane manufacturers' guidelines to help remove foulants physically.
- The system should be thoroughly flushed after the CIP procedure to ensure traces of CIP chemicals are removed before returning to service.

5.4 Innovations in membrane cleaning

The use of products formulated with multiple cleaning mechanisms offers enhanced cleaning performance. Conducting an effective clean rather than multiple partial cleans is a gentler and more efficient process to help extend membrane lifespan and reduce operational costs. The authors have completed a 6 year research programme into new cleaners and methods and have published that work. The main innovations are:

5.4.1 High ionic strength osmotic flush

The use of powder high ionic strength cleaners during an off-line clean causes normal osmosis to occur during periods of soaking; permeate water passes through the membrane surface to the feed side breaking up layered deposits. This allows the cleaning chemicals improved penetration to dislodge deposits. These powdered products have proven particularly effective against clay, biofilm and organic removal which make up 85% of the foulants in lead elements.

5.4.2 Effervescing reagents

Incorporating effervescent reagents into the cleaning chemical formulations produces chemical microbubbles that abrade, agitate and dislodge deposits at the membrane surface and in and around the feed spacer, which assists in deposit removal.

5.4.3 Air inducted microbubbles

Combining air with the correct cleaning chemical formulation causes a 10 mm air bubble to dissipate into thousands of microbubbles 5-50 microns in size. The microbubbles help physically dislodge deposits without damaging the delicate polyamide salt rejecting layer on the membrane. Smaller plants can easily and cheaply fit a microbubble Genairator™ device to the cleaning circuit which inducts air and creates microbubbles. If a pump forces a fluid flowing into the microbubble generator tube an increase in velocity occurs in the constricted part simultaneously with the decrease in pressure which leads to air being sucked in through the tube. Pressure recovery takes place further downstream and the air bubbles drawn in collapse forming bubbles which then have a tendency to coalesce into larger bubbles around the microbubble generator. In order to optimize cleaning it is preferable to have micro and macro bubbles. This can be achieved using specially formulated cleaning agents which minimize the coalescing of micro, mini and midi bubbles into larger bubbles. The cleaning reagents create a suspension of bubbles and cleaning solution which distribute evenly over the membrane surface in a pulsed fashion. Larger plant can use compressed air which reacts with the cleaning chemistry formulation to create microbubbles.

6. Conclusions

The benefits of using reverse osmosis membranes to clean up waste water streams for discharge have been known about since the 1970's. The first plant to recover metals using reverse osmosis membranes started operating in the 1990's. There has however been a slow adoption of the technology due to capital cost, operational cost, lack of published reference material and a shroud of secrecy. Due to the huge increase in production of membrane elements worldwide the real cost has reduced over the last ten years. Plant designs have become more reliable and 76% of the 67 operational membrane plant have come on line in the last 5 years. Specific mining companies Barrick and Newmont have favoured this technology and repeated successes around the world.

The authors have presented statistics and case study examples of where membranes can be used in mining. The ongoing problems of fouling and scaling still exist as the waters entering the membrane plant have a large amount of complex suspended and dissolved solids. New developments and tools to minimize the problems of scale formation, cleaning and fouling have been presented. These include:

- Scaling prediction software to identify likely scaling species and antiscalants to inhibit the scale
- High performance calcium sulphate, calcium carbonate and silica antiscalants
- Use of membrane autopsy to identify deposits and effective cleaning protocols and products

- Range of pre-formulated cleaning chemistries proven to remove different deposits
- Production of the correct cleaning protocols for individual plant
- High ionic strength cleaners to induce an osmotic flush of permeate water during the soaking stage of cleaning
- Effervescent reagents incorporated in cleaning compounds
- Microbubble generation in the cleaning solution to increase effectiveness of cleaning chemistry

The authors have embarked on a major project to develop mining specific chemical products for the unique challenges that membranes in the mining industry face and will publish subsequent findings in the future.

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Opportunities for Zinc Compound Recovery from Mining Influenced Water

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Abstract

The zinc value in mining influenced water (MIW) is lost when conventional alkaline water treatment process trains are employed for removal. Recovering the zinc value from MIW requires modifying the treatment sequence to produce a metal with a chemical form of value to a market/buyer. One market for zinc is the fertilizer industry, which requires feedstock that can be economically converted to zinc oxide or zinc sulfate.

This paper examines the constraints that should be considered when determining the potential value of zinc in MIW. Contaminant specifications for zinc fertilizer include limits on arsenic, cadmium, chromium, mercury and lead, metals that can co-occur with zinc in MIW. Selective recovery of zinc from MIW in the oxy-hydroxide or carbonate form has the potential to provide a usable feedstock for fertilizer manufacture. Additional processing is required of zinc feedstock to produce a salable product.

An evaluation of potential for zinc fertilizer feedstock recovery from the Nelson Tunnel drainage (Colorado, USA) is presented. The relative concentration of co-contaminants that may occur with zinc oxy-hydroxide or zinc carbonate precipitate formation is estimated. Low relative concentration of metal co-contaminants in MIW is an important factor in producing a zinc feedstock that can meet the acceptance specifications.

Key words: Mine water, resource recovery, metal sludge

Introduction

The US exported 85% of its zinc ore production and imported refined zinc equal to 91% of US production in 2013. Thus, there is a viable market for zinc chemicals and an opportunity to reduce imports by recovery of zinc from mining influenced water (MIW). Analysis of potential metal value based on individual metal concentrations in MIW by Smith et al. (2013) suggests that metal value could offset treatment cost. A next level of analysis requires that additional details related to technical constraints should be evaluated.

Zinc Markets

In 2013, the United States exported 670,000 Metric Tonnes (MT) of zinc and imported 713,000 MT of refined zinc. Zinc oxide and zinc sulphate were 21% of the imported refined zinc at 97,000 and 53,000 MT, respectively. In April 2016, zinc oxide prices per kg Zn were \$2.0 to \$4.4 at 93 to 99% purity; zinc sulfate monohydrate per kg Zn, \$1.5 to \$2.2 at 90 to >99% purity, at the point of shipping from China or India. The average London Metal Exchange price of zinc in April 2016 was \$1.9/kg Zn. The above costs give economic price points to target for the local production of zinc compounds in the US.

There are 4 common forms of zinc oxide/sulphate fertilizers. The chemical forms and nominal characteristics are presented in Table 1 (International Zinc Association, www.zinc.org/crops).

Table 1 *Characteristics of selected zinc fertilizer forms*

Zinc source	Formula	Water solubility	Soil type
Zinc sulfate heptahydrate	$ZnSO_4$-$7H_2O$	high	all
Zinc sulfate monohydrate	$ZnSO_4$-H_2O	high	all
Zinc oxysulfate	$xZnSO_4$-$xZnO$	variable*	variable*
Zinc oxide	ZnO	low	acidic

* depends on relative proportion of $ZnSO_4$ and ZnO

Zinc sulfate forms are the most commonly used zinc fertilizer due to high solubility and relatively low cost (Maltalvo et al. 2016). Zinc oxides have a specific niche for acidic soils and to control the rate of zinc release. Thus, details related to sulfate and oxide forms of zinc fertilizer were selected for further examination.

Zinc Fertilizer Feedstock

Zinc forms that have been produced by chemical treatment of MIW included: zinc carbonate, zinc hydroxide and zinc sulfide. Zinc sulfide of sufficient purity can be processed in a primary (Nyrstar, USA) or secondary zinc smelter (Horsehead Corporation, USA and Canada) to produce zinc metal. Horsehead Corp. also has the capability to produce zinc oxide from recycled zinc sources at selected facilities.

Zinc fertilizer feedstock can be zinc carbonate, zinc hydroxide or zinc sulfate. Zinc carbonate can enter the zinc sulfate fertilizer production line in the dry $ZnCO_3$ form. The use of zinc hydroxide requires roasting at 100 – 250 ˚C to form zinc oxide (ZnO). The use of zinc sulfide requires roasting at 700 to 1000 ˚C to produce ZnO and results in the formation of a sulfur dioxide (SO_2) byproduct. Zinc sulfide precipitate produced by the Wellington Oro Mine Water Treatment Plant (Breckenridge, Colorado USA) is sold to Nyrstar as a feedstock. Thus, carbonate and hydroxide are the two zinc precipitate forms from MIW treatment that have the most potential for fertilizer feedstock.

Zinc Fertilizer

An important consideration in using zinc precipitates from MIW treatment is the presence of trace heavy metals. In 2002, the EPA finalized regulations applied to the production of zinc fertilizer from recycled hazardous secondary materials (40 CFR Parts 261, 266, 268 and 271 [FRL–7248–3]). The rule established new product contaminant specifications. Metal contaminants potentially present in MIW sourced zinc carbonate and hydroxide precipitates are summarized in Table 2. Thus for zinc sulfate monohydrate (35% Zn by mass), arsenic content must be ≤ 10.5 ppm (by mass). The Table 2 values can be used to calculate the metal contaminant limitations for other forms of zinc fertilizer by using the relative zinc percentage of each form and the metal to zinc mass ratios derived from the EPA specifications.

Table 2 *Limits on selected metal contaminants in 35% zinc content fertilizer*

Metal	ppm
Arsenic	10.5
Cadmium	49.0
Chromium	21.0
Lead	98.0
Mercury	10.5

The production of zinc sulfate fertilizer is shown in detail (Figure 1) to show the purification steps that may be required based on the grade of the zinc oxide or zinc carbonate feedstock. The cost of producing zinc sulfate from zinc oxide or zinc carbonate MIW based feedstock may be reduced if metal contaminant limits are controlled in the MIW treatment process or if the relative trace metal concentrations relative to zinc are already below the EPA specification.

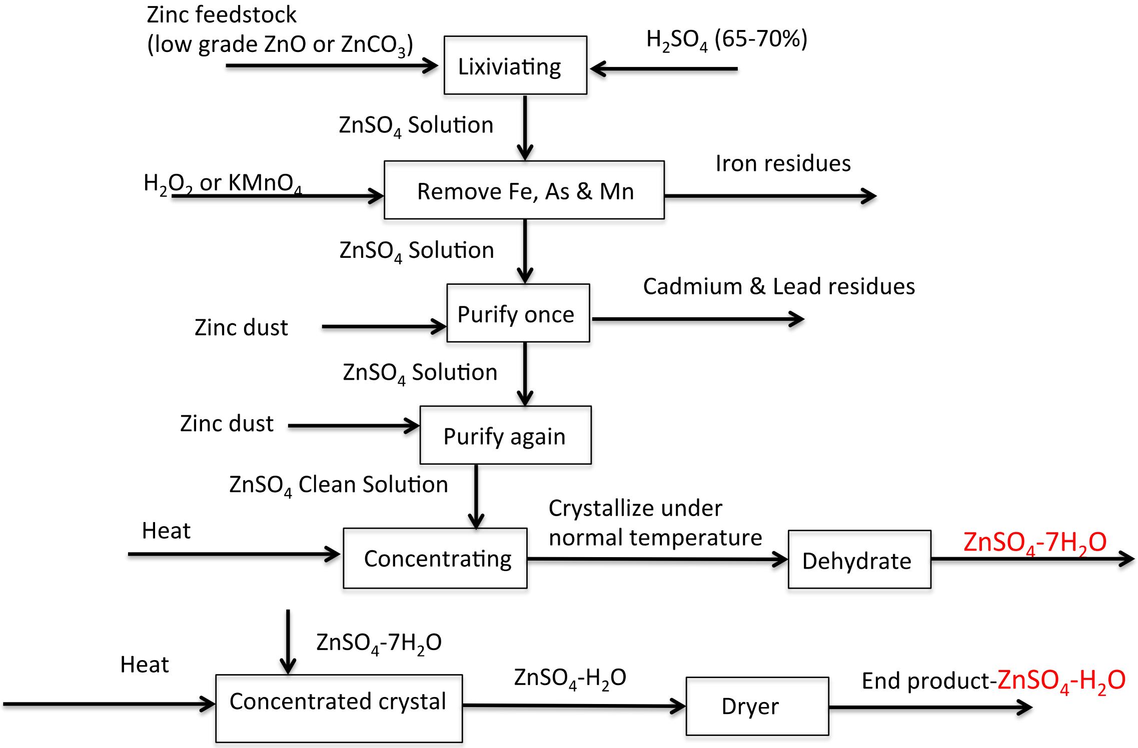

Figure 1 *Steps in the production of zinc sulfate fertilizers from zinc oxide and zinc carbonate feedstock.*

MIW Treatment Considerations

The cost of subsequent chemical processing by the manufacturer will be less if the amount of iron, manganese (nuisance) and arsenic, cadmium, lead (toxic) that co-precipitate with zinc are limited. The limits on iron and manganese will depend on the target product by the manufacturer. Iron and manganese are required micronutrients for plant growth. A multimicronutrient composition proposed by Bandyopadhyay et al. (2014) contained iron and manganese at relative concentrations of 333 mg Fe/g Zn and 167 mg Mn/g Zn. The co-precipitation of other metal micronutrients may have added value for some fertilizer feedstock producers or manufacturers.

The toxic metal limits for zinc fertilizer are fixed. A useful way to examine the potential concentrations of toxic metals relative to zinc from a MIW precipitation process is to assume complete co-precipitation. The equivalent of 1 ppm toxic metal for a 35% zinc material on a mg metal/g Zn basis is 0.00285 mg metal/g Zn. Thus, the standards for cadmium and lead from Table 2 can be rewritten as 0.14 mg Cd/g Zn and 0.28 mg Pb/g Zn.

Nelson Tunnel mine drainage is an attractive MIW to target for zinc recovery due to relatively low iron, manganese, cadmium and lead and no arsenic reported. A design flow of about 1000 liters per minute was used in a 2006 feasibility analysis with the following major metal constituents, Table 3.

Table 3 *Major dissolved metals in Nelson Tunnel MIW*

Constituent	**Concentration, mg/L**
Calcium	250
Magnesium	30
Cadmium	0.5
Copper	0.2
Iron	0.2
Manganese	15
Lead	1.0
Zinc	80
Aluminum	1.5

The K_{sp} values of selected metal carbonates and hydroxides are presented (Table 4) to elucidate the potential for nuisance and toxic metals to co-precipitate with zinc. Co-contamination of the zinc precipitate with Cadmium and Lead is expected for the Nelson Tunnel MIW composition for both carbonate and hydroxide zinc precipitate forms. The K_{sp} of Cadmium and Lead relative to Zn suggest that they may co-precipitate together. Manganese and iron based on K_{sp} may co-precipitate with the zinc carbonate and copper and iron may co-precipitate with zinc hydroxide.

Table 4 *Solubility product values for selected metal carbonates and hydroxides*

Metal	**Carbonates K_{sp}**	**Hydroxides K_{sp}**
Cadmium	$CdCO_3$ 1 x 10^{-12}	$Cd(OH)_2$ 7.2 x 10^{-15}
Lead	$PbCO_3$ 7.4x10^{-14}	$Pb(OH)_2$ 1.4 x 10^{-20}
Zn	$ZnCO_3$ 1.5x10^{-10}, $ZnCO_3$-H_2O 5.4x10^{-11}	$Zn(OH)_2$ 3x10^{-17}
Copper	$CuCO_3$ 1.5 x 10^{-4}	$Cu(OH)_2$ 4.8 x 10^{-20}
Iron	$FeCO_3$ 3.1 x 10^{-11}	$Fe(OH)_2$ 4.9x10^{-17} $Fe(OH)_3$ 2.8x10^{-39}
Mn	$MnCO_3$ 2.2x10^{-11}	$Mn(OH)_2$ 2x10^{-13}

The zinc precipitates will require reduction in moisture content to produce a saleable product. The zinc hydroxide form will require roasting for conversion to zinc oxide. The carbonate form would be most attractive for fertilizer feedstock as the carbonate sludge will require drying but not roasting. However, Sibrell et al. (2005) observed that aluminum and iron were removed but zinc and manganese were not in a pilot limestone treatment system with Argo Tunnel MIW (Colorado USA). Miller et al. (2013) found that the amount of zinc removed with limestone addition was a function of iron concentration in batch experiments. No zinc was removed when initial iron concentration was zero. For zinc at an initial concentration of 16 mg/L, 50% and 80% of the zinc was removed at initial iron concentrations of 48 and 480 mg/L, respectively. The relative amount of iron to zinc (6000 to 36000 mg Fe/g Zn) observed by Miller et al. (2013) are well above the micronutrient requirements of 333 mg Fe/g Zn proposed by B (2014). The zinc hydroxide form of MIW treatment sludge will have similar co-contamination issues as the carbonate form. An opportunity exists for the development of a process to selectively recover zinc from MIW in the carbonate and hydroxide forms with targeted co-contaminant levels.

The zinc precipitate derived from the Nelson Tunnel MIW will contain cadmium and lead in excess of the EPA fertilizer specification (Table 5) and thus the manufacturer will need to employ the zinc dust purification step for removal of cadmium and lead residuals (Figure 1). The MIW treatment and fertilizer manufacture could be more cost effective if a multimicronutrient fertilizer was the end goal.

Table 5 *Estimated cadmium and lead relative to zinc mass ratios and target limits*

Constituent	Metal/Zn in precipitate	Metal/Zn limits
Cadmium	6.25 mg Cd/g Zn	≤ 0.14 mg Cd/g Zn
Lead	12.5 mg Pb/g Zn	≤ 0.28 mg Pb/g Zn

The relative concentrations of copper, iron are well below the target levels for the multimicronutrient fertilizer composition proposed by Bandyopadhyay et al. (2014) and manganese is within 15% of the target ratio. The potential zinc product yield from the Nelson Tunnel MIW is 115.2 kg Zn/d or 42 MT Zn/yr. If the manufacturer valued MIW derived zinc feedstock at $1/kg Zn, then the annual value of the zinc product would be $42,000/yr.

Conclusions

The potential value of recoverable zinc from MIW will depend on the relative concentration of co-contaminants regulated by the fertilizer industry. Contaminant of concern in zinc fertilizer includes arsenic, cadmium, chromium, mercury and lead. Selective recovery of zinc from MIW in the hydroxide or carbonate form with controlled removal of co-contaminants has the potential to provide a usable feedstock for fertilizer manufacture. Evaluation of zinc recovery from the Nelson Tunnel drainage (Colorado, USA) suggests that a viable zinc feedstock can be produced.

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Integrating the Acid Mine Drainage Value Chain – Polluted Water Abstraction to Sustainable Environmental Conformance

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Abstract

The approach presented herewith suggests that AMD is viewed as a source of scarce commodities, namely water and valuable chemicals.

A proper sustainable business would take a view on minimising the life cycle cost of such recovery. A significant cost contributor is the extraction of the AMD from the mine.

Abstraction concepts revolve around the Ritz HDM pumping system. This pump is a free-hanging, double-suction submersible pump. The pump is supported only through a revolutionary piping column, which in itself is free-hanging from the top of the shaft or well. Such pumps can be located as deep as 1 km underground, so no underground pumping stations are required. The pumps are virtually maintenance free, through the balanced axial thrust design. Potential maintenance can be effected from surface.

The treatment technology entails addition of basic barium salt (carbonate or oxide), to the water and precipitating sulphates in the form of the very low soluble barite. This process happens at distributed AMD treatment sites. The water treatment plant simply receives water from lime neutralisation plants, basic barium salt is added, treated water is dispatched and formed solid barite is transported to a centralised chemical factory. The capital investment of such a water treatment plant is significantly lower than a membrane treatment plant.

At the chemical plant, the barite is converted to the basic barium salts required by the AMD treatment plants. Sulphur presents itself in numerous chemical forms, making itself available as a raw material for a number of different chemical products. These range from elemental sulphur, sulphuric acid and other higher value sulphur based chemicals, such as sodium bisulphide.

Key words: Mine water, abstraction, barite, sulphate removal, modeling, chemical reclamation, barium sulphate precipitation, sustainability

Introduction

AMD IS NOT A NEW PHENOMENON. One of the oldest documented mining regions in the world, the Rio Tinto region in Spain, had problems associated with AMD beginning over 2000 years ago (Balkau and Parsons, 1999; Boocock, 2002). Since then, there have been thousands of documented cases of AMD and it is becoming increasingly visible as more mines approach closure around the world.

Following the discovery of diamonds and gold in Southern Africa and the subsequent development of platinum, chromium, manganese vanadium, iron ore, and coal reserves, the country was transformed from a relatively underdeveloped region to a fairly modernised nation with widespread infrastructure and an increasingly diversified economy. In 1999, mining directly contributed to approximately 6.5% of GDP and 33.5% of total export revenues. To increase profits through the removal of minerals that would otherwise remain buried deep within the Earth's crust, elaborate pumping systems were employed in the beginning of the 20th Century to remove water from mine shafts, a process which has become known as mine dewatering. Although this method was successful, there were also many unintended consequences including but not limited to the modification of the water table, creation of sinkholes, and elevated levels of aquatic, air, and soil pollution (Adler and Rascher, 2007).

In the 120 years since mining activity began to unlock significant gold reserves, the impact on the Water Table in the Witwatersrand Reef's Western Basin has been dramatic.

Mining operations, to expose and remove the gold-bearing ore, has resulted in the following:-

- Dolomite formations in the area have been disrupted and the water that naturally filtered through them (en route to the Upper Vaal River and Tweelopies Spruit catchment) has begun to subside.
- Water that drained through the dolomitic rock, into the voids caused by mining operations, has mixed with the exposed ore (Pyrite) and combined to form a Sulphuric Acid solution known as Acid Mine Drainage (AMD). This has contaminated the water, making it unsuitable for drinking and other domestic uses.
- Reservoirs of contaminated AMD have collected in the mining voids and have begun discharging into nearby rivers at a rate of 15 Mega Litres per day.

This therefore poses a significant environmental threat – not only to the surrounding residential communities who rely on the rivers for their potable water – but also to the nearby Sterkfontein Caves which could be flooded, and irreversibly damaged, if the water seepage is not effectively addressed.

The Sterkfontein Caves - which form part of the Cradle of Humankind World Heritage Site - date back some 3.5 million years. It is sobering to note that to fill the Western Basin void, which potentially threatens their continued existence, has taken just 2.5 years.

The AMD Value Chain

Acid Mine Drainage is one of the serious legacies of our mining history. Whilst mining occur, water is generally pumped out as it is collected. Contamination levels are therefore not as significant, given rather protracted retention times.

The major challenge usually starts after mine closure, when exposed pyrite rock formations (containing primarily iron sulphide (FeS) is dissolved in water in the presence of oxygen. This microbiologically catalyzed process converts the sulphides to sulphuric acid through oxidation, whilst dissolving iron in the water, primarily as the divalent ion.

When the mining void eventually fills, AMD decanting commences, causing pollution to the environment.

It has long since been recognized that this water needs to be treated. Treatment schemes typically entails extraction, treatment and release to the environment. The major issue with such an approach is that it is not and cannot be sustainable. This approach also advocates the premise that AMD is a problem, and that the problem can only be solved by applying huge sums of money.

The first paradigm shift required to achieve a successful solution is to target a premise of self-sustainability of any solution applied to AMD treatment.

Wikipedia defines self-sustainability as follows:

“A system is self-sustaining (or self-sufficient) if it can maintain itself by independent effort. The system self-sustainability is:

- the degree at which the system can sustain itself without external support;
- the fraction of time in which the system is self-sustaining.

