These Proceedings of the International Mine Water 2019 Conference in Perm, Russia include the peer-reviewed papers of the vibrant community of scholars, practitioners, experts in mine water management, mine water treatment and environmental restoration on the global and local levels. Ten tracks of the Conference, ranging from mine water geochemistry and mine water hydrogeology to environmental monitoring and the future of the closed Kizel coal basin, are reflected in the conference theme “Mine Water: Technological and Ecological Challenges”. Over 200 participants from 42 countries come together to discuss the most burning issues of finding new solutions and bringing cutting-edge technologies into mine water treatment and preventing damage to the unique environments and ecosystems in different corners of the world. The Proceedings offer an outstanding opportunity to acquire the most advanced methods derived from interdisciplinary research and expertise in the field of mine water worldwide.
MINERAL WATER: TECHNOLOGICAL AND ECOLOGICAL CHALLENGES
in memoriam

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MINER WATER: TECHNOLOGICAL AND ECOLOGICAL CHALLENGES


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Welcome to Russia!

Dear Guests and IMWA 2019 Conference Participants, Dobro pozhalovat’! Welcome!

We are honoured and delighted to welcome you to the International Mine Water Association 2019 Conference at the Perm State University of the Russian Federation in Perm! On behalf of the Organizing Committee, it is our pride and honour to see you and IMWA here in Perm, a lively city of modern and classical culture, especially ballet and opera. Geologically, Perm is the Border between Europe and Asia, and the trans-national and multicultural gate to Asia. Perm is also the birthplace of the Ural Mining Civilization from the 16th century, founded on the first orders of Ivan the Terrible to discover the treasures of the Urals. This began with the first salt plants of the Permyaks (the salty-ears).

The Theme of the IMWA 2019 Conference is “MINE WATER: Technological and Ecological Challenges”. This is closely connected with the historic heritage of that Ural Mining Civilization but, unfortunately, also ecologically.

This international conference in 2019 offers, over ten sessions, talks on seventeen sub-disciplines, from mine water geochemistry and hydrogeology to environmental monitoring. Critical to Perm, it examines the future of the closed Kizel coal basin, the most environmentally challenging place in the Urals.

Over 200 delegates like you – scholars, practitioners, researchers, experts, and students, from 42 countries – will discuss new solutions and cutting-edge technologies for mine water treatment together with ways to prevent damage to the unique environments and ecosystems of the different corners of the world.

We hope that you will take advantage of our special events and outstanding speakers, along with the sessions within your own scholarly and professional expertise. We encourage you to explore the breadth of the Conference and drop in on sessions that offer cross-disciplinary perspectives on mine water remediation. We also hope that you will take the opportunity to learn about Perm and the Russian Urals, along with the talks from other global regions. We think that you will enjoy the new ideas and advanced methods, the results of interdisciplinary and international research and expertise in the field of mine water. These ideas and methods are treasures that show the way forward for cost effective and environmentally responsible ways to mine in the future and environmental remediation of areas mined in the past.

The real treasures of the International Mine Water Association are you, the real people doing vital work, and the abundant opportunities that this conference offers to discover and create new communities, new collaborations and friendships within the IMWA community, here in Perm. We hope you have a wonderful conference and a good time here in Perm!

Elena Khayrulina, Christian Wolkersdorfer, Svetlana Polyakova and Anna Bogush"
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MINE FLOODING
Secondary Water Saturation of a Carboniferous Rock Mass in a Abandoned Mines as the Cause Behind the Changes in Geomechanical Conditions and State of Hazards in Active Mines of the Upper Silesian Coal Basin

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Abstract

Mining activity, from the phase of exploration of the rock mass to the end of exploitation and abandonment of the mine, causes destruction of the rock mass and its dewatering. This is the resulting in changes of the original geomechanical properties of rocks and their strengthening during and after dewatering. These changes, in turn, affect the formation and an increase in number of manifestations of the main natural hazards (fire, gas, induced seismicity and rock bursts). The current mining situation in the Upper Silesian Coal Basin (USCB) causes that the active and abandoned mines coexist in the close vicinity. The process of flooding of the abandoned mines is ongoing up to re-saturation of rocks with water. It changes the geomechanical, and thus form the hazardous conditions. Some hazards (fire, gas, tremors and rock bursts) are limited, on the other hand among other hazards, it occurs an increase in symptoms (hazards: uncontrolled methane escapes, water, environmental, common like sinkhole, and other geomechanical ones, e.g. collapse). The reason for these changes, e.g. in the case of water hazards, may be the changes in the geomechanical properties of rocks, and conditions of safety measures, for example safety pillars or water dams. As presented in the article on the example of a safety pillar, the results of geomechanical research can be used for the design of safety measures.

Keywords: USCB, rock mass, rocks, mechanical properties, hydrogeological properties

Introduction

At different stages of development of hard coal mining in the USCB, various dependencies of mining activities and closure of mines were observed, with hydrogeological and geomechanical conditions changing in the life cycle of the mine. The changes in conditions of mining exploitation are strongly diversified in different phases of the mine operation, and also depend on the state of mining technologies, varying over time. On these changes, which rely initially on dewatering of the rock mass and the change in the rock properties, then on flooding of the abandoned mines and its effect on the rock properties, depend largely on the type, nature and intensity of mining hazards and environmental threats (Grmela, Rapantova 2002).
Characteristics of changes in hydrogeological and geomechanical conditions and development of natural hazards in the life cycle of the mine

The effect of variability in hydrogeological conditions and water saturation on the geomechanical conditions of the rock mass is presented schematically in 8 steps of mining activity development. The development of natural hazards and conditions determining the state of the rock mass has been considered in the system: hazards – sources and reasons – geomechanical and hydrogeological conditions and their changes. The sequence of hazards assumed below reflects the significance of the hazard in a given phase of the mine development (from dominant to marginal), including:

1) at the stage of exploration of rock mass before construction of the mine - lack of more important natural hazards of larger scale and substantial effects, except for gas and environmental hazards - hazards related to the process of the rock mass exploration and execution of drilling works to investigate the deposit (phase of hazards identification and assessment) - original state of the rock mass, undisturbed rock mass, at great depths triaxial compression stress state, under natural conditions of saturation and properties of the rocks,

2) at the stage of construction of the mine the following hazards may occur: water, geomechanical, geotechnical, as well as gas and environmental - these hazards are usually associated with first mining works and opening the deposit to the mining activity - state of the rock mass is predominantly close to triaxial compression stress state, under the near to natural strength-strain and hydrogeological properties of the rocks, the inflow of water to the excavations from static resources increases, the development of cone of depression occurs,

3) at the stage of development of operation, the following hazards may occur: geomechanical including induced seismicity of lower energy, and less frequently rock burst, geotechnical, water, gas, fire, dust and environmental - associated with the intensification of dewatering and drainage, process of the dewatered rock mass strengthening and increasing the depth of exploitation, and the spread of excavations. State of the rock mass is complicated and very changeable and dependent on actual mining activity and in close vicinity of excavations it changes from a triaxial compression stress state into a biaxial one, and in the vicinity of the pillars into a uniaxial one, an increase in strength and a reduction of rocks deformability, an increase in water inflow from static resources and small inflow from dynamic resources, an increase in degree of drainage and water absorption of the rocks, humidity strives to capillary saturation state and static resources of the water decrease, a clear destruction of the rock mass causes connectivity of aquifers - a cone of depression develops vertically and horizontally,