In the economics literature, a system that has the quality of being self-sustaining is also referred to as an autarky.

In order to successfully deal with the challenge of AMD handling, the AMD treatment system must therefore be an autarky, or be as close to an autarky as possible.

It is evident that to be fully autarkic, the total cost required to operate a system must be less than the total income derived by a system.

The traditional approach of abstraction, treat and release entails only costs, and no income. Such a system is therefore clearly not self-sustainable.

To drive to an autarkic system, all components of such a system must be considered, separately and jointly.

Overall for the system, two objectives are targeted to enable achievement of the overall goal, namely:

- Maximise revenue;
- Minimise costs.

Maximising revenue is dependent on identifying the potential revenue generating components in such a system. AMD is practically 99,5% water, with the remaining 0,5% being contaminants. The only thing making the water unusable, is the fact that the contaminants are in the water. Separation of the water and the contaminants will provide value to the water.

The water in the AMD is therefore a potential revenue generating item.

Likewise, the contaminants in the water are worthless while they are contained in the water stream. In the event, however, that they could be separated and purified, they could earn value and so contribute to revenue.

The components of a treatment system typically also comprises its value chain. In general, the three major system components are:

1. AMD extraction;
2. Water Recovery;
3. Contaminant Recovery.

AMD in underground basins possesses no value. AMD transport to surface is therefore the first item in the value chain. This is analogous to mining, where any mineral contained underground is worthless. This component therefore adds value to the AMD by getting it to the right place for processing. Transferring AMD to surface is generally a very high cost affair, having to overcome significant heads in a rather corrosive environment.

Water recovery is the process where contaminants are separated from the water, in this process making the water usable for some defined purpose. In this process, significant value is added to the water, at certain costs.

The contaminants that were removed from the AMD is now treated to a usable form and recovered as chemical components having a value, again at a certain cost.

The remainder of this paper reports on one approach to make AMD treatment self-sustainable by consideration of the proposed value chain.

Value Chain Component 1: Towards Sustainable Extraction

Both the water and contaminants have no value being underground. In order to have any value, the first step would be to transfer the AMD to surface.

The traditional approach for mine dewatering would be to install huge pumping stations underground, and pump AMD from sealed compartments to surface through piping installed in a vertical shaft. This would require operators and maintenance personnel to enter the pump station (which could be located more than 1000 m underground). This is clearly a high cost approach. In conjunction with maintaining the pump station, and associated equipment underground, the shaft and elevation systems also need be maintained and operated.

The Ritz Pump solution provides for a submersible solution, completely installed, operated and maintained from surface.

In order to apply centrifugal pump solutions to mine dewatering, multiple pumping stages are required to overcome the high pumping head requirements. Progressing beyond four pumping stages has traditionally disqualified the use of submersible pumping solutions, as the axial thrust became intolerable leading to frequent pump failures.

The Ritz solution provides for a fully submersible pump (see **Figure 1**) providing for two suction points (top and bottom), with the pumping stages so arranged to cancel the axial thrust. It also provides for 50% lower flow velocity. With this innovation, suddenly there is no limit on the number of stages that can be employed in a single submersible pump.

The resultant economic benefits are operational reliability, low wear, and a long service life (exceeding 20 years). These pumps can provide heads up to 1500 m and flow rates up to 6,000 m^3/h.

***Figure 1**: A Ritz HMD pump being placed in the test bay. Note the two suctions to combat axial thrust.*

Two such pumps were installed in Germiston, South Africa, each capable of pumping 1500 m3/h of water at a head of 450 m. The pumps each contains 15 stages.

Another novelty of these pumping systems is the manner in which they are installed. They are free-hanging on a vertical piping system. Piping sections are typically about 6m each. Each section is connected to each other with a novel ZSM™ coupling, depicted in the following figure. The couplings (see **Figure 2**) provide a leak tight seal and a tin chain is used to lock the two pipe sections onto each other.

The pump hangs at the bottom of this piping column in a protective shroud. Installations in excess of one km (1000 m) deep are possible.

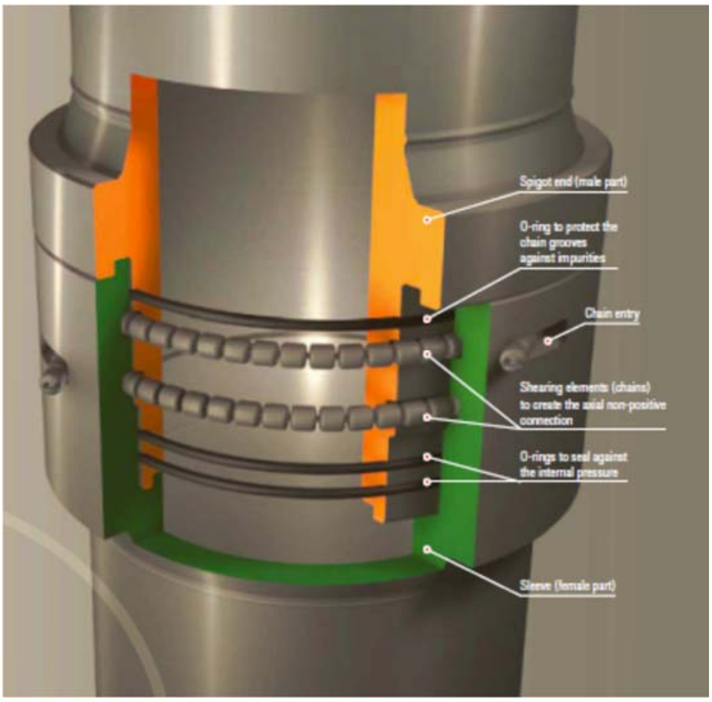

Figure 2 *ZSM Coupling for vertical free-hanging piping columns*

Value Chain Component 2: Water Recovery from AMD

The AMD has to be converted to a standard suitable for consumption, being potable or otherwise.

In general, AMD has three quality issues, namely pH (low and acidic), dissolved metals (primarily ferrous iron) and high levels of sulphate. The Alkali-Barium-Carbonate (ABC) process was developed to take care precisely of these three issues.

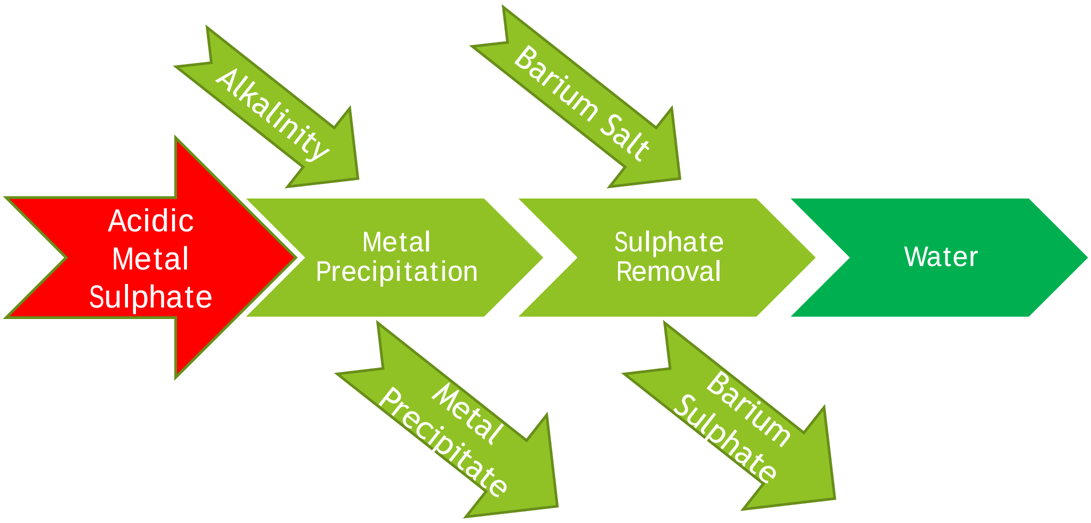

Figure 3 *The ABC water treatment process concept*

The first step is to add alkalinity to neutralize the acidity, comprising both the free acidity characterized by the pH and also the acidity associated with iron. The pH is controlled at a point where the solubility of the metal hydroxide is at a minimum.

Depending on the amount of free acidity in the water, neutralisation could be a two stage process. In the first stage, calcium carbonate could be used and hydrated lime could be used in the second step. In the second step, aeration is also provided to assist in oxidation of ferrous iron to ferric iron.

The net result is the precipitation of metal hydroxides and gypsum (depending on the sulphate levels in the feed).

The steps described thus far comprises the well-established High Density Sludge (HDS) process.

Further addition of lime to pH of about 11,5 results in the precipitation of magnesium hydroxide and more gypsum. The solid precipitates formed thus far in the process reports as a waste.

The second major process step entails removal of sulphate to a desired and acceptable concentration in the treated water.

The solution at this point in the process is saturated with respect to calcium sulphate. Sulphate can be removed to low concentrations making use of the very low solubility of barium sulphate in water. One way of achieving the precipitation of barium sulphate is through the addition of barium carbonate to a typical continuously stirred tank reactor (CSTR).

The sulphate removal reaction that takes place within the reactor is shown in the following equation:

$$Ca^{2+} + SO_4^{2-} + BaCO_3 \rightarrow BaSO_4(s) + CaCO_3(s)$$

Conductivity data is used to track the sulphate removal in the reactor. Based on the reaction equation, feed water is characterized by high conductivity due to the presence Ca^{2+} ions and free SO_4^{2-}. The treatment using $BaCO_3$ results in removal of these two species from solution, replacing them with insoluble $BaSO_4$ and $CaCO_3$. Carbon dioxide can be used to adjust the pH to desired values.

Through the different treatment stages proposed above, water suitable for reuse is produced, as indicated in **Table 1**.

***Table 1** Removal of contaminants through ABC treatment process*

Component	Unit	Feed	Treated
pH		3.3	7.9
Sulphate	mg/l	1910	90
Chloride	mg/l	44.5	49.5
Fluoride	mg/l	5.4	0.7
Sodium	mg/l	46.5	53.3
Magnesium	mg/l	124.6	0.98
Calcium	mg/l	205	75
Iron (II)	mg/l	180	0.3
Iron (III)	mg/l	2	0
Copper	mg/l	21	0.02
Nickel	mg/l	5.6	0.01

From the above, it is clear that the major operating cost of water treatment lie in the chemicals applied to the process, namely lime and barium carbonate.

Value Chain Component 3: Contaminant Recovery

The major portion of sulphate reports as $BaSO_4$ from the water treatment stage. This has been co-precipitated with calcium carbonate.

In the precipitated form as is, the contaminants are basically worthless. However, the collection of these precipitated compounds from various mine water treatment facilities is proposed for treatment in a centralised chemical recovery facility, as depicted in **Figure 4**.

The aim of this central facility is to produce lime and barium carbonate for use as chemical feed at the water treatment facilities, and also to produce Sulphur (or sulphuric acid) for sale in the chemical market.

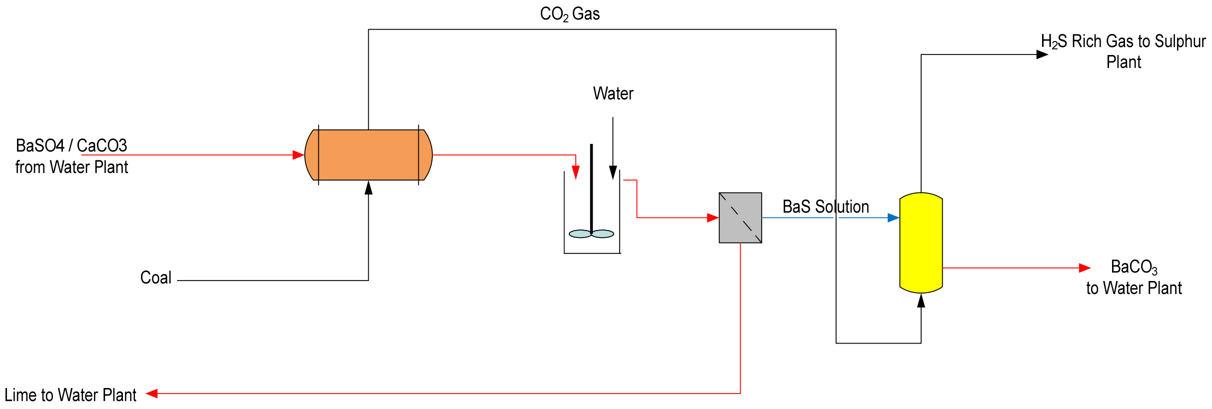

Figure 4 *The chemical recovery process*

Excess moisture is removed in a filter press. The precipitate is fed into a thermal reduction unit. Carbon or methane could be used as a reducing agent. The unit is typically operated at a temperature of 1100°C.

The following reactions occur:

$BaSO_4(s) + 2C \rightarrow BaS + 2CO_2$

$CaCO3(s) + heat \rightarrow CaO + CO2$

The carbon dioxide offgas is captured and compressed for use in the downstream carbonation stage.

The solid product (BaS and CaO) is mixed with water. The lime is hydrated to form Ca(OH)2 and filtered for reuse in the water treatment plants. The highly soluble BaS has reacted in the water as follows:

$$BaS + 2H_2O \rightarrow Ba(SH)(OH) + H_2O \leftrightarrow Ba(HS)_2 + Ba(OH)_2$$

This aqueous solution is characterized by high pH in excess of 12.

Compressed carbon dioxide (ex thermal reduction) is blown through this solution to produce barium carbonate, according to the following reactions:

$$Ba(HS)_2 + Ba(OH)_2 + 2CO_2 \rightarrow 2BaCO_3 + 2H_2S$$

The hydrogen sulphide gas can then be separately converted to either sulphur or sulphuric acid.

The barium carbonate is recycled to the water treatment plants as reagent.

Integrating the Scheme

The water treatment plants are clearly simple in concept and in design. They are significantly less capital intensive than alternative membrane treatment technologies. They also consume significantly less electricity. The only waste is in solid form, i.e. no brine to contend with. The downstream cost impacts are therefore significantly less.

The unit cost of water purification needs to be less than the price achieved for the selling of the treated water. This is achieved by limiting the cost of the chemicals used in the process. The chemicals will be obtained from a centralised chemical treatment facility, which receives its feed from multiple AMD treatment plants and supplies these same treatment plants with reagents.

The income for such a chemical plant is from the sales of the treatment chemicals to the AMD treatment plants (prices to be such as to make the treatment plants self-sustainable). Costs in the chemical plant is offset by the sale of Sulphur and high purity excess carbon dioxide.

The income of such a chemical plant can be further improved (and therefore the prices of reagent chemicals further reduced) by production of high value niche Sulphur containing chemicals. Within this chemical plant, Sulphur presents itself in all its possible valence states (-2 to +6).

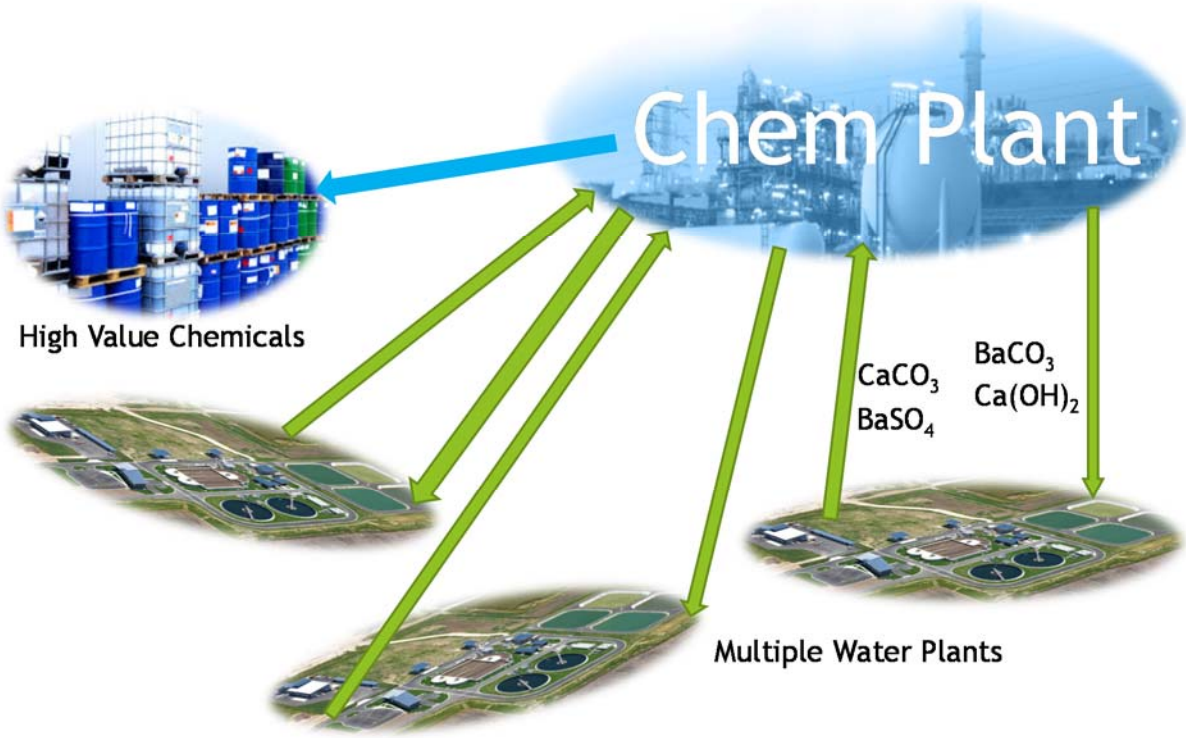

Figure 5 *Integrated AMD treatment and recovery scheme*

Conclusions

It is certainly possible through paradigm shifting to devise AMD Treatment schemes that are less costly and potentially even be financially self-sustaining. For this to occur, it is imperative that contaminants are viewed as valuable products for reclamation.

Acknowledgements

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REE behavior during evaporative precipitation in a severely affected-AMD creek (SW Spain)

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Abstract

The Iberian Pyrite Belt (IPB) covers a vast part of the SW of Spain and Portugal. This region is rich in sulfide deposits which have been exploited intensively. As a consequence, there is a large number of sources of acid mine drainages, characterized by very extreme pH conditions and high pollution load. Waters affected by acid mine drainage (AMD) can contain high concentrations of rare earth elements (REE) which have a great interest from the scientific and economic point of view. This work is focused on the REE behavior during evaporative concentration during the summer along the Agrio River, a small stream deeply affected by AMD coming from the Río Tinto mines. The pH varied from around 2.8 to 1.5 and the electrical conductivity from 5.8 to 15 mS/cm. Concentration of ∑REE varied from around 1.3 mg/L to around 5.3 mg/L at the end of the summer. In September, with the lowest discharges, most elements showed an increase along the reach (Al 12%, Zn 8%, Cu 4%) due to evaporation. REE also showed an enrichment, which varied from 7% (La to Nd) up to 10-11% (Ho to Lu), which seems to indicate a slightly higher affinity of the evaporative salts for LREE in relation to HREE. Although REE concentrations varied widely between the different samplings, the NASC-normalized patterns are very constant, showing a negative Eu anomaly together with the enrichment of MREE typical of AMD-affected waters. The amount of dissolved ∑REE transported by this small river was surprising, varying between 9 kg/day in September and 26 kg/day in May.

Key words: sulphides, rare earth elements, acid mine drainage, Iberian Pyrite Belt

Introduction

Nowadays, there is a great interest in studying the behavior of rare earth elements (REE) in acid mine drainage (AMD)-affected rivers with two main goals: 1) the possibility of recovery of these elements (Ayora et al., 2015) and 2) its use as tracers of hydrogeochemical processes (Noack et al., 2014). The Iberian Pyrite Belt is rich in sulphide deposits which have been exploited intensively since the mid-nineteeth century (Olías y Nieto, 2015), generating a huge problem of river contamination by AMD with highly-toxic concentrations of metals and metalloids.

Although the behavior of REE during Fe and Al oxyhydroxysulphates precipitation has received considerable attention (e.g. Gimeno et al., 2000; Delgado et al., 2012) their behavior during evaporative salt precipitation has been less studied. The main goal of this work is to study the variations of REE contents in a severely affected-AMD stream.

Methods

We have sampled four points along a small stream (~5 km long) deeply affected by AMD, the Agrio River coming from the Río Tinto mines, during spring and summer (March, May, July and September) The samples were filtered (through 0.2 µm), acidulated to pH <2 and refrigerated until analysis by ICP-AES for main elements and ICP-MS for trace elements and REE. Temperature, pH, electrical conductivity and oxidation-reduction potential (ORP) were measured in situ using an equipment CRISON model MM40+.

Results and conclusions

The river discharge decreased from approximately 200 L/s in March to 18 L/s in September. Concomitantly, the pH varied from around 2.8 to 1.5 and the electrical conductivity from 5.8 to 15 mS/cm (Fig. 1). Maximum concentrations were reached in September (up to 2048 mg/L of Al, 395 mg/L of Zn, 173 mg/L of Cu, etc.), except for Fe, whose maximum values (up to 693 mg/L) were reached in July. Concentration of ∑REE varied from around 1.3 mg/L (March) to around 5.3 mg/L (September), when there was a strong precipitation of evaporative salts over the river banks.

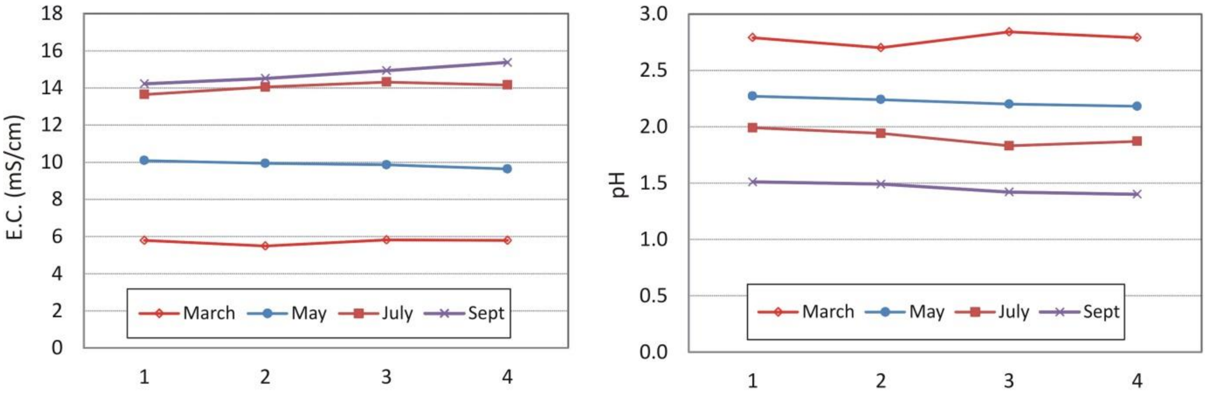

Figure 1 *Variation of electrical conductivity (E.C.) and pH along the reach from upstream (point 1) to downstream (point 4)*

From March to July, concentration of most elements, including REE, remained constant along the reach, showing a conservative behavior. However, Fe concentration diminished 17% in March, 10% in May and 12% in July indicating Fe precipitation. Arsenic also showed a decrease along the reach due to coprecipitation/adsorption processes.

In September, with the lowest discharges, most elements showed an increase along the reach (Al 12%, ∑REE 8%, Zn 8%, Cu 4%) due to evaporation. Concentration of Fe and As did not vary along the reach, showing a balance between precipitation and evaporative concentration. REE also showed an enrichment in waters, which varied from 7% (La to Nd) up to 10-11% (Ho to Lu), which seems to indicate a slightly higher affinity of the evaporative salts for LREE in relation to HREE. On the other hand, the amount of dissolved REE transported by this small river was surprising, varying between 9 kg/day in September and 26 kg/day in May.

Although REE concentrations varied widely between the different samplings, the NASC-normalized patterns are very constant (Fig. 2). It can be seen a negative Eu anomaly together with the enrichment of MREE typical of AMD-affected waters (Pérez-López et al., 2010).

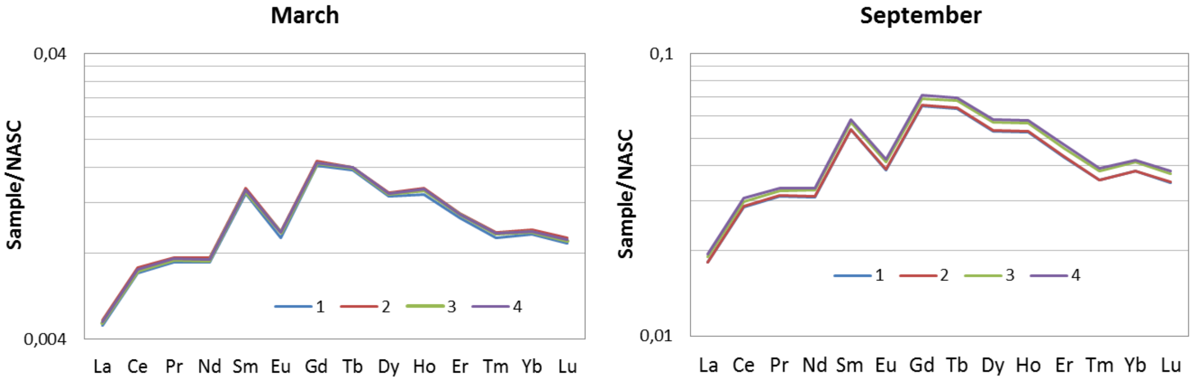

Figure 2 *NASC-normalized REE patterns of two samplings along points nº1 (upstream) to nº4 (downstream). Note the different Y-scale.*

The study on the mineral precipitation pathways that control REE mobility in AMD environments is of paramount importance in the search for possible sustainable and beneficial resources.In this sense, the high REE loads observed in this study and the longevity of AMD processes turn this polluted water course into a promising resource.

Acknowledgements

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Extracting value resources from acid mine drainages and mine wastes in the Iberian Pyrite Belt

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Extended Abstract

The Iberian Pyrite Belt (IPB), located in the southwest of Iberian Peninsula (Fig. 1), is well-known from its historic mining activity, especially for copper in volcanic-hosted massive sulfide deposits (VHMS). The exhaustion of richer ores together with market conditions determined the cession of activity by the end of eighties.

This historic activity has left numerous waste dumps, requiring environmental rehabilitation. Today, there are more than 4800 ha occupied by waste dumps, open pits, tailing dams, and mining facilities, corresponding to 88 sulfide mines (Pérez-Ostalé et al. 2013). Most of them are abandoned, comprising 200 million m^3 of abandoned wastes (Sáinz et al, 2004). The waste dumps are the main source of contamination when they are abandoned or improperly closed (Loredo and Pendás, 2005). In the IPB, the presence of sulfides has led to high levels of contamination by acid mine drainage (AMD), which has been widely described by different authors. The fluvial network is one of the most affected in the planet as a result of more than 5,000 years of mining history (Grande, 2015).

In association with sulfide ores, IPB is also known for historic exploitation of manganese. Currently, all these mines are abandoned. *However,* the gangue in such mine wastes may represent an opportunity for industry to extract valuable resources from the mining waste stream.

The rising value of some metals as a result of demand from emerging countries, combined with the presence of ore deposits, provide a strategic opportunity for metal, which would otherwise be rejected.

The legal framework (European Directive 2006/21/EC) defines waste from the extractive industries as products resulting from prospecting, extraction, treatment and storage of mineral resources as well as quarrying. From this perspective, the mine water should be considered a mining waste. Considering the magnitude of its impact proper management of AMD is now a basic condition for the viability of sulfide exploitations (Grande et al., 2005).

The present study addresses different issues in relation to the type of wastes in the IPB: inert wastes resulted from manganese exploitation and reactive wastes, with sulfides, from which acid mine drainage is derived. The level of knowledge and diversity of solutions is very different for both cases. The distinctive nature of these wastes implies different lines of action:

i) Intervention strategies for recovery of metals and non-metals in mine waters, which occur with unusually high concentrations in the river network of the IPB and justify the economic viability of decontamination. This work presents a prototype for the recovery of strategic metals from acid mine drainage.

ii) Other strategies focused on to the recovery of non-contaminant wastes, such as the gangue from manganese ores, with high potential reuse, particularly in construction and civil works industry.

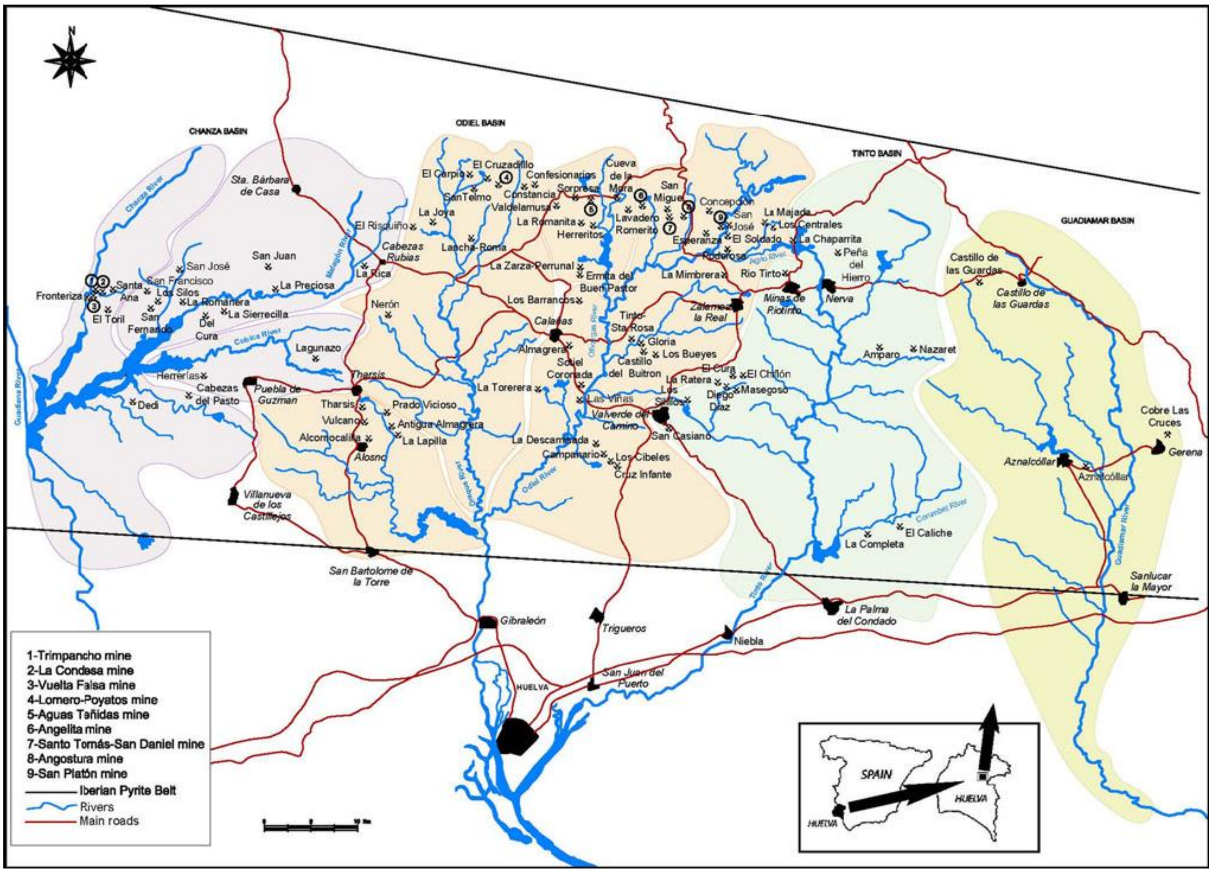

Figure 1 *Location of the Spanish sector of Iberian Pyrite Belt, with representation of watersheds and major mines.*

Key words: Mine water, wastes, strategic elements, economic potential

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Advanced (bio)hydrometallurgical methods for the optimized extraction and beneficiation of Rare Earth Elements from Ion Adsorption Clays

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Extended Abstract

Their physicochemical properties make Rare Earth Elements (REE) essential ingredients of renewable energy appliances such as wind-energy generators and electric vehicles. Whilst recycling only covers about 1 % of today's REE demand, the extraction from Chinese Ion Adsorption Clays (IAC) is still the main source of these critical raw materials (European Commission, 2014).

The significant impacts on environmental receptors such as surface and groundwaters, soils and sediments deriving from conventional extraction techniques of REE from IAC (e.g. Alfonso et al., 2012, Yang et al., 2013), emphasize the need for environmentally sustainable methods for the extraction and processing of these elements. Furthermore, about 200 comparable REE-rich deposits exist worldwide in regions such as Madagascar, Laos, Suriname and Brazil that so far have been little exploited for their REE content. Thus, any alternative and optimized mining technology for the REE extraction from IAC will bear on the resource efficiency and environmental sustainability in China and beyond.

The main objective of our project (Fig.1) is consequently to develop mining and processing methods for on-site leaching and (bio)hydrometallurgical extraction of REE from IAC.

In detail, we aim to:

i) enhance sediment permeability of IAC by **geotechnical conditioning** using cryotechnology to promote a more efficient and environmentally sustainable leaching process,

ii) optimize currently employed hydrometallurgical processes (e.g. in terms of reactant consumption) and **develop new (bio)hydrometallurgical processes** (e.g. based on lixiviants such as organic acids, complexing agents and chelators) in order to selectively leach and recover REE,

iii) develop **sorption processes based on bio-materials** such as algae and yeast to sequester and separate REE from solutions and

iv) study and optimize processes of the REE extraction and recovery (e.g. on different yeasts) by **numerical process simulation** based on **experimentally derived thermodynamic data** in order to evaluate and improve the newly developed methods.

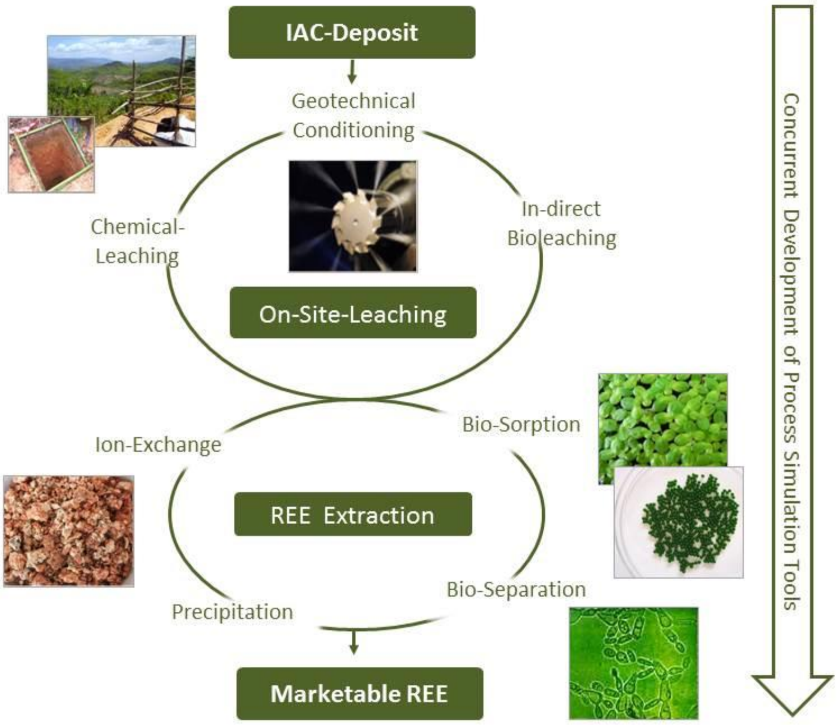

***Figure 1** Proposed process steps for the extraction of REE from Ion Adsorption Clays*

Key words: environmental impact, on-site leaching, biomining, modeling, geotechnical extraction

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Technologies for sulphate removal with valorisation options

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Extended Abstract

One of the major challenges confronting the mining and minerals processing industry in the 21st century is the management of water in an environment of ever decreasing water resources. Especially polluted mine water, from both active and abandoned mines represent a major problem worldwide. Discharge from the latter has been recognised as the main cause of 7% of failures to achieve the goals of the Water Framework Directive (2000/60/EC).

The treatment of mine water has generally focused on the removal of (heavy) metals. Less attention has focused on mitigation of dissolved sulphate levels due to its lower environmental risks and regulatory standards when compared to those for acidity and dissolved metals. However, regulatory agencies are becoming increasingly concerned over elevated SO4-concentrations in effluents with discharge limits sometimes as low as 10mg/L, but typically between 250 mg/L and 1,000 mg/l. The rationale for imposing sulphate discharge limits range from more generally accepted aspects of salinity contributions from high concentrations of sulphate, to more controversial aspects such as the putative effects of sulphate on mercury methylation by sulphate-reducing bacteria, or purported chronic aquatic toxicity.

Figure 1 gives an overview of the current commercially available technologies for sulphate removal. Mine location, climate, water characteristics, available utilities, footprint, and disposal areas all preclude a "one-size fits all" solution. Currently the most widely used method for mine water treatment is lime precipitation in which acidity is neutralized and metals precipitated as hydroxides by adding lime or limestone. Although this process successfully removes the metals and increases the pH to neutral levels, the resulting effluents contain high levels of sulphate (1 500 - 2 000 mg/l), well above the permittable discharge levels (Table 1).

Sulphate limits range from 2000 mg/L for surface water discharge in Finland and Chile to 10 mg/L in the US state of Minnesota (International Mining 2013; Minnesota Pollution Control Agency 2014). In British Columbia/Canada a 30-day average sulphate concentration guideline of 65 mg/L has been proposed , and other provinces are also considering lower limits for sulphate.

***Table 1** Sulphate discharge levels.*

Authority	Sulphate Concentration (mg/L)
USA	10-500
Canada	500
Finland	2,000
South Africa	200-600 (evaluated on a case-by-case basis)
Australia	1,000
World Health Organization (drinking water)	250

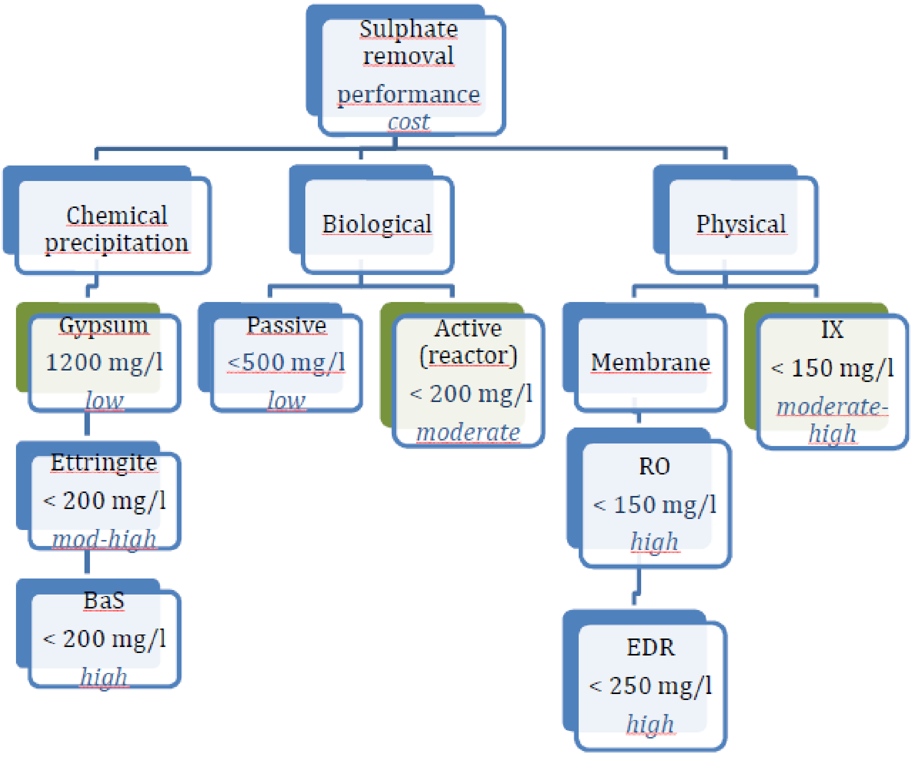

Figure 1 *Sulphate removal technologies, average removal efficiency and costs. Based on e.g. Mattson (2014) and Mierzejewski (2014). Technologies in green indicate possibility for solids productification or valorisation*

Further reduction in the sulphate levels is well below the capability of lime precipitation. However, achieving low solute concentrations to comply with discharge limits in an economically viable process is challenging and additionally requires sustainable and economically viable solids waste management. Biochemical methods have mainly been used as an inexpensive passive treatment system for removal of metals and sulphate by reducing sulphate to hydrogen sulphide using sulphate-reducing bacteria with concomitant precipitation of metals within the pit or passive reactor. However, compared to active processes performed in controlled reactors, metal removal from passive systems is difficult and does currently not result in recovery of metal values.

All treatment technologies produces a residual or by-product which will require additional treatment. It is thus somewhat surpising that the valorisation aspect of sulphate laden mine water treatment seems to only be in the beginning phases of development and little work has been published in this field. Examples of successful recovery of Cu and Zn from process streams are described using the Paques ThIOTEQ^{TM} and SULFATEQ^{TM} technologies. Elemental sulphur can also be recovered from biological sulphate reduction processes and could be potentially re-used for sulphuric acid production.

Tests have been conducted at Mintek in multi-stage columns (Figure 2) at ambient around 20°C using cellulose-based substrates. The pH levels of the water could be successfully increased to levels >6. Reducing conditions could be maintained and removal of sulphates (80-90%) and base metals were demonstrated. The work will continue developing the with recovery of elemental sulphur from the reactors.

Figure 2 *Multi-stage column system used for test work*

Figure 3 gives the results of sequential precipitation of the water from a Finnish Gold mine. It gives a clear indication of the optimal pH for precipitation (10.5) and further analysis of the generated sludge (10.5). Detailed chemical analysis of the generated solids will form the base for developing the valorisation concepts. The generated solids contain little base metals but the minerals of potential industrial value are magnesium and manganese.

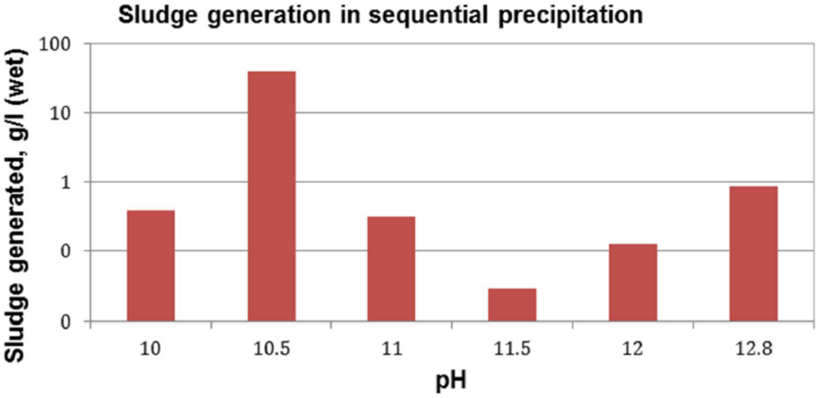

Figure 3 *Sludge generated in sequential precipitation*

Although there are a number of technologies available for producing an effluent that can be reused or safely released into the environment, the focus should in future be on the development of concepts that can enable valorisation of the components of the effluent or solid waste generated, focusing on recovery of beneficial metals and development of less energy consuming processes.

Key words: IMWA 2016, full paper, writing, tables, figures, reference

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CHAPTER 13

Secondary Mining – In-situ Recovery

Hydrological Characterization and Optimization of In-Situ Recovery

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Abstract

The performance of in-situ recovery (ISR) of technology metals is mainly determined by the appropriate control of both hydrological (flow) regimes and geochemistry (Märten 2015). This paper focuses on the hydrological optimization of ISR with regard to wellfield design for maximizing recovery in an economic context on the one side and minimizing environmental impacts as an important precondition for regulatory procedures on the other side.

Hydrological modeling for ISR performance is presented for both real site and hypothetical conditions in three respects: (i) optimization of wellfield design in local scale for maximum recovery in dependence on ore morphology and hydrogeological conditions, (ii) control of mining fluid inside the wellfields and minimization of its migration in ongoing ISR operations, and (iii) evaluation of post-mining aquifer restauration in terms of natural attenuation and active measures in a regional scale.

In this context, challenging and limiting factors for ISR hydrology are addressed with regard to confinement condition, porosity/permeability, aquifer pressure conditions, and saturation (also considering ISR within the vadose zone). It is demonstrated that ISR simulations in this general scope require the application of 3D hydrological modeling, in particular in the case of irregular and massive deposit morphologies and/or heterogeneous hydrological conditions. The simulations were conducted with the finite element software FEFLOW (Diersch 2014).

Key words: In-situ recovery (ISR), wellfield design, 3D hydrological modeling, aquifer restoration

Introduction

ISR is applied to extract metals from (typically sedimentary) subsurface ore bodies by injecting a chemical leaching solution (leachant) into the ore zone to mobilize the metal(s) of interest and pumping the pregnant leach solution (PLS) to the surface for further processing. ISR is an alternative to conventional mining technology (underground and open-pit mining). It has many advantages including less environmental impact (no destructive changes to the landscape, no waste rock piles, and no tailings), less labor requirements and reduced total costs, provided that the hydrogeology and mineralogy/geochemistry of the ore deposit enable its application.

The development and testing of ISR for uranium mining has started in the early 1960s in the former USSR and USA. Later ISR of uranium has been successfully applied in Australia, Kazakhstan, Uzbekistan, Ukraine, Czechoslovakia, former Eastern Germany and China (Taylor 2004). Attempts to use ISR for other metals like copper and gold are ongoing, e.g. there are several copper ISR prospects in the USA like the Gunnison Project (Excelsior Mining), Van Dyke Project (Copper Fox Metals) and Florence Project (Taseko Mines). Martens (2012) and Wang (2013) investigated gold mining using ISR. Currently, several international research programs focus on the development/application of ISR technology (including aspects of bioleaching) to (critical) technology metals, e.g. EU-funded BioMOre project, German r^4-SEM^2 project (recovery of rare earth elements REE from ion-adsorption clays), the British SOS RARE project and others, cf. relevant websites.

The applicability (and risks) of ISR has to be examined for each deposit individually in dependence on host-rock characteristics, orebody specifics and other site conditions. Hydrological modeling is a valuable tool to investigate ISR fluid-flow regimes in regional (aquifer) and local (ISR wellfield) scale. The outcome from hydrological modeling of ISR is typically used to setup reactive transport simulations to optimize ISR geochemistry. A consistent combination of 3D hydrological modeling of ISR wellfield performance with reactive transport approaches is a promising but highly complex and challenging task. Nicolai et al. (2016) consider essential aspects of geochemical reactive transport modeling of ISR in more detail. The present study focuses on the hydrological characterization of ISR.