4) at the stage of the mature phase of the mine development, the following hazards may occur: tremors and rock bursts, other geomechanical, gas, fire, dust, climatic and environmental - the water hazard loses its importance and it is mainly related to underground sources (underground reservoirs, boreholes, fault zones), associated with strong drainage of the rock mass from water. State of the rock mass: clear strengthening of rocks, while reducing their deformability, and at the same time, strong transformations associated with intensive influence of mining and transition of the rock mass into a uniaxial compression stress state, or intermediate between uniaxial and triaxial one, an inflow of water to excavations from static and dynamic resources is balanced, an inflow from dynamic resources increases and the degree of drainage of rocks increases, approaching it to the value of specific yield coefficient, water capacity of rocks approaches the maximum values, humidity of the rock mass approaches the value of capillary saturation state, static water resources are substantially reduced, the shaped cone of
depression strives to reach its maximal range,

5) at the final stage of mining activity, the following hazards may occur: tremors and rock bursts, other geomechanical, gas, fire, dust, climatic and environmental - in the conditions of drained rock mass, and great depth and range of the cone of depression, water hazard occurs but of marginal importance - it is mainly related to the loss of precaution and human factor (a source may be: underground reservoirs, boreholes, fault zones, and technical state of the drainage system) – they are associated with a clear strengthening of rocks and the rock mass, as a result of dewatering, but also with strong destruction processes. State of the rock mass: with high strength, low deformability of rocks and transition of the rock mass into biaxial or uniaxial state, or the state close to them, inflow of water comes from disappearing static resources, and predominant dynamic resources and its intensity decreases and stabilizes, the degree of drainage approaches the value of specific yield coefficient and water capacity of rocks reaches the maximum values, humidity of the rock mass reaches approximately the values of capillary saturation state of rocks, static water resources are substantially reduced, the maximum range of the cone of depression is stabilized vertically and horizontally,

6) at the closure stage, the following hazards may occur: uncontrolled mine gases migration, fire, water and geomechanical, geotechnical, among them less frequently seismicity, common (sinkhole, uncontrolled mine gases migration)environmental, gas, fire – hazards are related to erroneous safety assumptions, errors in the mine flooding conceptual model and hydraulic model, errors in the mine abandonment scenarios. State of rock mass, determined by occurrence of three zones of flooding (entire flooding, transition states on the level of water table, and the secondary state of saturation due to flooding – Bukowski 2010), state as in the phase 6, and additionally in the flooded part of the mine: re-saturation and clear weakening of the rocks by water, and increasing their deformation (Bukowska 2015a,b, Li et al., 2005), especially on the level close to water table and in the area of boundary and safety pillars, dams and insulation plug, etc. – possible changes in directions and intensity of flow, blurring and soddening of rocks, a decrease in water capacity of free voids in the mining excavations, possible reactivation of goaf, pushing out the mine gases towards the surface, physical and chemical changes of waters, including “first flush” effect (Younger 1997, Younger, Wolkersdorfer 2004), an increase in pressures and differential water pressures in the reservoirs, an increase of hydraulic gradient in the border areas and saturation of the rock mass by water, including one-sided saturation of the boundary and safety pillars, transition of the rock mass under water from the uniaxial state to close to the hydrostatic state, saturation
...zero degree of drainage and water absorptivity of the rocks, a reduction or cessation of water inflow below the water level and a clear reduction in the diameter of the cone of depression.

8) after complete water table rebound, the following hazards in abandoned mines may occur: common and environmental, gas and fire, with low residual seismicity, implicating reactivation of goaf, shaft backfillings, damage to the pillars subjected to water influence, and water hazard for neighbouring mines etc., associated with the geomechanical and geotechnical processes, processes of re-saturation of the rock with water and pressure recovery. It is related to erroneous assumptions for safety, errors in the assessment of geological and mining conditions, properties of the rock environment covered by water table rebound processes, errors in the model of flooding of the mine and the method of the end of drainage, errors in determination of conditions of water circulation and hydrodynamic model, water quality and position of water piling up ordinate, errors in the mine abandoning scenarios. Exposed: surface of terrain, abandoned, backfilled and unabandoned, unbackfilled shafts, and boreholes, neighbouring mines and deposits intended for exploitation, investments based on the underground infrastructure of the abandoned mine and on water and mine gas. State of rock mass – state of saturation close to original – description as for step 7 below the water table.