In general, ISR is being applied to sedimentary hosted deposits that meet well-defined conditions for ISR amenability including (i) confined aquifer hosting the deposit with no critical hydrologic connectivity to adjacent formations (e.g. due to tectonic faults), (ii) effective (free-fluid) ore porosity and corresponding permeability, and (iii) appropriate mineralogy/geochemistry enabling the effective leaching of metals of interest with regard to both thermodynamic conditions and kinetic rates (Märten 2015). In addition to typical ISR applications, the present paper addresses conceivable options to use ISR in alternative cases, high-lighting the limits and possibilities of modifications from the perspective of 3D hydrological modeling:

(i) Application conditions and constraints of ISR with regard to deposit morphology and hydrogeology (emphasizing heterogeneity, porosity/permeability limits and conditions to improve permeability by fracturing),
(ii) Specific options for optimizing the wellfield design in order to maximize the contact of mining solution with the orebody at sufficiently high pore volume exchange rates,
(iii) Embedding the (local) wellfield simulation in a regional scale model to examine potential environmental impacts, investigate different post-mining scenarios for aquifer restoration as well as to evaluate long-term effects, e.g. natural attenuation.

Application Conditions and Limits of ISR

Hydrogeological Conditions. A detailed understanding of hydrogeological conditions in and around the formation hosting the deposit is required to investigate the efficiency of ISR operation and to estimate potential environmental impacts. The porosity and permeability (hydraulic conductivity) of the mineralized formation is one of the decisive factors for ISR feasibility, determining the leachant contact with the ore, leaching rates and recoveries. The (free-fluid) porosity determines the total volume of leachant in the ore formation (effective pore volume V_p) and the residence time inside the orebody at given flow rate Q, expressed in terms of the pore volume exchange rate $q = Q/V_p$ (typical values in the order of 10^{-1} d^{-1}). Efficient ISR performance can be achieved for hydraulic conductivities exceeding 1 m/d, but ISR could also be operated at somewhat lower values (IAEA 2001) depending on other conditions (mentioned below) and wellfield design. The higher (and more uniform) porosity/permeability, the better is the contact between leachant and ore, the higher is ISR efficiency.

Preferably, the aquifer of interest meets confinement conditions, i.e. it is enclosed by impermeable layers (aquitards) to assure that there is no hydraulic connectivity to adjacent aquifers or surface waters. In addition to appropriate stratigraphic conditions, there should be no (tectonic) faults or fractures causing unintentional spreading of leaching solution. Further hydrogeological conditions for efficient ISR performance include (IAEA 2001):

- Sufficient hydraulic head above the extractor screens (in the order of 10^1-10^2 m);
- Adequate thickness (up to 10 m) of the mineralized zone (too low thickness impedes targeting, too high thickness requires staged screening of wells);
- Moderate depth of deposit from surface (costs for drilling and well construction);
- No or minor interference by impermeable intersections (e.g. shale, clayey layers, cemented sediments) that could disturb hydraulic connection between injection and production wells.

Deposit Morphology. The morphology of (typically sedimentary) orebodies amenable to ISR can be highly variable. It results from geological-mineralogical, hydrogeological and geochemical conditions (IAEA 2001). Sedimentary uranium deposits are classified in the following categories: (i) rollfronts, e.g. distributed at continental basins, mixed fluvial-marine genesis, or multi-episodic distal rolls (fig. 1 a-b), (ii) stratiform or tabular (lenticular) shape (fig. 1 c-d), (iii) basal channels e.g. distinctive paleodrainage or complexly braided fluvial systems, and (iv) tectono-lithologic e.g. redistributed primary uranium, e.g. hosted close to a fault (Dahlkamp 2009). ISR is applicable mainly to categories (i) to (iii). Usually, rollfront-like deposits have the highest concentrations of minerals within the central, most massive part that can reach a thickness from a few meters up to a few tens of meters (IAEA 2001).

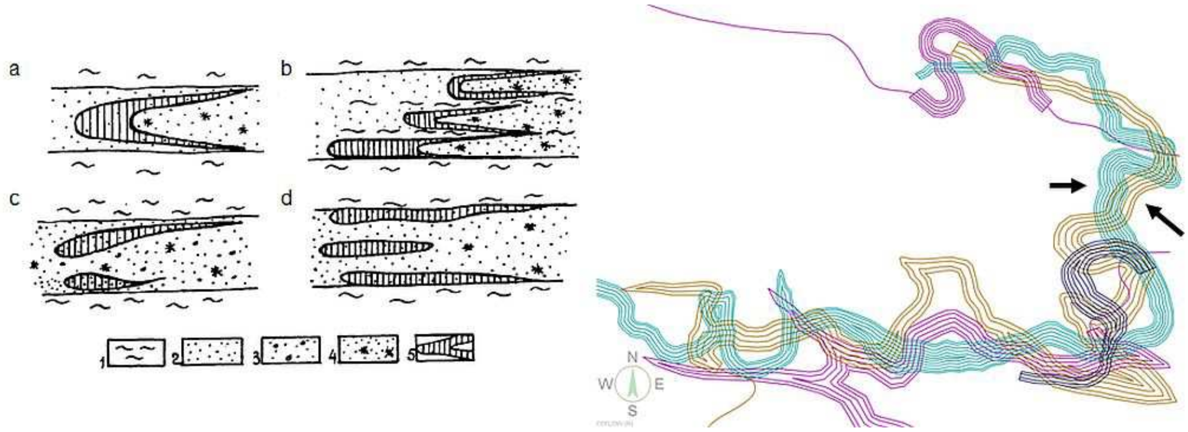

Figure 1 *(Left) Morphology of roll-type deposits: a) simple roll-type deposit, b) series of simple rolls within aquifer with zones of reduced permeability, c) stratiform deposits with no roll, d) lenticular deposits at several levels: 1 - clay, 2 - sand, 3 - gravel, 4 - limonitizations, 5 - ore deposit (modified after IAEA 2001), (Right) Map of multilevel rollfronts in aquifers with different groundwater flow directions.*

Optimization of Wellfield Design

Hydrological modeling is usually applied for (i) wellfield design (injection, extraction and monitoring wells), and (ii) specification of operational parameters. Wellfield design comprises the geometry of injection and extraction wells, including depth intervals of screened sections, in accordance to the hydrogeological conditions and outline of the orebody. In order to appropriately design ISR wellfields the comprehensive knowledge of stratigraphy, comprising the mining zone and relevant adjacent layers, as well as any irregularities (e.g. tectonic faults and impermeable beds) and heterogeneities is essential. Stratigraphic irregularities are a major concern with regard to environmental impacts and subject to scrutiny by regulatory organizations (Märten 2015).

Most common wellfield designs are 5- and 7-spot patterns of injection/extraction wells, alternate well lines and free setups adjusted to irregular orebodies. Design criteria include optimum contact (pore volume exchange) of leachant and ore (in 3D), minimized migration of leachant, minimum dilution (groundwater) and uniformity of leachant flow (IAEA 2001). Arrangements of 5- and 7-spot patterns are characterized by a central extraction well surrounded by 4 or 6 injection wells, respectively. Depending on hydrogeology and ore characteristics spacing between wells range from 15 to 50 m typically.

Operational parameters include injection pressures, injection and extraction flow rates, and pore volume exchange rate (q). The achievable flow rate in a wellfield pattern is mainly determined by permeability, hydraulic head of mining aquifer above extraction screens, relevant aquifer interval and injector-extractor spacing. Typical extraction flow rates range from a few 10^0 to 10^1 L/s. The injection/extraction flow regime is carefully balanced to avoid/minimize the excursion of mining fluid. Typically a bleed from the leachant cycle in the order of 0.5 to 2 % is applied for better flow balance.

Fig. 2 demonstrates the wellfield optimization for a rollfront ore deposit, performed by the use of a 3D hydrological model with FEFLOW. A typical 5-spot well pattern is set up with a well spacing of 30 m between injectors and extractors. As shown in the 3D image (fig. 2, below), screening sections of the wells are positioned according to the morphology of the rollfront, resulting in longer screens within the rollfront nose and intervals of shorter screens within the limbs. Further, fig. 2 represents the travel times of fluid flow (streamlines) from injection towards extraction wells for a time period of 30 days showing the pathways lengths for the defined well design and specified flow rates. The optimization of ISR is based on the variation of flow rates, well spacing, and filter lengths in an iterative process.

The exact vertical placement of well-screens is critical for realizing a uniform leachant flow through the entire ore body (within the pattern) and, hence, a precondition for maximizing ISR efficiency.

The hydrological modeling of ISR wellfields enables the evaluation of potential “dead” zones where leachant solution either bypasses or PLS accumulates along the peripheral (slower) flowpaths. Such zones could be predicted and (temporary) alternative flow regimes investigated by applying reversed scenarios where injection wells are converted to extraction wells and vice versa (role reversals).

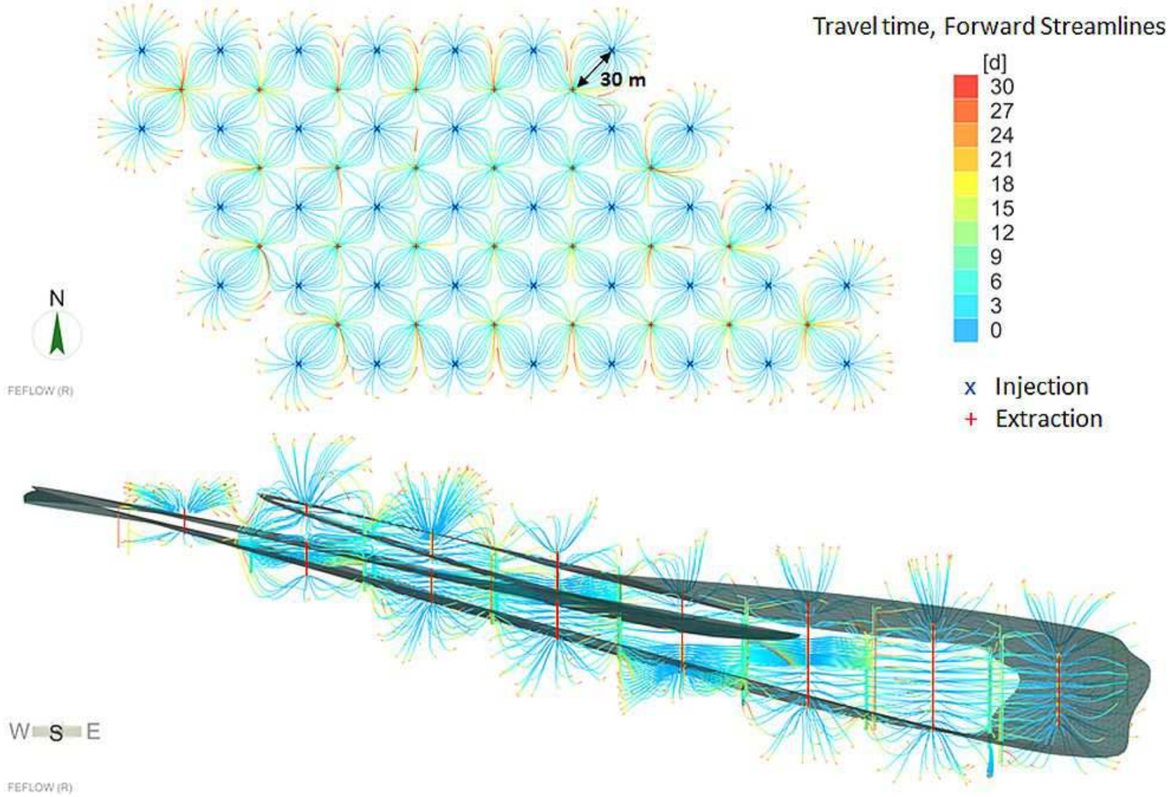

Figure 2 *Optimization of wellfield design for a mineralized rollfront; lixiviant streamlines within a 5-spot well pattern as top view (upper image) and 3D view within the rollfront (lower image). Streamline color is indicative of travelling time (cf. legend).*

Deposit Heterogeneities with Regard to Hydraulic Permeability and Ore Morphology

Massive rollfronts (‘noses’) with a thickness in excess of 10 m are a challenge for ISR operation with regard to setting up optimized (effective) filter screen lengths and positions. Too long filter screens may not provide uniform flow of leachant caused by the natural heterogeneity within the mineral deposit. Ore layers with higher permeability are likely to be leached more preferably, resulting in a poor recovery from less permeable ore layers accordingly. This scenario is illustrated by a comparison of two numerical simulations that model the pumping from a single well in a 3D model domain (fig. 3). In both simulations the extraction well is defined by the same total flow rate (~6 L/s) and a well screen of 10 m length that is positioned in the center of a mineralized, confined aquifer. The two simulations differ regarding the specification of hydraulic conductivity K (permeability) of the mineralized ore zone that is divided into 5 sublayers. Simulation (a) considers a homogeneous conductivity along the screen length, while in simulation (b) hydraulic conductivity differs from layer to layer (fig. 3, top right), thus, defining a vertical distribution of K.

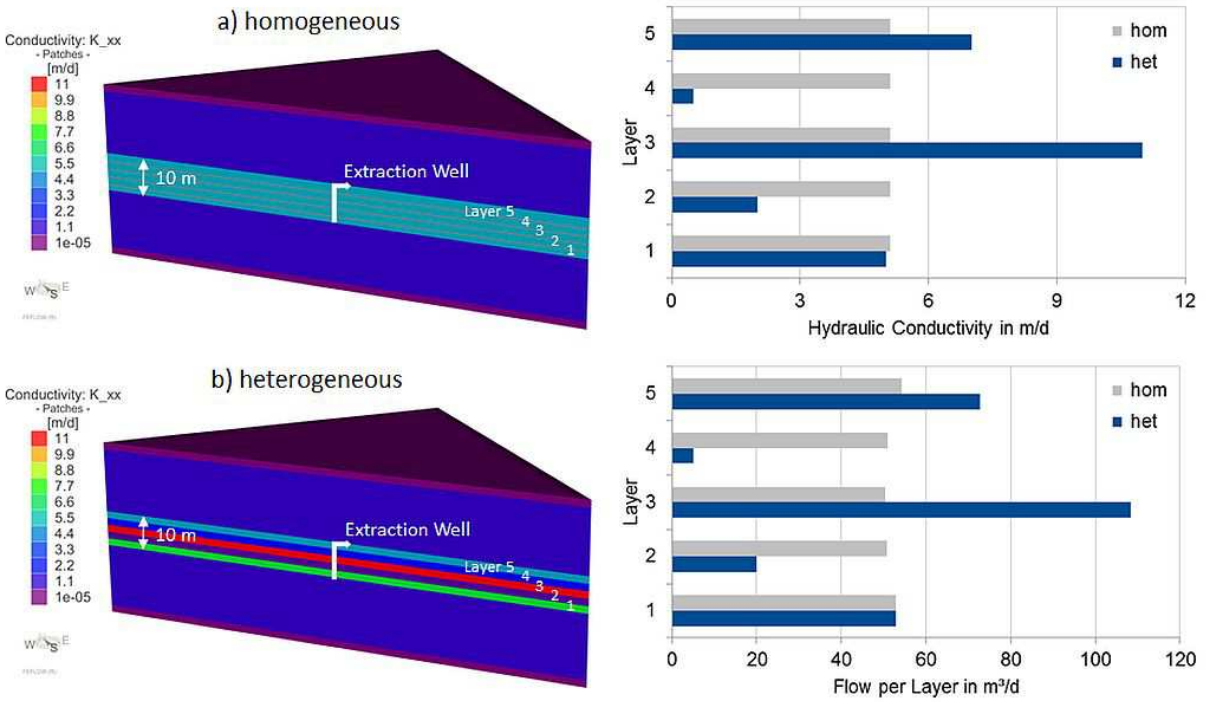

Figure 3 *(Left) 3D model design of a single extraction well (10 m screen) embedded within a (a) homogeneous and (b) heterogeneous aquifer hydraulic conductivity. (Right) Hydraulic conductivity (m/d) and flow rates (m³/d) per layer along filter screen for homogeneous (hom) and heterogeneous (het) model.*

Fig. 3 (bottom right) represents the resulting flow rates in the 5 layers along the filter screen. As expected, the vertical flow rate profile reflects the variation of K in the heterogeneous model. In the present example, the metal from the less permeable layers 2 and 4 would be recovered at a very low rate. Under real world conditions, the screening of ISR wells can be adjusted in accordance to the vertical permeability profile measured by using advanced borehole logging techniques (Märten 2015) to optimize recovery. In particular, effective leaching along massive ore zones can be achieved by changing screening intervals (so-called ‘rescreening’) consecutively during the lifetime of the wellfield. The same would apply to staggered ore formations (roll fronts) shown in fig. 1 b (left image). Rollfronts could form quite variable morphologies in superposed layers as a consequence of different groundwater flow regimes during the deposition of such sedimentary ore bodies (see fig. 1, right image). Here the challenge is to set-up a wellfield design that could be applied in different depths consecutively by the readjustment of flow regimes (e.g. role reversals/modifications) in general and filter screens of individual wells in particular. Thus, drilling and well construction costs could be minimized. In summary, provided the mineralized ore zones are well mapped, 3D hydrological modeling is a powerful tool to optimize the design of ISR wellfields to realize an efficient/economic recovery and, by the same token, to minimize the probability of leachant excursions.

Modified/Adjusted ISR Applications

ISR Application in Vadose Ore Zones. If the ISR amenability criteria are not met entirely, modifications or adjustments of the classical ISR operation by wellfields are conceivable, subject to feasibility and efficiency. Such non-ideal application cases include (i) unconfined deposits with low to moderate hydraulic heads, (ii) deposits hosted in the vadose (unsaturated) zone, or (iii) deposits characterized by low porosity and permeability. Modeling ISR under such (originally) unfavorable hydrogeological conditions is a valuable tool to investigate new technological approaches. In the case of unconfined conditions along with low hydraulic heads, hydrological modeling is suitable to estimate appropriate well configurations and flow regimes, in particular to prevent pumps from running dry. Hydrological conditions are quite different for ISR applied to an ore zone within the (unsaturated) vadose zone. A possible leaching approach is gravity-driven, percolate leaching regime combined with the extraction of the PLS via drainage systems (ADEQ 2004). Depending on the specific site conditions, the ore zone could be located above, below or partly below the water table. A water table above the level of extraction would induce a higher dilution of PLS (impacting metal recovery). Modified ISR regimes are conceivable if the ore body is located in a formation with a natural gradient and an impermeable underlying layer to prevent leachant migration. An exemplarily simulation performed by the use of FEFLOW (Diersch 2014) is demonstrated in fig. 4. The injection and extraction wells are set up for an ore body located in the vadose zone. The original groundwater table is below the ore zone within the underlying impermeable layer. The simulation shows the gradual saturation of the ore zone and the surrounding area at two different time steps t1, shortly after startup, and t2, when the PLS is reaching the extraction site. The model allows the variation of injection/extraction rates and pressures to achieve hydrologic control of leachant flow to meet ISR objectives and environmental requirements.

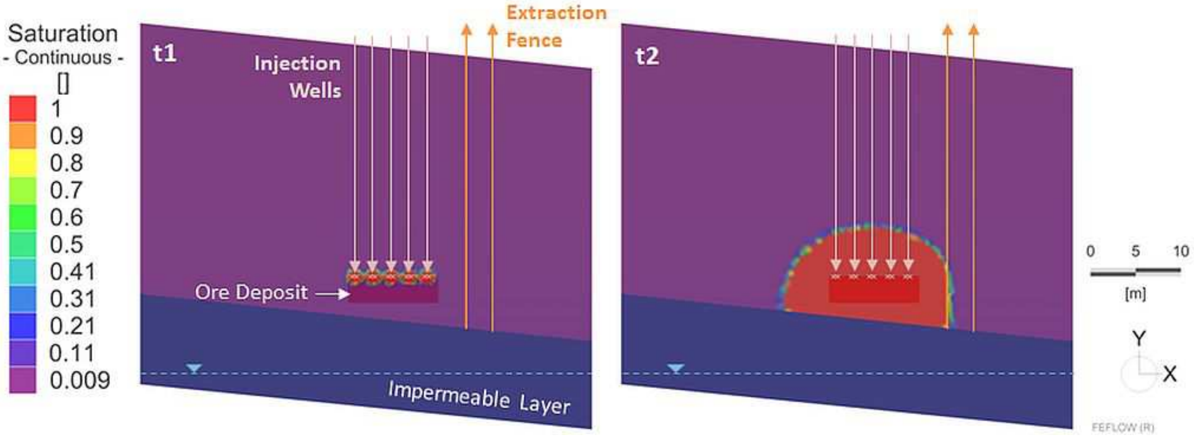

Figure 4 *ISR application within the vadose zone; gravity-driven saturation of the ore deposit and adjacent area for two different time steps t1 (shortly after startup) and t2 (reaching extraction).*

Fracturing of Less Permeable Ore Formations. In order to overcome the technical challenges of low porosity and permeability, fracturing by different means (hydraulic, chemical, thermal, high-voltage, blasting, etc.) has been considered to achieve the leachant-ore contact required for an economic recovery (Robinson 2016). Fracturing and fracture modeling approaches are known from the oil and gas industry, like discrete fracture network (DFN) modeling (Dershowitz 2011). Its transferability to ISR operations needs to be evaluated with regard to the different flow characteristics of oil/gas and leachant. Another challenge in fracture modeling is the proper replication of the fractures within the model due to their difficult visualization that is subject of ongoing testing. Whereas high-permeable sedimentary ore formations, e.g. hosted in sandstone, are characterized by a rather uniform free-fluid porosity enabling an ideal contact of the leachant with the metal-bearing minerals, the flow through fractured ore formations is preferential. In the latter case, the kinetics of leaching is by far more controlled by diffusion, thus, retarding recovery. An economic recovery is only conceivable for very high ore grades of very valuable metals.

Regional Scale Model

So far, we considered the advantages of hydrological modeling in a local (ISR wellfield) scale in terms of maximization of metal recovery. In regional scale, hydrological modeling is used to investigate environmental impacts of ISR in general, monitoring in the vicinity of operating ISR wellfields, post-mining monitoring and restoration strategies as well as relevant long-term effects such as natural attenuation (NA). For these applications, the wellfield hydrology is embedded into the regional groundwater model to simulate the effect of temporary ISR operation in a wider scale. Potential environmental impacts during ISR operations include (i) the migration of mining solution along the natural groundwater flow within the mining aquifer, (ii) unintended excursions caused by (tectonic) faults, discontinuous sealing layers (aquitards) and other exceptional hydraulic connectivity in both horizontal and vertical direction. Potential impacts and risks can be addressed within a regional-scale hydrological model. In particular, such simulations support the design of a representative monitoring systems (observation wells) during and after ISR operations.

The setup of the regional-scale hydrological model with embedded wellfields requires the following data input and procedures (calibrations) to be followed for reliable simulations:

- The appropriate representation of the regional geological stratigraphy is fundamental. Additionally, possible hydraulic connectivity between strata and along tectonic faults or thinning of confining layers should be considered. Input data can be derived from geophysical surveys (in particular, seismic) and borehole data (logging data, core assays).
- The permeability and porosity of all relevant formations (strata) including the mineralized ore zone are deduced from (i) geophysical borehole logging, (ii) laboratory assays of available core samples, (iii) aquifer pumping tests. Whereas the first data categories refer to smaller scale conditions, pump tests provide wider-scale information for aquifers and other strata.
- The initial hydraulic head data (potentiometric surfaces) is used for the calibration of the hydrological model and for simulating natural groundwater flow (baseline conditions).
- The anisotropy of permeability (lateral versus vertical) is quite significant for sedimentary formations. It can be determined by testing core samples.
- All relevant boundary conditions need to be considered appropriately, in particular sink and source terms that contribute to the groundwater flow regime like recharge/discharge, precipitation/evaporation, pumping/injection, surface water boundaries.

Post-mining conditions inside former ISR mining aquifers were studied by simulating the propagation of a mining solution body in 3D. For this purpose, the 3D hydrological model was first generalized for mass transport calculations incorporating a non-reactive species. Most important transport parameters including porosity and dispersivity had to be adapted. Representative results of such a 3D mass transport simulation are shown in fig. 5. The fate of mining fluid is indicated by time-dependent SO_4^{2-} concentration profiles considering horizontal and vertical cross-sections. Essentially, the mining fluid moves along the natural groundwater flow, spreading in 3D according to permeability and dispersivity conditions.

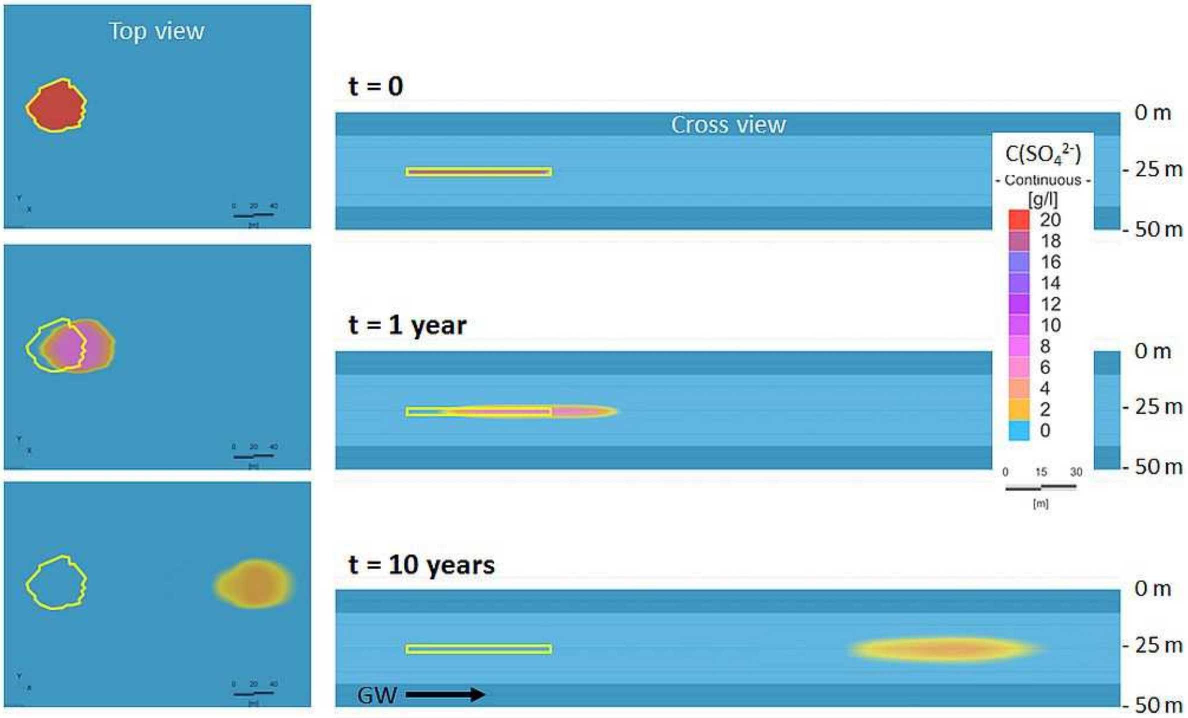

Figure 5 *Fate of tracer solution (SO_4^{2-} in g/L) from an abandoned mine site in horizontal (top view) and vertical (cross view) direction caused by groundwater (GW) induced dilution (non-reactive species transport).*

FEFLOW offers two possible approaches to incorporate *reactive* transport in 3D. First, geochemical reactions can be incorporated by user-defined reaction rate specifications, which require a comprehensive understanding of the main geochemical reactions and species derived from more sophisticated 1D reactive transport models (Nicolai 2016). Second, the piChem plug-in could be applied that allows for coupling FEFLOW with PHREEQC (Parkhurst 1999). These two approaches to 3D reactive transport modeling were studied for a homogeneous 5-spot ISR wellfield by Nicolai et al. (2015) showing that both approaches produce reasonable results, however, extensive computation times and numerical constraints restrict the applicability of the piChem approach for ISR optimization.

Conclusions

3D hydrological modeling is a state-of-the-art approach to support ISR projects with regard to feasibility studies, regulatory procedures, ISR wellfield design, optimization of ISR performance, monitoring/control of aquifer conditions during and after (post-mining) ISR, and aquifer restoration. Based on incorporating the comprehensive input from 3D structural models of the ISR district, the consistent embedment of (local) wellfields into a regional-scale hydrological model has been demonstrated for setting up and optimizing ISR operation as well as studying environmental impacts by applying the software FEFLOW (Diersch 2014). It is also suitable to investigate the 3D mass transport of main chemical species considering the kinetics of determining mineral-solute interactions.

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Geochemistry of In-Situ Recovery of Metals

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Extended Abstract

The applicability of in-situ recovery (ISR) of (technology) metals is mainly determined by ore body characteristics as well as hydrogeological and mineral/geochemical conditions in the mining aquifer. In addition to optimizing wellfield operation, the environmental impacts need to be addressed by considering hydrological and long-term geochemical processes within the *regional* scale. Whereas 3D hydrological modelling of ISR wellfields embedded into the relevant stratigraphic system is a state-of-the-art approach [1], the complex understanding of geochemical conditions by computer simulation is often constrained by the limited availability or uncertainty of kinetic and thermodynamic data of rock-solution interactions.

Based on the long-term experience in planning, operating and optimizing acidic ISR of uranium in saturated aquifers the main geochemical parameters determining the recovery and economics of ISR mining have been identified and characterized by studying both field data and results from dedicated lab-tests with ore samples from various deposits. In addition to basic simulations using PhreeqC [2], several categories of reactive transport models have been developed to study both uranium recovery from wellfields and environmental impacts [3]. In particular, well-calibrated models are available to *control* the geochemistry of ISR operation.

This paper describes the methodology of geochemical, reactive transport modelling of ISR in practical terms and represents applications to both acid and alkaline leaching of various ore rock types. Results are generalized to detail the ISR applicability criteria for technology metals.

In addition to the geochemical aspects of recoverability, the potential environmental impact of mining solutions in the vicinity of ISR wellfields have been studied in several application cases. Post-mining scenarios include both natural attenuation of mining fluids and aquifer restoration measures.

Key words: In-situ recovery, wellfields, geochemistry, reactive-transport modelling, post-mining

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Nanofiltration – A new separation pathway in secondary mining

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Abstract

Since decades, the demand of strategic elements is increasing. On the one hand, the industrialization of emerging countries is advancing due to the desire of a higher standard of living. On the other hand, the technical progress of the industrial countries leads to an enhanced provisioning of raw materials, such as strategic elements. Therefore, the supply is becoming increasingly difficult and supply bottlenecks might occur. Hence, the potential of secondary mining has to be exploited to uncover yet untapped resources. In the present study, the potential of a Theisenschlamm mono-landfill, a residue of German copper smelting with various strategic elements (e.g. Co, Ge, Mo, Re, Sb) included, shall be illustrated. By means of a hybrid process, consisting out of bioleaching and downstream processing, the target elements shall be mobilized and processed. As part of the element-specific procedures, the presented study investigates the applicability of nanofiltration to separate mono- and divalent metal ions in aqueous solution. Three thin-film polymeric nanofiltration membranes were investigated to determine the pH-dependent separation performance of Ge, Mo, and Re. Membrane screening experiments were conducted in dead-end set-up (15 bar, 25 °C) with the single and combined elements and aimed at identifying a suitable membrane for the proposed cross-flow set-up. The results demonstrate that rhenium could be separated from the multicomponent solution by the utilized RO90 membrane, which accounts for a market potential of approx. 19 Mio. $.

Key words: Secondary mining, Theisenschlamm, strategic elements, bioleaching, nanofiltration

Introduction

The investigated mining residual, the so-called Theisenschlamm, is a fine-grained flue dust with a mean particle diameter of 1.55 µm. It remained from top gas scrubbing during copper shale smelting in a blast furnace. Approximately 220,000 t of this by-product were deposited between 1978 and 1990 in Saxony-Anhalt in Germany (Weiss et al. 1997; Lorenz et al. 1992; Lorenz 1994). Besides the main components zinc and lead, various critical and candidate critical raw materials (European Commission 2014) are included from very small but right up to very significant amounts (see Figure 5A). Pyrometallurgical and hydrometallurgical attempts were applied to extract valuable components from the Theisenschlamm matrix, but until today a suitable process is missing (Weiss et al. 1997; Lorenz et al. 1992; Leipner et al. 1991). With beginning of 2015, the interdisciplinary r^4-joint research project was commissioned to develop an energy-efficient, economical, and eco-friendly process to extract and process the target elements from the Theisenschlamm (see Figure 1).

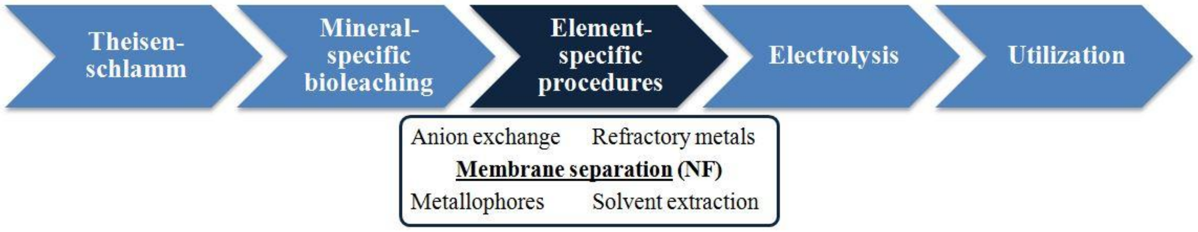

Figure 1 *Proposed process chain of the r^4-joint research project to extract, separate, and concentrate the target strategic elements from the Theisenschlamm matrix by bioleaching and downstream processing.*

As shown in Figure 1, a variety of element-specific procedures like nanofiltration (NF) shall be conducted to separate and concentrate the strategic elements from the obtained multicomponent leaching solution. By bioleaching even low-grade sulfidic mining residuals can be solubilized. Acidophilic microorganisms like *Thiobacillus* and *Acidithiobacillus* are able to oxidize sulfides, sulfur and iron(II) and mobilize sulphate, iron(III), and other soluble metal compounds (Bosecker 1997; Das et al. 1999). Initial bioleaching experiments were performed in a 2 L stirred-tank bioreactor with *A. ferrooxidans*, a $9K_{25}$-medium, and 4 % (w/v) Theisenschlamm. The leaching solution was analyzed with ICP-AES (Zn, Cu, Sb, Pb, Mo) and ICP-MS (Co, Ge, Re, Ag). An excerpt from the analysis is shown in Figure 2 (Klink et al. 2016).

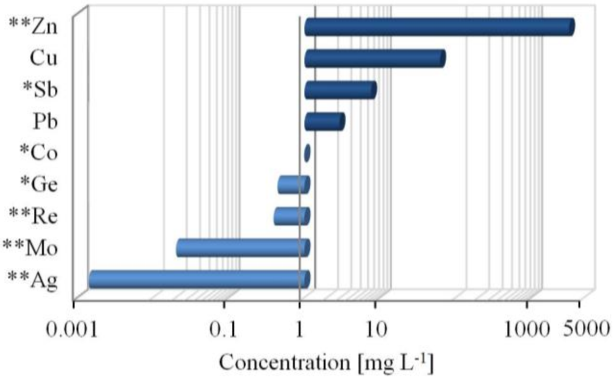

Figure 2 *The chemical composition of the bioleaching solution of Theisenschlamm (Klink et al. 2016); *critical, **candidate critical raw material (European Commission 2014).*

Figure 2 illustrates that the bonded metals can be solubilized from the Theisenschlamm matrix by bioleaching, but the concentration of the extracted elements is strongly varying (Klink et al. 2016). As a new environment-friendly pathway in secondary mining, the nanofiltration enables a selective separation and concentration of dissolved metals in aqueous solution. Based on adsorption and convective (size exclusion), diffusive, and electromigrative (charge interaction) transport mechanisms (see Figure 3), the retention of dissolved components is influenced. It is possible that the different retention mechanisms exist alongside and affect each other (Mulder 1996; Shen and Schäfer 2014).

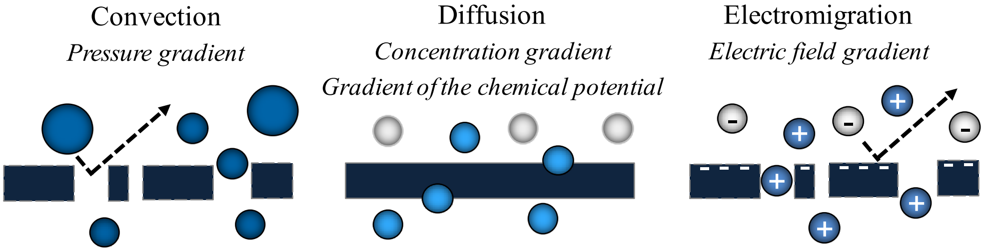

Figure 3 *Simplified retention mechanisms and related driving forces of the nanofiltration according to Shen and Schäfer (2014).*

For years, the membrane technology is used for water and wastewater treatments and synthetic nanofiltration membranes are in focus due to their high selectivity towards mono- and multivalent ions, wide pH range, and high permeability (Mulder 1996). The presented study investigates the pH-dependent separation performance of three polyamide nanofiltration membranes towards Ge, Mo, and Re in dead-end set-up. The aim is to examine occurring retention mechanisms and to identify a suitable membrane for processing the multicomponent leaching solution in the planned cross-flow set-up.

Materials and methods

Analytical investigation of Theisenschlamm

Theisenschlamm was sampled from the mono-landfill in Helbra (Saxony-Anhalt, Germany) at a depth of 4 m in May 2015. The total element concentration of Cu, Mo, Pb, Sn, Sb, and Zn was analyzed by energy dispersive X-ray fluorescence spectrometry (EDXRF; SPECTRO XEPOS HE, X-Lab Pro 5.1

Software). The trace elements Ag, Co, Ge, and Re were analyzed in an *aqua regia* extract of the Theisenschlamm using ICP-MS (Agilent 7700) due to the limitation in determination of EDXRF.

Synthetic feed solutions

On the basis of the bioleached Theisenschlamm (see Figure 2), synthetic feed solutions were prepared, which contained 1 mg L^{-1} Ge (GeO_2, 99.999 %, metals basis), 0.5 mg L^{-1} Mo ($Na_2MoO_4 \cdot 2H_2O$, 98 %), and 1 mg L^{-1} Re ($NaReO_4$, 99+%, metals basis, Re 68 %), either as single element or in combination. The aim was to investigate the pH-dependent retention mechanisms with and without mutual interferences. Due to the fact that bioleaching is carried out between pH 1.5 – 3 (Bosecker 1997), experiments were conducted at pH 2 and 4. Moreover, pH 7 was examined to investigate the influence of varying ionic species and changing membrane surface charge. The requested pH was adjusted with 0.1 M NaOH and 0.1 M H_2SO_4. The feed concentration was verified with ICP-MS (Agilent 7700). In advance, the samples had to be acidified with 20 µL HNO_3.

Polymeric nanofiltration membranes

Three nanofiltration membranes from the Alfa Laval Corporate AB (Lund/Sweden) were investigated to examine the retention mechanisms of Ge, Mo, and Re in dependence of pH. A summary of the membrane characteristics is given in Table 1.

Table 1 *Characteristics of the utilized polymeric nanofiltration membranes. Unmarked information has been provided by the manufacturer.*

Membrane	NF (NF99, NFT-50)	NF99HF	RO90 (NF97)
Material	Active Layer: Polyamide Support Layer/Paper: Polysulphone/Polyester		
MWCO	≥200 Da	≥200 Da	≤200 Da
Operating conditions	5 – 50 °C | 15 – 42 (max. 55) bar | pH 3 – 10		
IEP	pH 4.3[a)]	pH 4.12 – 4.42[b)]	pH 4.1[c)]
Nominal retention	NaCl 76 %[d)] $MgSO_4$ ≥98 %	NaCl 72 %[d)] $MgSO_4$ ≥98 %	NaCl ≥90 % $MgSO_4$ ≥97 %
Pure water permeability [kg m^{-2} h^{-1} bar^{-1}] [L m^{-2} h^{-1} bar^{-1}]*	10[d)] 8.3 ± 0.2*	9 – 18[d)] 18.7 ± 0.8*	1 – 6[d)] 4.4 ± 0.5*

MWCO – molecular weight cut-off , IEP – isoelectric point
*Measured with deionized water (15 bar, 25 °C, 500 rpm), calculated after Eq. 3
[a)]Nilsson et al. (2008), [b)]Oatley et al. (2012), [c)]Malmali et al. (2014), [d)]Restolho et al. (2009)

As can be seen in Table 1, the polymeric membranes are distinguished by their MWCO and therefore by their permeability and nominal retention towards mono- and divalent ions. Furthermore, the membranes have a positive, negative, or neutral zeta potential in dependence of pH, which can affect the retention mechanisms due to charge interactions.

pH-dependent nanofiltration experiments

The membrane screening was conducted in dead-end set-up (see Figure 4) with a constant filtration pressure of 15 bar and constant temperature of 25 °C. The utilized thin-film composite flat-sheet membranes had an active surface area of 40 cm² and were pretreated for 45 min in Ultrasil®. All experiments were performed in double determination.

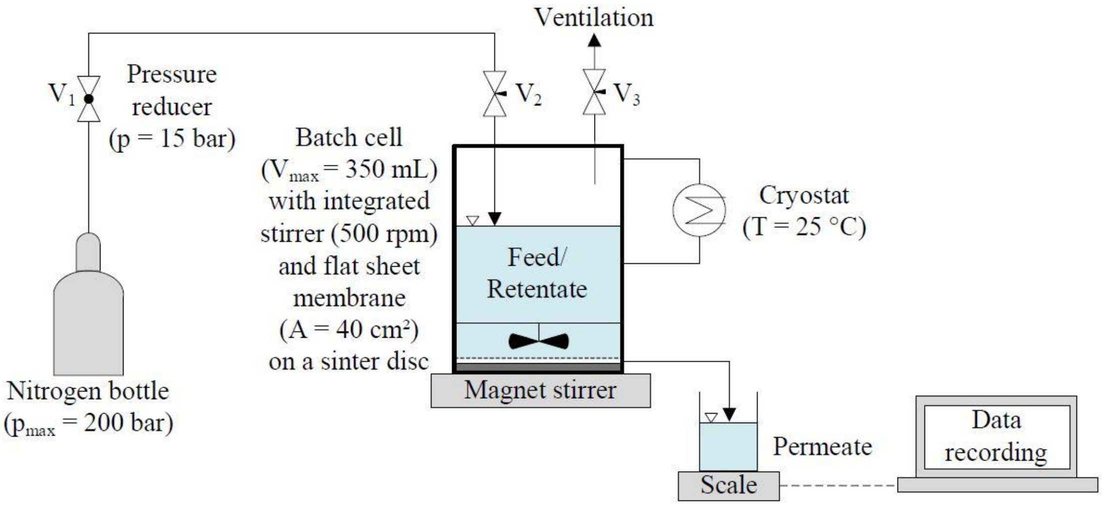

Figure 4 *Schematic presentation of the dead-end set-up.*

Filtered permeate was let out pressureless and was weighted on a precision balance (Kern & Sohn GmbH, readout: 0.01 g). Similar to the feed, the composition of the permeate and retentate was analyzed by ICP-MS. The separation efficiency during filtration was evaluated by the retention, which was calculated according to Eq. 1 (see ‘mathematical equations’).

First, the pH-dependent single element retention of Ge, Mo, or Re was investigated with a recovery of 85.7 % (see Eq. 2). After a membrane preselection, the pH-dependent separation performance of the combined elements was examined, while testing different recoveries (25, 50, and 87.5 %). The aim of the investigations was to identify the optimal process conditions and a suitable membrane, which separates the combined elements from each other with a high selectivity and high permeability (see Eq. 3).

Mathematical equations

$$\text{Retention}[\%] = \left(1 - \frac{c_{i,P}}{c_{i,R}}\right) \cdot 100\ \% \tag{1}$$

$$\text{Recovery}\ [\%] = \frac{V_{P,t=end}}{V_{F,t=0}} \cdot 100\ \% \tag{2}$$

$$\text{Permeability}\ [\text{L m}^{-2}\ \text{h}^{-1}\text{bar}^{-1}\ ] = \frac{V_P}{A \cdot t \cdot p} \tag{3}$$

A – Membrane surface [m²]
c_i – Concentration of element i [mg L^{-1}]
V – Volume [L]
p – Pressure [bar]
t – time [h]

F – Feed
P – Permeate
R – Retentate

Results and discussion

The chemical composition of Theisenschlamm

The sampled Theisenschlamm was analyzed by EDXRF (Zn, Pb, Cu, Sn, Sb, Mo) and ICP-MS (Ag, Co, Re, Ge) to determine the chemical composition. Figure 5A shows the mean concentration values of selected elements. The current market value of these elements is illustrated in Figure 5B. Furthermore, the expected sales value was estimated.