As it results from the above, the change in hydrogeological and geomechanical conditions occurs at every stage of the mine's operation, while the changes in the hydrogeological conditions in a large approximation are inversely proportional to the changes in geomechanical conditions. Both changes, in the hydrogeological conditions including changes in flooding of mines, as well as the changes in geomechanical conditions, if they are not a direct cause of water hazards, tremors and rock bursts, roof collapse and sinkhole, largely indirectly shape these and other natural hazards in the underground mine, from the beginning of mining.

**Interdependence of geomechanical and hydrogeological conditions and their effect on the state of hazards to active mines**

The evaluation of the relationship between hydrogeological and geomechanical conditions, as well as the assessment of their effect on the formation of various hazards, are based on analytical, geophysical, drilling, etc. methods of testing. In every case, the key to such an assessment are analyzes of changes in geological and mining situations and conditions, based on observations and results of hydrogeological and geomechanical studies of the rocks and rock mass. Progressing since the 1990s in Poland, and in the Czech Republic, abandonment of unprofitable mines, is most often associated with their partial or total flooding, with water from the natural inflow. Regardless of the course and rate of this process in the abandoned mines in Poland, most often bordering with the active mines (Figure 1), there arise huge water reservoirs, with capacity counted in millions of cubic meters of water. These reservoirs constitute a serious source of hazard to the active mines, operating in their vicinity.

An important element of a prognosis of the mines flooding is an assessment of the possibility of water flow from one mine to the another one. It is necessary to determine critical parameters of the protections, e.g. safety pillars, and condition and transmissivity for all hydraulic connections. The safety of active mines operation, located in the vicinity of the flooded mines depends on correctness in determining above-defined conditions (Figure 1). In the USCB coal mines, the dimensions of safety pillars are determined in adaptation to the mining situation, based on the examined geomechanical properties of the rocks that build them. For this assessment, the so-called theory of limit range of excavations is used, as well as the Russian calculation formulas according to Slesariev, adapted to Polish conditions (vide Konstantynowicz et al. 1974, Maksimov 1967). However, due to the repeated changes in saturation of rocks of the disturbed rock mass in the vicinity...
of mining excavations and within the rock debris in the goaf (occurring at different rates in phases 6 ÷ 8), necessary corrections have to be introduced.

The loosened water-absorptive rocks within disturbed rock mass are saturated with water from the air-dry state and then capillary saturation, to the saturation state, while the non-water-absorptive rocks are surface wetted and subjected to the processes of blurring and soddening. Considering the occurrence of constant vertical pressure of the rock mass of value resulting from the depth and density of the above rock mass, and the reduction in rock strength due to the destruction and effect of water, it is necessary to consider these processes e.g. in calculating the critical dimensions of the safety pillars. The calculation formulas developed in Russia had been proved in mining practice and in their application since the 1970s in Poland and the Czech Republic. Then, the conditions for conducting laboratory tests of the rocks (in the air-dry state) were adapted to the condition of the rock mass, described in phases 2 ÷ 5 of the mine development. It was not until the first decade of the 21st century, despite performing earlier tests for different humidity states, that an attempt was made to relate the results of strength-strain determinations to the moisture content state close to the natural one (Bukowska Kidybiński 2002, Bukowski, Bukowska 2008, Bukowska 2015a,b). The broader physical-mechanical laboratory tests were carried out, which indicated the ranges of variability of some of the strength-strain parameters of the USCB Carboniferous rocks, due to their capillary saturation with water. The uniaxial tests were carried out in full stress-strain characteristics, stating that the main loss of compressive strength of rocks (nearly 80-90%) occurs already at the transition of the sample from the air-dry state to the capillary saturation state. The decreasing of compressive strength, depending on the type of rock, for the USCB rocks may vary from a few percent for siltstones, 20-30% for sandstones, to nearly 50% for some claystones. The Carboniferous coals lose their strength on average from a few to about 20% under conditions of water saturation.