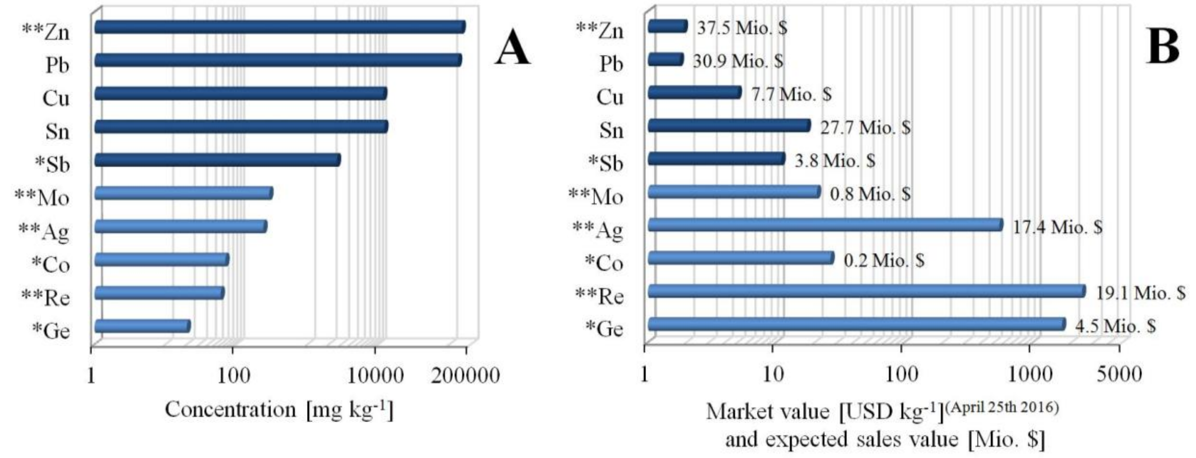

Figure 5 *(A) The chemical composition of Theisenschlamm (B) Current market value and expected sales value (assumed density 0.6 kg m^{-3}); *critical, **candidate critical raw material (European Commission 2014).*

Zinc and lead are the major components of Theisenschlamm (see Figure 5A). The market value of both elements is currently below 2 USD kg^{-1}. However, the expected sales value exceeds 68 Mio. $. As shown in Figure 2, zinc can be mobilized by bioleaching but it can be assumed that lead mainly remains as precipitate ($PbSO_4$) as the leachate concentration is below 3 mg L^{-1} (Klink et al. 2016). The solid concentration of the trace elements Mo, Ag, Co, Re, and Co varies between 20 – 290 mg L^{-1}. Silver is promising a high profit but similar to lead it seems to precipitate because the leachate concentration is little (1.4 µg L^{-1}) (Klink et al. 2016). Therefore, the nanofiltration cannot be used as element-specific procedure to separate Ag. Rhenium and germanium are present in low concentration in the Theisenschlamm matrix but an extraction and separation seems worthwhile due to the high market value. The recovery of both elements shall be increased by mineral-specific bioleaching. On this assumption, nanofiltration experiments with 1 mg L^{-1} Ge and 1 mg L^{-1} Re were conducted. Furthermore, the pH-dependent separation performance of molybdenum (0.5 mg L^{-1}) was investigated. Currently, only the separation performance of the anion-forming species is examined. Further investigations are aimed to extend the synthetic feed solution by the addition of other elements (e.g. Zn, Cu, Co).

pH-dependent nanofiltration experiments

The pH-dependent retention of the single elements Ge, Mo, and Re is illustrated in Figure 6A–C for the three tested polymeric membranes. Respective literature data is missing at the moment and the conducted research should clarify the influence of pH, MWCO, ionic species, and zeta-potential on the separation performance.

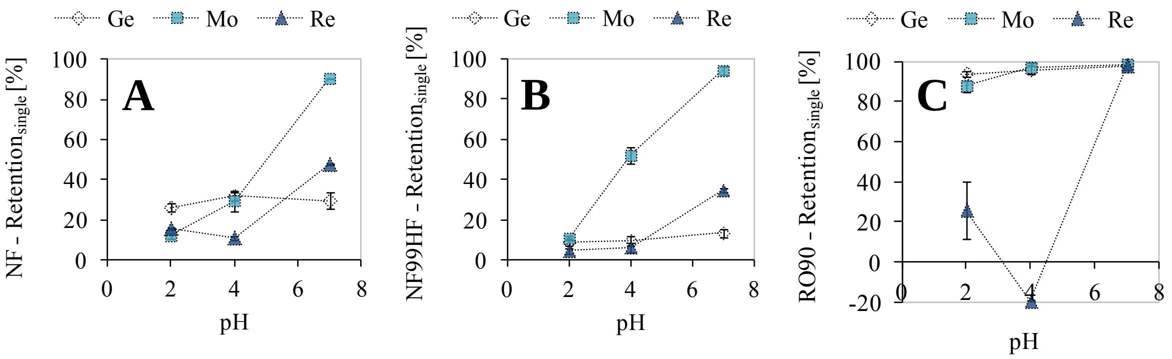

Figure 6 *The pH-dependent retention of the single element Mo (0.5 mg L^{-1}), Ge (1 mg L^{-1}), or Re (1 mg L^{-1}) using the membrane (A) NF (B) NF99HF (C) RO90 (15 bar, 25 °C, 85.7 % recovery).*

As shown in Figure 6A–C, the separation performance is obviously affected by the pH and the MWCO. The membrane RO90 (see Figure 6C) has the smallest MWCO and therefore, the highest Ge and Mo retention (>88 %). Germanium is present as $\mathrm{Ge(OH)}_4^0$ in the investigated pH range (Pokrovski and Schott 1998; Virolainen et al. 2013). For this reason, charge interactions can be excluded and convective transport mechanisms dominate here. The same applies for molybdenum at pH 2 because $H_2MoO_4^0$ is present in the aqueous solution. With increasing pH, the ionic species is transforming into MoO_4^{2-} (Ozeki et al. 1988) and charge interactions become relevant as can be observed in Figure 6A and B. The molybdenum retention is significantly increasing (pH 7 >90 %) caused by repulsion between negatively charged membrane surface and the dominating MoO_4^{2-} anion above the isoelectric point. Different molybdenum retentions at pH 4 are attributable to the varying location of the IEP (see Table 1) and the more or less pronounces retention of the present ionic species.

Rhenium is present as ReO_4^- in the investigated pH range (Magee and Blutstein 1985; Srivastava et al. 2015) and therefore charge interactions are more pronounced. Similar to Mo, the Re retention is enhanced at pH 7 due to repulsion, which can be seen in Figure 6A–C. Conspicuous is the low rhenium retention of the RO90 at pH 2 and 4 (see Figure 6C). Although this membrane has the smallest MWCO and Ge as well as Mo is rejected, Re can permeate nearly unimpeded. The IEP at pH 4.1 enables a convective transport without charge interferences and therefore, the Re retention is even lower than for the NF and NF99HF. At pH 2, an attraction of ReO_4^- towards the positively charged RO90 membrane surface seems more likely for the low Re retention.

According to the manufacturer´s information, the MWCO of the membranes NF and NF99HF should be similar but the experimental results conclude that the NF must have a smaller cut-off due to the fact that the retentions are increased compared to the NF99HF. However, derived from Figure 6B, it can be assumed that the selectivity of the NF99HF is even enhanced for the combined elements and a separation at pH 7 seems feasible. Before testing the separation performance of the combined elements for NF99HF (see Figure **7**B), the single element retention was evaluated with a recovery of 50 % (see Figure **7**A) because a lower recovery might improve the performance efficiency.

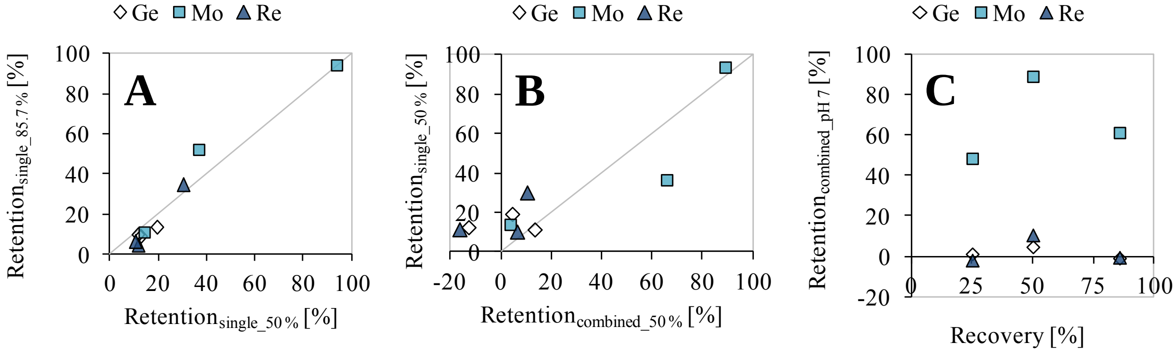

Figure 7 *(A) Retention of the single elements – varying recoveries (B) Single and combined element retentions – 50 % recovery (C) Retention of the combined elements at pH 7 – varying recoveries (NF99HF, 15 bar, 25 °C).*

As can be seen in Figure 7A, the retention of the single elements is nearly unaffected by varying the recovery. However, if the elements got combined, the retentions are changing (see Figure **7**B) caused by the Donnan equilibrium. The charged membrane strives towards electroneutrality and in case MoO_4^{2-} is rejected at pH 7, more ReO_4^- can permeate because the equilibrium needs to be established. Due to this fact, the recovery has a significant influence on the combination experiments as a concentration of the bulk solution forces the gradient of the chemical potential (Mulder 1996). This becomes clearly evident in Figure 7C. Neither a recovery of 25 or 85.7 % shows a satisfying separation selectivity. Using a recovery of 50 % enables a separation of Mo from the three-component solution. A separation of rhenium would be more desirable because the estimated sales value exceeds 19 Mio. $. This seems feasible with the RO90 at pH 4 and can be seen in Figure 8.

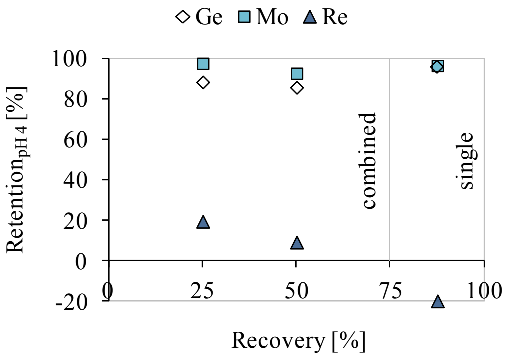

Figure 8 *Retention of the single and combined elements testing different recoveries for the RO90 at pH 4 (15 bar, 25 °C).*

Figure 8 shows that Re can be separated from Ge and Mo at pH 4 with the best efficiency using a recovery of 50 %. Combination experiments with a recovery of 85.7 % were not performed because the permeability was very low (see Figure 9). It can be assumed that the addition of divalent cations (e.g. Cu^{2+}, Co^{2+}, Zn^{2+}) should not be detrimental for the rhenium separation because in general they have a high retention (Mulder 1996). For example, the manufacturer indicates that the $MgSO_4$-retention is above 97 % for the RO90. However, the presence of other monovalent metal anions (e.g. $Sb(OH)_6^-$) might be disturbing for the selective separation of Re but further combination experiments have to examine these hypothesis.

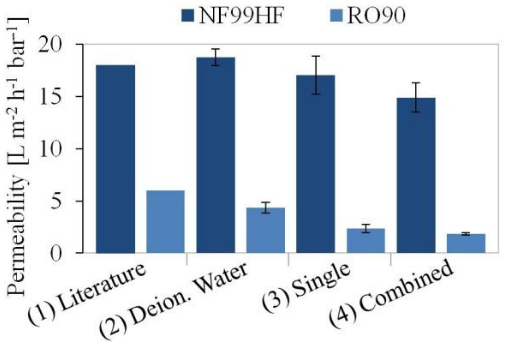

Figure 9 *Permeability of NF99HF and RO90 in comparison (1) Literature data from Table 1(2) Deionized water (3) Single element feed solution (4) Combined element feed solution (15 bar, 25 °C).*

The permeability of NF99HF and RO90, which was measured with deionized water, is similar to the literature data (see Figure 9). It was observed that the permeability is decreasing in case Ge, Mo, or Re was added to the feed solution. If the elements got combined, the decrease is even higher. The permeability of the NF99HF achieves higher values compared to the RO90 due to the enlarged MWCO. In the planned cross-flow set-up, the transmembrane pressure shall be increased and as consequence, the permeability should be enhanced especially for the RO90. The utilized dead-end set-up is restricted to 20 bar.

Conclusion

The influence of pH (2, 4, 7) on the retention of the single and combined strategic elements Ge, Mo, and Re by nanofiltration using three different polymeric membranes (Alfa Laval: NF, NF99HF, RO90) was studied. The NF (≥200 Da) and NF99HF (≥200 Da) show a similar separation performance but the selectivity of the NF99HF is increased. Currently, Mo can be separated from Re and Ge at pH 7 using the NF99HF. The highest Ge and Mo retention (>88 %) was measured for the RO90 due to the smallest MWCO (≤200 Da). Nevertheless, this membrane shows a high selectivity towards rhenium, which can be separated from the synthetic multicomponent solution at pH 4. However, the permeability of the RO90 was below 2 L m^{-2} h^{-1} bar^{-1} in the combination experiments but it can be assumed that a higher filtration pressure will lead to an increased permeability. This will be verified in further cross-flow experiments.

The following dead-end investigations are aimed to examine the retention mechanisms of Co, Cu, and Zn in single element experiments and in combination with Ge, Mo, and Re using the NF99HF. Moreover, other membrane materials like poylethersulfone shall be screened. Furthermore, cross-flow experiments shall be conducted to verify the dead-end results and to receive reliable data for a scale-up. The ascertained data shall be processed in a mathematical model to predict retention mechanisms, even for similar separation problems. Multicomponent solutions could be treated by a nanofiltration membrane, which was intended as suitable in advance.

Acknowledgements

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Economic Potential for reprocessing Copper Mine Tailings in Chile

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Abstract

Four copper mine tailings in Chile were investigated for their elemental and mineral composition, in order to evaluate the potential for economic reprocessing. The sample material, taken for processing had Cu-contents between 0.1 and 0.5 %. Copper was abundant in various primary (mostly chalcopyrite) and secondary (cuprite, atacamite, brochantite and chrysocolla) minerals. This report includes tests of laboratory size. Chemical sulfuric acid leaching was assessed in comparison to bioleaching. Copper bioleaching resulted in recoveries between 20 % and 70 %. For chemical leaching the recovery was 4 % to over 80 %. The recovery was strongly dependent on the mineralogical composition of the copper minerals. Secondary copper minerals were very scarcely abundant in the solid leaching residues. Using chemical leaching a very low copper recovery for one sample could be explained by the presence of the recalcitrant mineral chalcopyrite as the almost unique copper bearing mineral. In contrast, a significant copper bioleaching was found instead. Almost one third of all chalcopyrite grains showed clear signs of alteration investigated by scanning electron microscopy. Overall, the study shows that the economic potential for tailings reprocessing is strongly dependent on the composition of the valuable metals hosting minerals in connection with the applied processing technology.

Key words: Tailings, reprocessing, bioleaching, conventional leaching

Introduction

In Chile copper mining started in the middle of the 19th century. During the 20th century the country became one of the most important copper producing countries and since the early 1980s Chile is the most important copper producer with a share of more than 30 % of the world production (BGR data base). Concerning the production of waste,Chile is annually producing 350 million t of waste from copper mining and processing, according to conservative estimates. This lead to a total volume of 6.8 billion t over the last 30 years. These waste materials still contain copper and other metals and minerals of potential economic value. In this study we investigated the elemental composition, mineralogy and (bio)hydrometallurgy processing of mine waste tailings for an evaluation of their economic potential for reprocessing.

Methods

The Mineral Liberation Analysis is an automated mineral analysis, using back scatter electrons (BSE) from a scanning electron microscope (SEM). The **MLA** software automatically identified individual minerals at a high spatial resolution (0.005 mm) and quantified their respective proportions.

X-ray fluorescence (XRF) was used for measuring major and trace element composition.

Magnetic separation was applied on the concentrates obtained from the mechanical tailings processing on a wet shaking table (see below).

Concentrates were produced using **gravity sorting on a wet shaking table**. This technique uses the different densities of minerals to sort them. The higher the density of the material, the more the grains tend to be moved by the back and forth movement of the table, than by the water. As copper minerals have a higher density, compared to quartz and feldspar, they could be separated from these common rock-building, barren minerals.

For **bioleaching** experiments in shake flasks, 4 g of sample material were mixed with 200 ml medium. Additionally a 1 molar Fe^{2+} solution was added, to get a final concentration of 50 ppm Fe^{2+} for each assay. Each flask was inoculated with a mixed culture of acidophilic iron(II)- and sulfur-oxidizing bacteria (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*). The bioleaching was performed for approximately 28 days.

The **chemical leaching** experiments were done by IBZ-Salzchemie GmbH in Halsbrücke, Germany. Around 100 g of material was put in PVC beaker glasses, together with 1000 ml of water and a H_2SO_4 concentration of 49 g/L. Leaching was performed for 24 h.

Since tailings are highly heterogeneous bodies, hand driven core drills were performed, to sample 12 objects at several spots. The obtained samples were geochemically analysed (XRF). Based on these data four objects for taking a larger sample (about 20 kg) were choesen and gravimetric processing tests were carried out to produce concentrates. Subsequently both, the unprocessed tailings and the resulting concentrates were taken to execute conventional leaching and bioleaching tests.

Mineral Libaration Analysis (MLA) using an SEM was applied, in order to analyse the mineralogy of all samples, to obtain an optimal beneficiation scheme. The leaching residues were also analysed using MLA, to evaluate differences in the mineralogical composition of the ore minerals.

Results and Discussion

A total of 81 tailings samples were analyzed using XRF, during the survey sampling. The copper grade of the tailings varied between 0.1 % and 1.7 %. Further elements of interest were iron, gold, molybdenum and zinc.

This data and the tonnage of the tailings ponds was the basis to select four sites for a more detailed analyzes (Minera Carola, Minera Clarita, El Salado and Taltal). Around 20 – 25 kg of material were taken from each tailings dump and further processed in order to obtain concentrates and/or to do leaching tests.

Very large differences in the elemental and mineralogical composition of the tailings were discovered, causing an enormous effect on the Cu extractability that was revealed in laboratory studies of mechanical processing as well as bioleaching and chemical leaching.

For the El Salado tailings bioleaching gave a recovery of 60 % for the unprocessed sample. The copper grade of the sample taken for processing tests was only 0.4 %. Substantially less, than discovered during the survey samples (0.8 and 1.7 %). The tailings should be investigated in more detail to reveal the average grade of the material.

The Cu recovery of the tailings material from Taltal was high for both leaching techniques. With bioleaching around 70 % of the copper went into solution. This was substantially more than in the control experiment with slightly higher than 50 %. In the chemical leaching more than 80 % could be extracted. Iron, abundant as magnetite in this tailings pond, could be a significant by-product, as it can easily be concentrated, using magnetic separation.

Evidence of bioleaching was observed for about 1/3 of the analyzed chalcopyrite grains of the residue material. Nevertheless, the results exhibited a very poor recovery. If flotation should turn out to be feasible on the remaining chalcopyrite in the concentrates of Minera Carola, separate magnetite, chalcopyrite and pyrite concentrates could be produced. If all, including the pyrite concentrate, were marketable, a reprocessing could be of interest.

Tailings will be a marginal deposit in almost all cases from the economic point of view. Nevertheless for the tailings of Taltal our analysis resulted in an ore value of 24 US$/t (at a copper price of 6000 US$/t), not taking into acount credits from possible by-products like a magnetite concentrate. This is still a relatively low value compared to primary ore deposits, but the tailings are already crushed and milled, reducing the processing costs (energy needs). Additionally the production of a magnetite concentrate could substantially reduce the volume of the tailings, as the iron content was up to 53 % in one tailings pond.

Investigations on Heap leaching material and potential recovery of strategic elements

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Extended Abstract

The importance of rare elements, especially for the industry sector of renewable energies is well known. Our research group collaborates with a Chilean company that leaches ore using the method of conventional heap leaching with sulfuric acid to extract copper. The dumped residuals of the leaching process have been investigated for their potential concerning the content of strategic elements. Strategic elements in this context are minor and trace elements of economic interest. One important question is whether these elements are recoverable by using simple and inexpensive processes.

Initial studies of recently dumped material were started on-site and continued later in the laboratory. The heap material is a mixture of coarse-grained to fine-grained ore chunks. With this material, pure water eluates were prepared in the field to investigate milieu parameters and element content. As expected, extremely high electrical conductivities (22.9 mS/cm) and low pH-values (down to 2.9) were measured in the solvent. Besides that, liquid phase samples were taken for ICP-MS analyses of elemental concentrations.

In the lab, sequential extraction was performed as an analytical method, providing information about the extractability and thus mobility of the different elements. Sequential extraction is an enhanced type of leaching of granular material, treating the same material with progressively stronger leaching solutions in order to determine extractable metal concentrations of each step. Furthermore, the sequential extraction method was firstly simplified and secondly modified to estimate strategic element extraction from the residual dump material. Therefore, cheap extraction agents, coming from the proximity of the mining area, were tested. In our case, the cost-effective solvents seawater and sulfuric acid were used.

The article presents the results for three different (sequential) extraction methods:

1. Complete sequential extraction (SE) of 5 g of residual material with 50 ml extracting agent (see Tab. 1 Overview of extraction steps of the altered sequential extraction method (Zeien (1995) [2] and Graupner et al. (2007) [1] modified by Kassahun, Hache) as an "analytical method"
2. Shortened sequential extraction reduced only by certain steps
3. Modified and shortened sequential extraction with special extraction agents

Shortened sequential extraction

The shortened SE consists of four steps of the "complete SE": step I - water solubles, step II - exchangeables, step III - carbonates and the last step IV (corresponds to step Va in Tab.1) - poorly crystallized iron and aluminum hydroxides. The extractions were carried out under aerob conditions: 5 g of sample were mixed with 50 ml of extracting agent (2h in an overhead shaker).

Modified and shortened sequential extraction

The modified and shortened SE consists of four steps: step I - water solubles, step II – exchangeables, seawater instead of Ammonium nitrate, step III - carbonates and last step IV - sulfuric acid.

***Table 1** Overview of extraction steps of the altered sequential extraction method (modified from Zeien (1995) and Graupner et al. (2007))*

Step	Extracted phase	Leaching solution	Conditions
I	Water soluble	Ultrapure water	
II	Exchangeable	Ammonium nitrate	pH 7
IIIa	Carbonates and specific bonds	Ammonium acetate	pH 6
IIIb	Reducible	Ammonium acetate Hydroxylamine hydrochloride	pH 6
IV	Organically bound (Oxidizable)	EDTA	pH 4.6
Va	Amorphous and poorly crystallized iron and aluminum hydroxides	Ammonium Oxalate Oxalic acid	pH 3.25
Vb	Crystalline iron and aluminum hydroxides	Ammonium Oxalate Oxalic acid Ascorbic acid	pH 3.25

Summarized results of the SE method comparison:

Three different SE methods were tested on different Chilean heap and tailing materials. In general, the first (analytical) SE method is the most effective but also the most time-consuming and cost-intensive method. The effectiveness varies depending on the matrix of the original/raw material – e.g. tailing material is relatively homogeneous compared to the heap material. Depending on the (ore) deposit and the elements that should be extracted, each SE method shows a different behavior. In the case of the heap material, the release of elements shows a greater variance due to the heterogeneity of the raw material. Therefore, an accurate evaluation of the extraction results and SE method comparison is less clear in the case of heap material. However, the following results are observed for the SE method comparison with respect to the heap material:

- Step I – Water soluble: relatively high Copper contents (625 ppm); Li (40 ppm) but also REE: Ce (8 ppm), Dy, Sc, Y, La, Nd (< 3 ppm) and Sr (6 ppm)
- Step II - Exchangeable: still Cu released, but in smaller amounts (50 ppm); similar range of extracted element content in 3.5% NaCl and NH_4NO_3
- Step III – Carbonates and specific bonds: e.g. Ca, S, Si
- Step IV – (oxalate or acid step): similar range of extracted element content, acid mobilizes - as expected - some REE: Ce, Dy, Sc, Y, La, Nd and also Mo, Ti, V, Sr
- After two hours of exposure to the extraction agent, the aluminum and silicium contents are already showing the attack of the acid and the oxalate on the silicate structure (of the minerals). Iron is released from sulfidic and hydroxide phases.

Summarized results of the extracting experiments with 200 g of heap material:

For a better evaluation of that kind of extractive mining, new experiments with 200 g of residual material (instead of 5 g) were started to estimate a potential yield. The samples were taken at three different sampling sites (ES1/ES2/ES3) of the same dumping site. For each sampling site exists a shallow (0.5 meters depth) and a deep (4 meters depth) sample. The Material was separated during the water step into a fine (<1 mm) and a coarse fraction. For this extraction experiment a further simplified extraction method was applied, composed of three extraction steps: H_2O, NaCl and H_2SO_4. General results:

- Copper contents up to 1400 ppm were observed in the water soluble fraction (Fig. 1), and about 100 ppm again with NaCl extractant (see SE method comparison results)
- H_2SO_4-step: aluminum and silicium contents clearly indicate an attack on the silicates (see SE method comparison), copper release in fine fraction 300 ppm, in coarse fraction 3700 ppm, release of cerium in both fractions of about 9 ppm. Clear differences between fine and coarse fraction noticeable, release of REE in small amounts Ce, Dy, Y, La, Nd (Fig. 2) and Ti, V, Sr (Mo is probably contained but not measured)
- Comparison fine and coarse fraction: similar range of extracted element content, but Cu and Zn (and Mn and Si) significantly higher contents in the coarse fraction; for Al, Fe higher contents in the fine fraction (clays, Fe-hydroxides)
- Comparison deep and shallow samples: the element contents for extraction agents H_2O and NaCl show no significant trend, H_2SO_4 step: higher contents extracted out of the shallow samples
- Comparison sampling sites (ES1/ES2/ES3): Values previously available only for H_2O and NaCl step - significantly higher contents of location ES3 for the elements Al, Cu, Fe, Li, Mo in the water soluble fraction; NaCl step: Cu and Al content increased in orders of magnitude
- Sampling site ES1 and ES2 are located close together. ES3 is further away and at a slightly higher altitude. This may explain the difference in elemental content, whereas ES1 and ES2 seem to have the same raw material and the same weathering conditions.
- To estimate the real recovery, more investigations and extractions experiments and especially the total extraction analysis results are needed.

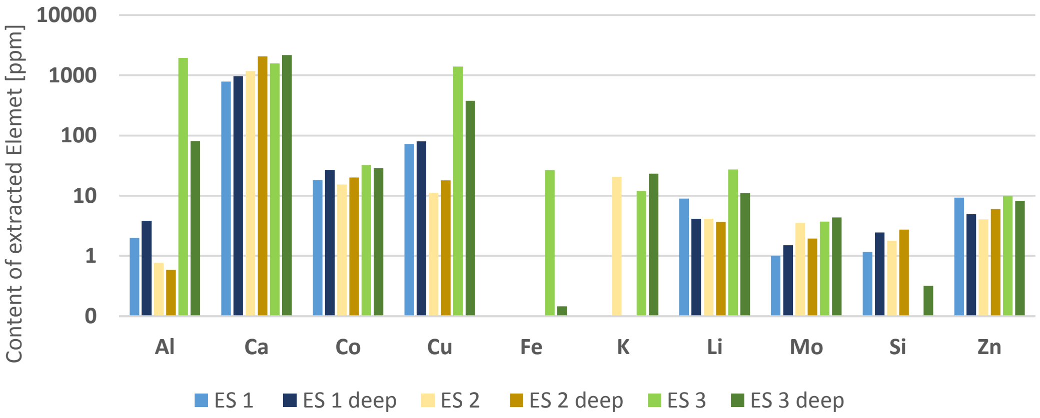

Figure 1 *Extraction experiment - H_2O step: release of main elements for different heap material samples*

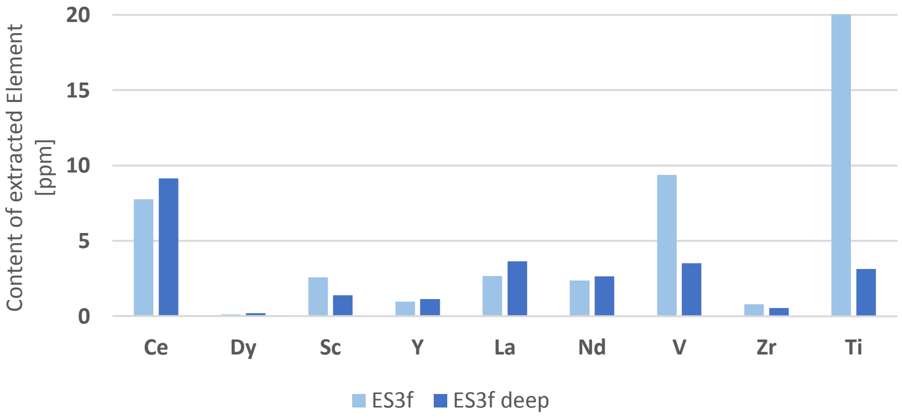

Figure 2 *Extraction experiment - H_2SO_4 step: release of several REE*

Derived from previous experiments, the main result is a high mobility of copper and aluminum. There is evidence to suggest that aluminosilicates have been attacked long-term (heap leaching takes about 60 days) and there is a release of strategic elements and rare earth elements in connection to that. These were also detected in the residual liquid phase of the first extraction step (pure water). For example Y, La, Nd, Ce and some Dy, Gd, Sc were detected. In the further extraction steps also Dy, Sc can be found.

Key words: heap leaching, strategic elements, sequential extraction

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Specific Retention of Copper and Strategic Elements from Chilean Mine Water with Zeolites and Peat-Based Sorption Media

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Abstract

Acid mine drainage (AMD) and their high element contents is a common problem in mining. One promising possibility to remove these elements from the AMD is ion exchange. Zeolites are reported to have a high exchange capacity for cations like copper, cadmium or zinc. Furthermore, they are low cost (Babel und Kurniawan 2003). Peat-based materials such as APTsorb (American Peat Technology) also retard copper very efficiently (Eger et al 2015).

Column experiments were carried out to reproduce the conditions in the real system. In this case, original Chilean tailing material was used to generate a representative tailing water. All experiments were done for a zeolite containing rock and for APTsorb. The changes in hydrogeochemistry and element content of the water while passing the different zones were observed via respective sample ports. After the experiments, the solid filling materials were removed from the column and investigated by hXRF analyses and SEM-EDX. Furthermore, sequential extractions were performed on the reactive materials to obtain information about the mobility of elements.

In the mobilisation zone of the column, copper concentrations range up to 2 g/L. In the paper, detailed results for both reactive materials will be presented. A main conclusion is that APTsorb is more efficient in comparison to zeolite. It was able to retard nearly 100% of the released copper. Both reactive materials have a good buffer capacity. They increased the pH of the tailing water (pH=3.8) up to values between 5.5 and 7.

The investigated zeolite as well as APTsorb seem to be appropriate retention materials for Chilean mine waters. Further investigations have to be done to extend the results, determine the sorption capacity for each material and to clarify if desorption of the attached elements is possible. The main focus here is on the reprocessing of copper and strategic elements. Furthermore, the applicability for other mine waters can be tested.

Key words: Chilean mine water, Zeolite, Peat (APTsorb), copper retention

Introduction

Mining activity is often related to acid mine drainage (AMD) with discharge of mine waters contaminated by environmentally relevant metals. Therefore, it is important to remove these elements from the released waters to protect the surrounding ground and surface waters. One promising possibility for the retention of these contaminants is ion exchange. There is a large variety of materials which are well known to function as ion exchange material. One auspicious ion exchange material which will be mentioned are zeolites. They are micro porous aluminum-silicates which have a large specific area (Foo und Hameed 2011) and reported to have a high exchange capacity for cations like copper, cadmium or zinc. Furthermore, they are low cost absorbents and occur in natural deposits all over the world (Babel and Kurniawan 2003). Motsi et al. (2009) reported for zeolites a high absorption speed after 40 minutes the main part of elements was absorbed by the zeolite. An Other promising ion exchange material is peat. It has an extremely high specific area up to 200 m²/g and very good absorption capacities to various elements (Couillard 1994). Peat-based sorption materials such as APTsorb (American Peat Technology) are also reported to retard copper very efficiently (Eger et al 2015).

Chile is one of the largest producer of copper ore worldwide. Due to that and the long period of time since ore processing in Chile is done there are large amounts of legacies which causes the already mentioned problems for the environment. Except for the environmental problems the legacies represent also a raw material body because of the enhanced metal production techniques now days. Therefore, the tailings are interesting for secondary mining approaches. Because they still contain significant amounts of minor and trace elements and metals of economic interests (Ussath et al 2015).

Column experiments are an appropriate instrument to reproduce real earth system conditions in a laboratory scale. Therefore, this experimental setup was chosen for the investigations of the absorption materials. Because they should be investigated under as realistic conditions as possible to get an impression how they can handle such complex systems and if they are an appropriate option for Chilean mine water treatment.

Sequential extraction is a type of leaching of solid material, which differentiates the mobility of elements. The same material is treated successively with stronger leaching solutions in order to determine extractable metal concentrations of each step. There are up to seven pH-dependent extraction steps incipient with water, followed by saline, complexing, reducing and oxidizing reactants were carried out. Due to that, a correlation between sequentially dissolved minerals and extracted element contents is possible. This allows inferences to the mobility's. An evaluation of the selective extraction method provides information about the extractability and thus mobility of different major and trace elements (Ussath et al 2015). These information are matter of particular interest for the evaluation of secondary mining approaches.

Methods

Column experiment

Column experiments were carried out to reproduce the conditions in the real system. In this case, Chilean tailing material was used to generate a representative tailing water. To investigate the reactive materials, the column was divided into three zones. The lowest zone represents the mobilisation zone and is filled with the original Chilean tailing material. To reach better flow through it was mixed with 37 % mass of pure quartz sand (inert dilution material). Above that, is the reactive "retention zone" located which consists of one of the ion exchange materials. Both materials were diluted by 50 % mass of pure quartz sand. The third zone was filled with quartz sand and characterises the outlet. All experiments were done for a Chilean rock which contains approximately 15-20 % of zeolite and for APTsorb. Changes in hydrogeochemistry and element content of the water while passing the different zones were observed via respective sample ports. To get information about the composition of the generated mining water the first sample port was located in the upper third of the mobilisation zone. The retention zone was monitored by two sampling ports one at the beginning and the other at the end of the zone. Ultrapure water was pumped through the column from the bottom to the top with speed of 20 ml/h. According to that takes the exchange of one pore volume 7.5 h with an effective pore volume of 10 %. All water samples were analysed by photometry in matters of their copper und sulphate concentrations. After the experiments, the solid filling materials were removed from the column and stored at -20°C.

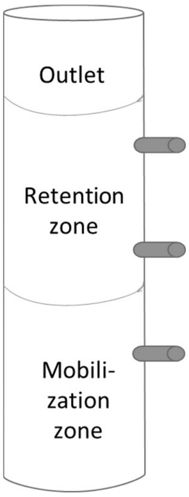

Figure 1: *schematic diagram of the column experiment*

Sequential Extraction

To get information about the mobility of the retarded elements on the ion exchange materials a sequential extraction was done. An abbreviated variation from the method of Zeien (1995) was used, developed by the project partner GFI (Kassahun, Hache). In

Table **1** the steps used in the sequential extraction are shown. For all steps a solid:liquid ratio from 1:10 was used. To conserve the mineral phases and bonded main and trace elements, step I to IV were done under nitrogen atmosphere. For each step the eluates were analysed for pH, electric conductivity, redox potential, total inorganic carbon (TIC), ferric iron and element content (by ICP-MS analysis).

Table 1: *overview of the steps of the sequential extraction (modified after Zeien (1995) and Graupner et al. (2007))*

Step	Extracted phase	Leaching solution	conditions
I	Water soluble	Ultra-pure water	pH 7
II	Ion exchangeable	Ammonium nitrate	pH 7
IIIa	Carbonates and specific bounded	Ammonium acetate	pH 6
IV	Organic bounded	NH_4 EDTA	pH 4.5
Va	Amorphous and poorly crystallized iron and aluminum hydroxides	Ammonium Oxalate Oxalic acid	pH 3.25

Results and Discussion

Column experiment

Former own investigations on the tailing materials have already shown a high mobility of copper. This can be confirmed by the current experiments. In the mobilisation zone of the columns, copper concentrations range up to 2 g/L during the first 24 h (17 h without and 7 h of pumping with a pump rate of 20 ml/h). But it also decrease very fast. For example after two days only 0.1 g/L copper was measured in the mobilisation zone of the APTsorb column. In figure 2 is the pH-development of each column zone for both reactive materials (APTsorb and zeolite) shown. Due to that it can be estimated that the Chilean tailing material used in the mobilisation zone behaves in both columns similar and is homogenous. Both reactive materials have a good buffer capacity. APTsorb were able to increase the pH-value of the tailing water over the whole time of testing in a range between 5.5 and 6. In comparison to that is the zeolite able to increase pH of the water up to a pH-value of 7.5 but not constantly over the complete time (see fig. 2). After one exchanged pore volume the buffer performance decrease and settle down to a pH of 5.5. This high buffering of the zeolite at the beginning of the test may related to contained calcite.

Both materials have a good retention potential (fig. 3) but APTsorb is more effective than the zeolite. The first two cm of APTsorb in the column retard the copper completely over the whole period of time. As in figure 3 shown does the first centimeters of the APTsorb (A retent 1) retard already the complete incoming copper. The zeolite accomplished the complete copper retention only up to three pore volumes and then decrease constantly. But a breakthrough in the outlet cannot be observed. The first time when copper can be detected in the outlet was in the last sample of the experiment after 5.5 pore volumes. But it has to be considered that in the experiments no pure zeolite was used. The zeolite content was estimated of 15-20 %. In comparison to APTsorb is the content of reactive material in case of the zeolite much lower. This can be one reason for these considerably differences between APTsorb and the zeolite. APTsorb has also a much higher adsorption capacity for copper than zeolite. Babel and Kurniawan 2003 reported for typical zeolites adsorption capacities between 1.64 and 5.10 mg/g (batch experiments) in comparison to that, have peat capacities from 6.4 to 19.56 mg/g (batch experiments). According to our results of the column experiments the adsorption capacities for copper can appraised for APTsorb on 286 mg/g and for zeolite between 120 and 160 mg/g (depending on assumed zeolite content). These obvious difference between the literature value and the experimentally observed value might be explained by possible precipitation and filter mechanisms which are only occur in column experiments.

The comparison of figure 2 and 3 show some similarities between copper retention and buffering. In case of the zeolite the buffer capacity decreases temporally delayed when the retention decline. When no retention can be observed the pH commute to a constant value. APTsorb indicates an analogue behavior.

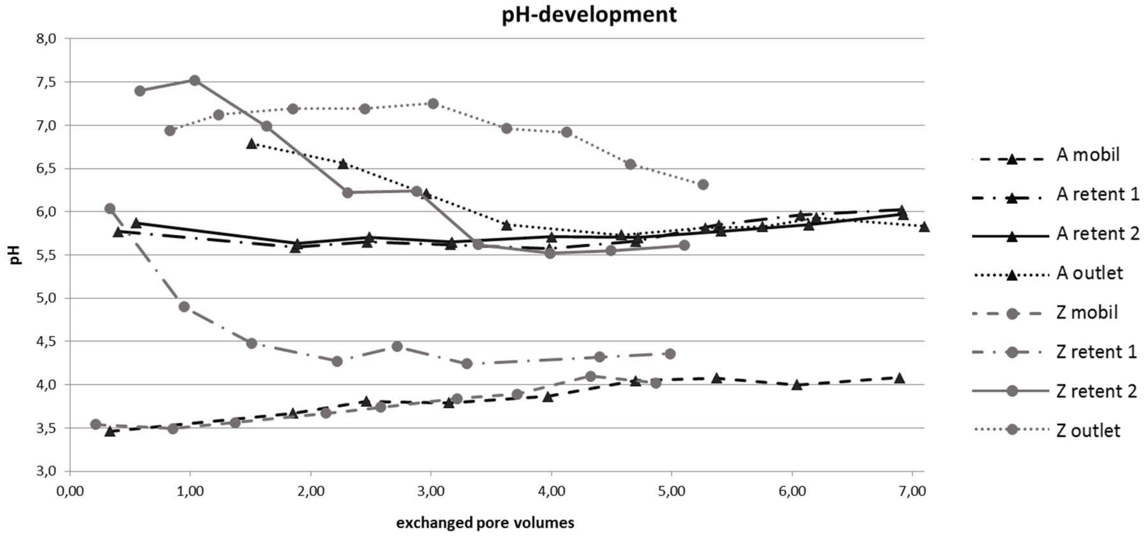

Figure 2: *Development of the pH-values in each column zone as a function of exchanged pore volumes.* ▲*Column A (retention material: APTsorb).* ●*Column Z (retention material: zeolite); mobil (mobilisation zone), retent 1 (retention zone first sample port), retent 2 (retention zone second sample port)*

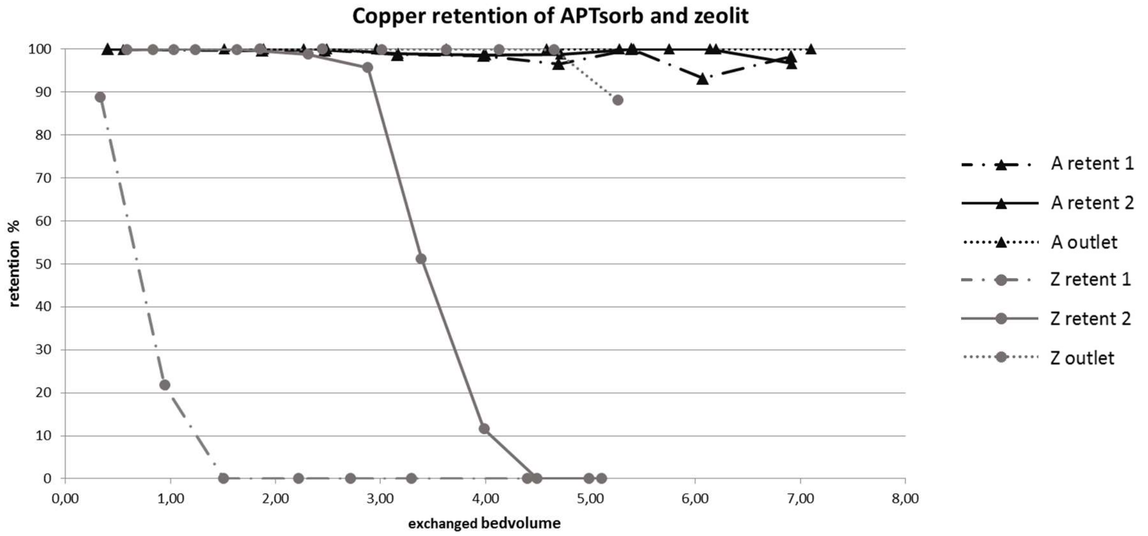

Figure 3: *Copper retention in % for zeolite and APTsorb.* ▲ *Column A (retention material: APTsorb).* ● *Column Z (retention material: zeolite); retent 1 (retention zone first sample port), retent 2 (retention zone second sample port)*

Sequential extraction

To get some information's about the strength of the element attachment to the sorption media and if they can be desorbed from materials afterwards a sequential extraction was done. Due to that the materials can be assessed if they are suitable for secondary mining approaches. Both retention materials bond the copper strong enough that it could not be desorbed by ultra-pure water from the ion exchange material in significant values. In figure 4 is the copper release from both sorption medias for each extraction step shown. For the zeolite the sequential extraction show that the copper is bonded by a variety of binding types but mainly to the ion exchanger (ammonium nitrate solution) and carbonate fraction (ammonium acetate solution). Due to the results the strength of bonding seems to be a function of contact time in case of the zeolite. The zeolite sample from Port 1 is near the mobilization zone and so exposed to the copper for a longer time than the material from the second Port. According to that the copper attached stronger to the zeolite with increasing contact time as in the figure 4 shown. In the ion exchangeable fraction released the zeolite from the second port higher copper amounts. For the stronger bonded carbonate fraction a reverse behaviour was observed. This assumption is supported by the results from the desorption behavior for the ammonium EDTA solution and the oxalate buffer. Both solutions release more copper from the zeolite of the first sample port than of the second. Due to these results the zeolite seems to be appropriate for secondary mining approaches because the main part of the released copper in the experiment was with quite cheap and unproblematic solutions.

In case of the APTsorb the results from the column experiment can be confirmed because there was no significant copper release from the material of the second sample port. As expected most of the copper attached to the APTsorb could be desorbed by the ammonium EDTA solution (see fig. 4) which represents the organic bounded fraction. The oxalate buffer was also able to release large amounts of copper. But for ammonium nitrate and acetate the copper amounts were very low. For the reclamation approach of attached elements to the ion exchange material, the APTsorb seems not to be the best possibility because ammonium EDTA is quite pricey and so the economic yield would be too low. One possibility is to look for a cheaper extraction solution as an alternative for ammonium EDTA.

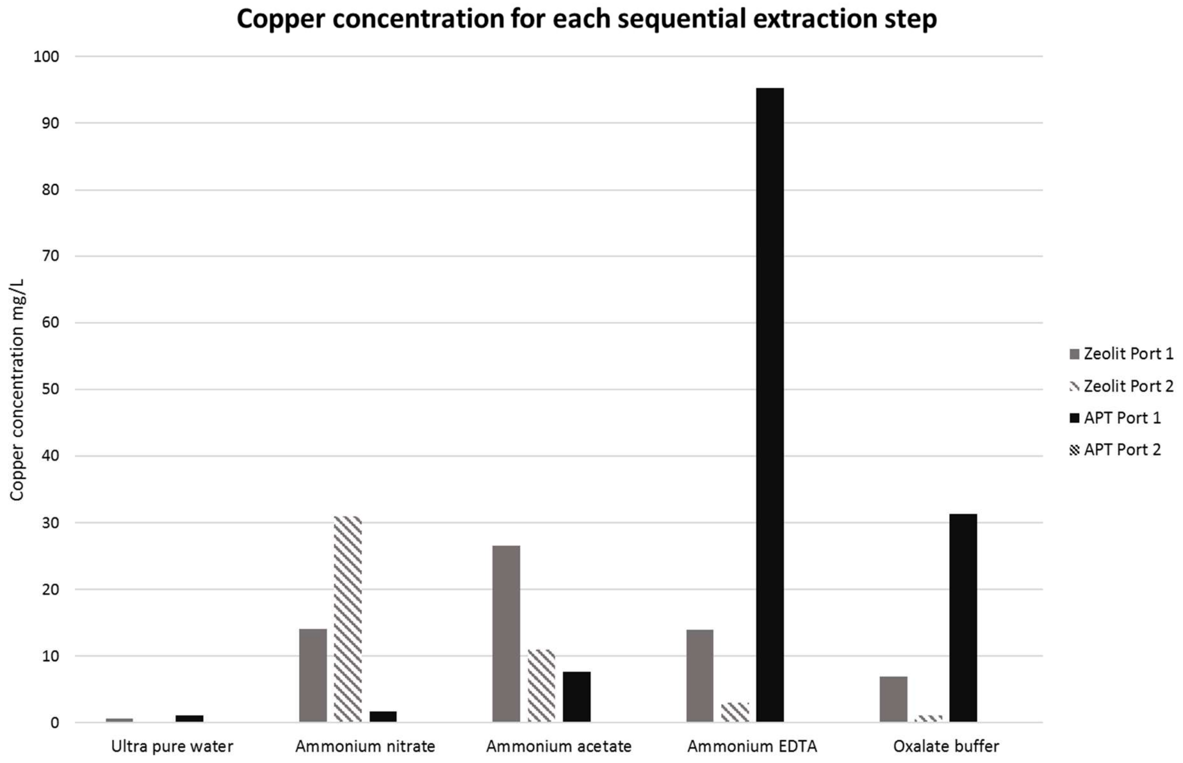

Figure 4: *distribution of the copper release from the loaded sorption materials (zeolite and APTsorb) subjected to the extraction solutions.*

Conclusion

The investigated zeolite as well as the APTsorb seems to be appropriate retention materials for Chilean mine waters. Both were able to increase the pH-values of the incoming tailing water up to environmental unproblematic values and retard large amounts of copper and other contained elements. Additionally, the developed experimental setup for the column experiment worked out well. Nevertheless, further investigations have to be done to extend the results and determine the sorption capacity for each material. Furthermore, the applicability for other mine waters can be tested.