As it results from the above, the assessment of physical-mechanical properties of rocks, with the simulation of re-saturating the rock mass with water in the process of flooding of the mine, is of key importance for the border areas. The assessment of stability of safety pillars with the application of different calculation formulas, using the results of strength-strain tests on rock parameters, repeatedly decides about the safety of the neighbouring mine, which conducts mining exploitation. For the conditions of capillary

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**Figure 1** Scheme of actual hydrodynamic situation of mining in the Upper Silesien Coal Basin and their possibility of influence on geomechanical and hydrogeological conditions and their changes
saturating with water of the rocks of safety pillars, an example of the calculations according to Slesariev, presented below was used:

\[ D = G \times \sqrt{\frac{4p}{\eta \times \left(\sigma_{rw}/G\right)}} \]

\( D \) – critical dimension of the pillar in hard coal, m, \( G \) – height of exploitation = 4.0 m, \( p \) – pressure of water in the reservoir = 3.0 MPa, \( \sigma_{rw} \) – tensile strength of hard coal in capillary saturation state = 0.85 MPa, \( \sigma_{rd} \) – tensile strength of hard coal in air-dry condition = 1.15 MPa, \( \eta \) – dimensionless coefficient according to Slesariev – regular deposition = 1.33 and variable deposition of layers = 2.0.

As can be seen from the above, the critical width of the hard coal pillar for the active mining excavations, with a given operating height and water pressure, at the level of floor of the excavations, made in the area of the reservoir in the abandoned mine, for rocks in the air-dry state will amount to \( D^d = 25.84 \div 31.68 \) m. The flooding and filtration process will cause saturation of the rock mass between the flooded and dewatered rock mass (Figure 1). It will also reduce the strength of the rocks, separating the active mine from the abandoned one. This is illustrated by the results of calculations contained in Table 1, which indicate the need to consider an increase of about 5-6 m in the critical width of the safety pillar for the planned excavations, or to lower the water table and water pressure in the reservoir in the abandoned mine, to the level safe for the existing pillars. When determining the width of the safety pillar, it is necessary to take into account all hazards and natural conditions, occurring in the given location, as well as the effect resulting from the existing and planned mining exploitation.

### Conclusions

Experience, gained in the Polish and Czech co-existing active and abandoned mines, indicate the need to adjust the approach to the assessment of natural hazards, especially the water hazard, to the changing hydrogeological and geomechanical conditions. The process of flooding of the mines undoubtedly changes the geomechanical properties of the rock environment, leading to reduction of its strength parameters and to increase of deformability. It makes, that the planning of abandonment of mines and the ordinate of water table in process of water table rebound should be done not only applying the knowledge of mining hydrogeology, as to the hight of water rebound, directions, method and quantity of water flow, but also with the use of knowledge of geomechanics. Interdisciplinary research in this field is the only and modern approach to the assessment of the interaction of risk factors, associated with the change in geomechanical conditions, as a result of the changes in hydrogeological conditions. These studies are used in the planning of monitoring and assessment of potential consequences for the surface area of the abandoned mine and in the assessment of hazards in the active mine, located in the area of the being created, or already created water reservoir.

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under the influence of water and their possible consequences in the areas of abandoned mines in the Upper Silesian Coal Basin Poland 10th Congress Mine Water and the Environment, Karlovy Vary, Czech Rep. 


Surface Water Inrush Mechanisms of Shallow Buried Coal Seams: A Single Crack Experiment and Discussion

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Abstract
The mechanism of water inrush from ground surface channel is a scientific challenge in shallow buried coal mine safety issue, fully understanding the rule of water inrush is substantial to mine water disaster in shallow coal seam. Variable controlling approach is used to discuss crack water volume with different variables including channel slope angle, crack width and flow volume. The experiment results show that crack width has a positive correlation with crack water volume, while channel gradients has a negative correlation with it. The crack water volume can be calculated by the binary non-linear equation. The results may reduce the risk of water inrush accident.