In case of the secondary mining approach the main focus is on the reprocessing of copper and strategic elements. Therefore, the zeolite seems to be more suitable than the APTsorb because of the relatively pricy extraction solution needed for the APTsorb which would reduce the economic profit. With further investigations other extraction solutions or techniques should be tested.

Acknowledgements

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Application of a Peat-Humic Agent for AMD Remediation and Element Removal

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Abstract

The given work focused on solving the fundamental problem of environmental geochemistry and material science related to developing a new environmentally safe technology for AMD remediation and extraction of strategically important metals. A new peat-humic agent (PHA) using mechanical, chemical, and thermobaric treatment of peat from the Krugloe deposit (Novosibirsk Region, Russia). The PHA effectively removed potential pollutants (e.g., Zn, Cu, Cd, Pb, Ni, Co, Hg, Al, Fe, etc.) forming metal–organic residues, and neutralized moderately acidic acid mine drainage (AMD). The amount of the PHA to be added depended on the AMD composition. For instance, an AMD/PHA ratio of 500-1000 was effective for the Karabashmed tailings AMD, while an AMD/PHA ratio of 100-500 was effective for the Belovo sludge pond water. The metal concentrations of these treated AMDs met water quality standards. From 1 to 10 L of PHA would be needed to treat 1,000 L of moderately acidic and contaminated AMDs. Moreover, PHA would be a low cost material for contaminant removal considering the production cost and the anticipated price. The PHA can be used to modify kaolinite clay in order to create an organic-mineral complex and to intensify sorption properties of clay. The modified materials (PHA and organic-mineral complex) can be considered for developing an artificial complex organic-mineral barrier in sludge pond base. The PHA can be used to prevent sulfide tailings dusting. A novel, alternative method for AMD remediation and element removal using a PHA with subsequent thermal treatment of the metal–organic residue to minimize waste sludge production was proposed.

Key words: Acid mine drainage, peat-humic agent, AMD remediation, clay and peat modification, element recovery from waste, sulfide tailings dusting

Introduction

The waste products of the ore mining and processing industry are usually disposed off in landfills, tailing ponds, and dumps (Tchobanoglaus and Kreith 2002), where sulphide minerals, if present, can be oxidized by atmospheric oxygen and microbial activity in the presence of water, forming acid rock drainage (ARD) with potentially high concentrations of SO_4^{2-}, Fe, Al, Zn, Cu, Cd, Pb, and other contaminants (GARD/INAP; Hudson-Edwards et al. 2011; Lottermoser 2007; Nordstrom 2011; Nordstrom and Alpers 1999; Nordstrom et al. 2000; Wolkersdorfer 2008; Younger 2002). AMD can also acidify and pollute soils located near mining areas and in floodplains downstream of them (Blair et al. 1980; Jambor et al. 2003; Lottermoser 2007; Thornton 1996; Williams 1975). The total global cost for remediation of AMD has been estimated at around US$10 (Tremblay and Hogan 2001). Various agents such as limestone, lime, caustic soda, ammonia, clay, activated carbon, zeolite, cellulose, fly ash, peat and waste green sends have been applied for AMD treatment (Bogush et al. 2015; Gaikwad and Gupta 2008; GARD/INAP; Johnson and Hallberg 2005; Skousen and Ziemkiewicz 1995).

In this work, we would like to discuss a potential application of the peat-humic agent as an alternative material for AMD remediation and element removal. Humic substances contained in peat play a significant role in element accumulation (Stevenson 1994; Varshal et al. 1993). Humic substances are complex mixtures of natural, high molecular weight, dark-colored, organic products of chemical-microbiological synthesis occurring during decomposition of mortal remains of living organisms (Orlov 1990; Perminova et al. 2006; White 2013). They can be found almost everywhere in nature, with the highest content (up to 85%) observed in biogenic rock, such as peat, coals, sapropel and black shales (Perminova 2000 and 2008). Humic substances have an irregular and heterogeneous structure with a high surface area (Kleinhempel 1970). They consists of an aromatic core with numerous functional groups (carboxyls, hydroxyls, carbonyls, and others) and of peripheral aliphatic units composed mostly of polysaccharidic and polypeptidic chains, terpenoids, etc. (Stevenson 1994; Perminova et al. 2006). Therefore, humic substances can bind potential pollutants such as heavy metals, polar and hydrophobic organic compounds (e.g., pesticides and polychlorinated compounds) (Perminova et al. 2006).

Material and Methods

The liquid peat-humic agent (PHA) was developed by chemical (alkaline hydrolysis), mechanical, and thermobaric treatment using hydrodynamic cavitation of peat from the Krugloe deposit (Novosibirsk region, Russia) which contained about 60% of organic substances including humic and fulvic acids (43.5 and 26.8% of the total organic content, respectively).

Drainage water from the tailings produced by the Belovo zinc processing plant (Belovo, Kemerovo region), the gold concentration plant (Ursk, Kemerovo region), the Altay polimetal Ltd. plant (Gornyk, Altay region), and the Karabashmed plant (Karabash, Chelybinsk region) were used for AMD treatment experiments.

The following materials were also used in the experimental work: 1) kaolinite clay (Dorogino deposit, Novosibirsk region); 2) peat ("Krugloe" deposit, Kochenevski area, Novosibirsk region); 3) limestone (Chernorechensk deposit, Iskitim area, Novosibirsk region); 4) haydite sand (particle size ≈ 1-3 mm); 5) activated carbon (State Standard 6217-74).

Laboratory researches were carried out in the analytical center of the Institute of geology and mineralogy SB RAS. The combination of field, experimental, mineralogical, physical and chemical research has been applied. Various methods, such as sieve analysis, AAS, ICP-OES, ICP-MS, XRF, IC, FTIR, XRD, STA and SEM/EDS were used for our investigation.

Results and Discussion

Clay Modified by the PHA (organic-mineral complex)

The micro addition of the peat-humic agent was used to modify kaolinite clay in order to create an organic-mineral complex. Element adsorption (Zn, Cd, Pb, and Cu) onto peat, kaolinite clay, PHA, and organic-mineral complex was investigated.

Formation of the organic-mineral complex mainly depends on electrostatic interaction, hydrogen bonding (-OH…H) and interaction between carboxyl group of the PHA ($Hu\text{-}COO^-$) and hydroxyl group of kaolinite (HO-Al-):

$$\text{-Al-OH} + H^+ \leftrightarrow \text{-Al-OH}_2^+$$
$$\text{-Al-OH}_2^+ + \text{Hu-COO}^- \leftrightarrow \text{-Al-OH}_2^+ - {}^-\text{OOC-Hu}$$
$$\text{-Al-OH}_2^+ - {}^-\text{OOC-Hu} \leftrightarrow \text{-Al-OOC-Hu} + H_2O$$

Ion exchange and cation bridging also play significant role in the organic-mineral complex formation:

$$2\text{Hu-COOH} + Me^{2+} \leftrightarrow \text{Hu-COO-Me-OOC-Hu} + 2H^+$$

During this process solid particles are getting bigger, easily settling out from solution (fig. 1).

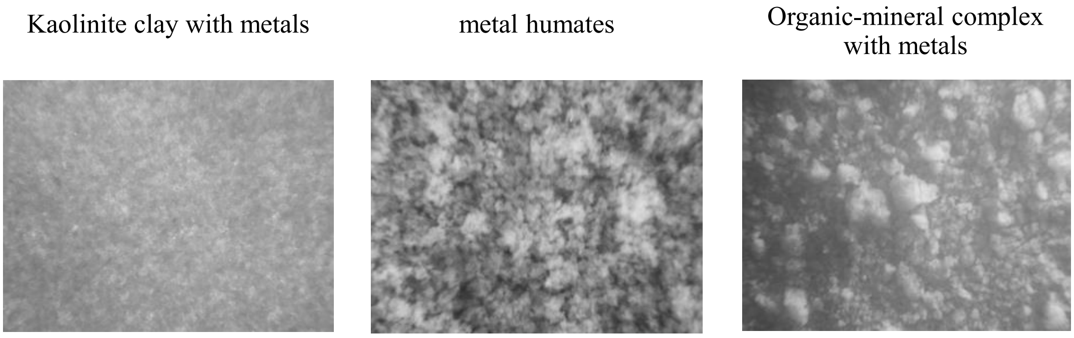

Figure 1 *Light microscopy images of kaolinite clay, PHA, and organic mineral complex with adsorbed metals in solution.*

Binding of potentially toxic elements with the PHA usually goes via the exchange mechanism with formation of poorly soluble humates. Carboxyl groups in the PHA play an extremely important role for element sorption (Bogush et al. 2007; Bogush and Voronin 2011). Humic acid (Hu-COOH) and sodium humate (Hu-COONa) dissociate to form a humate ion, a hydroxonium ion, and a sodium ion. The humate ion reacts with a metal ion and forms a humate complex:

$2\text{Hu-COOH} + \text{Me}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Hu-COO-Me-OOC-Hu} + 2\text{H}_3\text{O}^+$
$2\text{Hu-COONa} + \text{Me}^{2+} \leftrightarrow \text{Hu-COO-Me-OOC-Hu} + 2\text{Na}^+$

Additionally, humic substances are usually strong chelators with stability constants in excess of 10^{10} (White 2013).

The PHA has a highest q_{max} value comparing to other investigated materials (tab. 1). It was shown that peat adsorbed elements better than kaolinite clay. Elements were well adsorbed onto kaolinite clay at pH from 6.5 to 8.5, but onto peat at pH from 4.5 to 6.8. The organic-mineral complex has adsorption capacity in about 2 times higher than natural clay and can adsorb metals in extended interval of pH from 5 to 8.5. Also the element desorption is less than 3% for all investigated elements.

Table 1 *Element adsorption on natural and modified materials.*

aterial	Kaolinite clay	peat	PHA	Organic-mineral complex (kaolinite clay + PHA)
		q_{max}, mg/g		
Zn	14±0.6	39±0.4	155±5	22±0.8
Cd	10±0.7	44±1.1	170±9	17±1.2
Cu	11±0.9	38±0.6	150±6	21±1.1
Pb	23±1.2	109±0.3	390±12	46±3

q_{max} is the amount of sorbate necessary to complete a monolayer

Prevention of Sulfide Tailings Dusting

The big issues concerning with sulfide tailings are prevention of acid mine drainage generation and aeolian transportation of fine tailings particles on surrounding territories (forest, reservoirs, cropland, and local residential lands). We have already known some solutions of this problem, for example, tailings could be covered by break stone, clay or cement. We propose alternative solution that is covering sulfide tailings by peat-humic agent. Sulfide tailings mainly consist of fine particles (less than 0.25 mm), approximately 70-80%.

The unoxidized waste from the gold concentration plant (Ursk, Kemerovo region) and the oxidized waste from the Altay polimetal Ltd. plant (Gornyk, Altay region) were used. Two fine particle size fractions of solid waste (SW) of sulfide tailings (0.16-0.25 mm and <0.16 mm) which gave the greatest contribution to the particle size distribution of investigated wastes (approximately 65-85%), were used for lab experiments. The PHA was added to solid waste at the different liquid to solid ratio (L/S: 1, 0.5, and 0.2). The particle size distribution was determined by sieve analysis.

Table 2 shows particle size distribution after addition of PHA to the fine particle fractions of sulfide wastes. The fraction of >2 mm particles was considerable and formation of aggregates were observed. The percentage of >2 mm particles was higher for oxidized waste because it contained iron oxides/hydroxides which may easily interact with the PHA forming organic-mineral complex.

***Table 2** Particle size distribution in the experiment with PHA addition to the fine particle fractions of sulfide tailings.*

Particle fraction, mm	> 2	1-2	1-0.25	0.25-0.16	< 0.16
Experiment	Particle size distribution, %				
Ursk SW (<0.16 mm); L/S=1	51.89	5.72	2.21	0.9	39.3
Ursk SW (<0.16 mm); L/S=0.5	50.58	5.89	2.82	1.11	39.6
Ursk SW (<0.16 mm); L/S=0.2	43.83	6.32	4.56	2.18	43.1
Ursk SW (0.25-0.16 mm); L/S=1	36.33	3.89	3.99	55.78	-
Ursk SW (0.25-0.16 mm); L/S=0.5	38.89	3.76	5.32	53.99	-
Ursk SW (0.25-0.16 mm); L/S=0.2	38.22	4.25	10.91	46.62	-
Oxidized waste from Gornyk					
Gornyk SW (<0.16 mm); L/S=1	82.78	3.14	1.86	2.16	12.78
Gornyk SW (<0.16 mm); L/S=0.5	77.71	5.52	3.71	1.1	11.95
Gornyk SW (<0.16 mm); L/S=0.2	56.23	10.56	2.62	1.6	28.98
Gornyk SW (0.25-0.16 mm); L/S=1	71.41	5.15	6.16	17.27	-
Gornyk SW (0.25-0.16 mm); L/S=0.5	42.89	7.11	10.62	39.38	-
Gornyk SW (0.25-0.16 mm); L/S=0.2	48.39	1.91	5.93	43.76	-

These results were confirmed by the field experiment (fig. 2). It was shown that the particle size distribution of tailings material was changed after treatment by the PHA. Fraction of >2 mm particles was increased to approximately 50-80%. The complex geochemical barrier was formed at the top layer of sulfide tailings (pH increase, formation of organic-mineral complex). Thus, a complex geochemical barrier was formed at the top of sulfide tailings (pH increase, formation of organic-mineral complex).

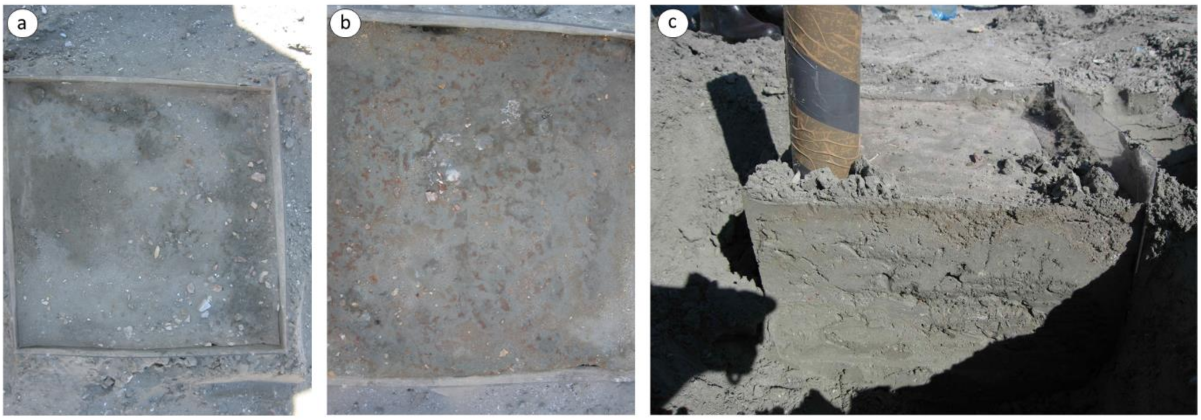

***Figure 2** Images of the field experiment on prevention of aeolian transportation: a) blank experiment; b) addition of the PHA with limestone; c) visual changes in top layer after treatment.*

AMDs treatment by the PHA

Drainage water from the tailings produced by the Belovo zinc processing plant (Belovo, Kemerovo region), the gold concentration plant (Ursk, Kemerovo region), the Altay polimetal Ltd. plant (Gornyk, Altay region), and the Karabashmed plant (Karabash, Chelybinsk region) were treated by the PHA (Bogush and Voronin 2011; Bogush et al. 2015).

The PHA effectively removed potentially toxic elements (Hg, Cd, Pb, Zn, Cu, etc.) and increased the pH of all treated AMDs. Complete neutralization was achieved for the AMDs from the Belovo sludge pond and Karabashmed tailings. The amount of the PHA to be added depended on the AMD composition. For instance, an AMD/PHA ratio of 500–1000 was effective for the Karabashmed tailings AMD, while an AMD/PHA ratio of 100–500 was effective for the Belovo sludge pond water. The metal concentrations of these treated AMDs met water quality standards. Using tested AMD/PHA ratios, partial acidity and metal removal was obtained after treatment of the highly acidic and contaminated AMDs of the Ursk tailings, the Belovo clinkers, and the old waste deposit (Gornyak). An increased AMD/PHA ratio was required for the more highly acidic and contaminated AMDs (Bogush et al. 2015).

The flaky sediment (metal-organic residue (MOR)) that was formed after AMD treatment by the PHA can be removed by filtration through activated carbon or haydite sand. Activated carbon is best to use after treatment of highly contaminated solutions. However, it is cheaper to use haydite sand, especially for slightly acidic drainage (Bogush and Voronin 2011).

Element Removal from AMD Using the PHA with Subsequent Thermal Treatment of the Metal–Organic Residue

Thermal treatment of MOR was proposed in order to produce a metal-concentrate residue and avoid waste sludge disposal to the environment. Organic matter can be removed completely from MORs by heating them at 450–500°C. Using higher temperatures would increase costs, loss of strategically important metals, and secondary environmental pollution by volatile harmful impurities.

The metal-concentrate residues generally contained aggregates with different size range (20–350 lm). These aggregates were mainly composed of metal oxides and sulphates. Hematite (Fe_2O_3), which can be potentially applied as a pigment in colored concretes or as a raw material in cement clinker production, was detected as a main phase in the residue after thermal treatment of the PHA-Ursk AMD precipitate. Tenorite (CuO) was detected as a main phase in the residue after thermal treatment of the PHA-Belovo AMD precipitate. Thermal decomposition of the organic matter in the PHA and metal-organic residues is an exothermic process with significant calorific value (9–15 kJ/g).The metal-concentrate residues can be used for metal production by the blast-furnace, pyroprocessing, and hydrometallurgical methods (Bogush et al. 2015).

A novel, alternative method for AMD remediation and element extraction using the PHA with subsequent thermal treatment of the MOR (fig. 3) to minimize waste sludge production was proposed (patent RU N2011139274; Bogush et al. 2015).

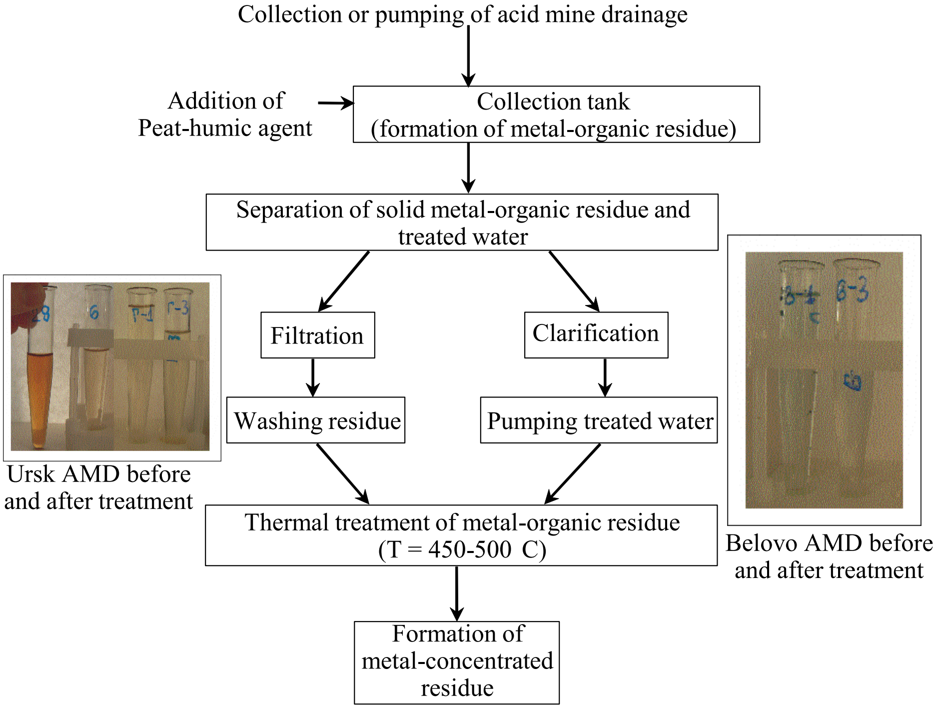

Figure 3 *The schematic technological process for metal extraction from AMD using the PHA with subsequent thermal treatment (modified from Bogush et al. 2015).*

Conclusions

Potential application of the new peat-humic agent as an alternative material for AMD remediation and element removal was discussed in this work. The PHA effectively removed potential pollutants from AMD and neutralized moderately acidic acid mine drainage. The amount of the PHA to be added depended on the AMD composition. The PHA would be a low cost material for contaminant removal. On average, 1.7 L of the PHA can be produced from 1 kg of this peat. The production and transportation cost of 1 m3 of peat in Russia is about $ 10 (US). On average, 1.7 L of PHA can be produced from 1 kg of peat, and up to 1,000 L/h can be produced in a single reactor. At this rate, the production cost of 1 L of PHA is about $ 0.5, and so the sale price would be about $1. Two litres of PHA would be needed to treat 1,000 L of slightly acidic mine drainage (Bogush and Voronin 2011).

The PHA can be used to modify kaolinite clay in order to create an organic-mineral complex and to intensify sorption properties of clay. The organic-mineral complex has adsorption capacity in about 2 times higher than natural clay and can adsorb metals in extended interval of pH from 5 to 8.5. The modified materials (PHA and organic-mineral complex) can be considered for developing an artificial complex organic-mineral barrier in sludge pond base. This barrier can consist of natural (clay, limestone, peat) and modified materials (PHA and organic-mineral complex) which may considerably reduce penetration of drainage solution into bottom layers and ground water, neutralize AMD and concentrate potentially toxic elements.

The PHA can be used to prevent effectively sulfide tailings dusting. The particle size distribution of tailings material was changed after treatment by the PHA. Fraction of >2 mm particles was increased to approximately 50-80%. The complex geochemical barrier was formed at the top layer of sulfide tailings.

A novel, alternative method for AMD remediation and element removal using a PHA with subsequent thermal treatment of the MOR was proposed. This new method can solve two problems: 1) effective treatment of AMD from potential pollutants and production of treated water which can be used in mining industry; 2) extraction of strategically important metals (Cu, Zn, Pb, Ni, Co, Ag, Au, etc.) from AMD.

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