Keywords: mine water disaster; Water inrush; Variable controlling approach; crack water volume; binary non-linear equation

Introduction
Water inrush from surficial channel is a one of mine water inrush disasters and it seriously threatens the safety in mine production of shallow buried coal seam (Hu and Tian 2010). Recently, with the development of coal mining technology, the comprehensive mechanized coal mining method of large-scale working face has been widely used and its disturbance damage intensity to the overburden of coal seam roof has also increased. In the surface gully and other shallow buried coal areas, cracks may develop up to the surface and then lead the channel flow water down to the coal mine, resulting in the mine water inrush accident. Surface water inrush has become one of the four main types of mine damages (Zhu et al. 2014).

The areas, which may cause surface channel water damage, generally with the shallow buried coal seam, high height of water guide crack zone, and good connectivity in fluid flow etc. (Wu et al. 2006; Wu et al. 2007; Wu et al. 2004). The researches on coal mine water damage and control technology mainly focus on the damage of groundwater source but are lack of analysing water damage caused by surface waters. The water damage caused by surface water happened frequently with large water quantity (Wu et al. 2013).

Researchers indicate that the coal seams mining with shallow buried, thin bedrock and thick loose layer is often accompanied by the occurrence of accidents such as broken water and sand and surface step sinking (Hou and Zhang 2005; Zhang and Hou 2005; Xu et al. 2009). Therefore, it is of great significance to analyze the law of surface channel in shallow buried coal seam. The study on the mechanism of surface collapse and the movement law of overburden mining in shallow buried coal seam shows that shallow buried coal seam mining often causes serious overburden failure and surface collapse, forming penetrating fractures and surface cracks (Hu et al. 2012; Wang et al. 2007; Zhang et al. 2002).

Methods
1. Experiment devices
In the experiment, water leakage experiment system has been performed to measure the water inrush volume from ground surficial channel. The system consists of water supply...
part (Fig.1: 1,2,3,4,5), water inrush part (Fig.1: 7,8,9,12,14,17) and water volume measurement section (Fig.1: 10,11,13,15,16).

It is important to correct the water level needle (Fig.1:13) and ensure the needle is back to zero before the measurement.

Fig.1 The experiment device of water insush: 1 Reservoir; 2 Water supply pipes; 3 Flange; 4 Valve; 5 Water pump; 6 Backflow pool; 7 Leaky sink(1); 8 Leaky sink(2); 9 Movable baffle; 10 Pitot tube; 11 Movable needle detector; 12 Changeable crack; 13 Fixed needle detector; 14 Backflow channel; 15 Triangular weir; 16 Rectangle weir; 17 Backflow channel; 18 Steady flow velocity grilling

Fig.2 Schematic diagram of leaking sink device

Fig.3 Schematic diagram of reservoir and water supply system installation

2. Experimental methods

Variable controlling approach is an effective method to reduce prediction errors of unknowns scientifically. In the paper, variable controlling method is used to analyze the influence factors on crack water discharge quantitively. The crack water volume is affected by many factors, including channel slope angle, crack width, water flow volume, crack roughness and media permeability. But in the same study area, cracks with the same width, their roughness and permeability often have little effect on crack water volume. Thus, crack roughness and permeability are considered as constants in the experiment. In the experiment, two sinks with 5% and 5‰ slope angle were selected, while the crack width at the bottom of the sink were set to 5 mm, 10 mm, 15 mm, 20 mm and 25 mm respectively, and the flow discharge was controlled. Firstly, crack water discharge is obtained by measuring the water flow discharge under conditions of fixed the value of the crack width and slope angle. Secondly, crack water discharge is measured with the change of water flow and crack width. Thirdly, crack water discharge is measured with the change of water flow, crack width and slope angle. Then, the crack water discharge with different slope angle, crack width and water flow can be obtained.

The experimental data of crack water discharge under the experimental conditions of different slope angle, water flow and...
crack width are obtained, and the crack water discharge has a linear correlation with water flow when the crack width and slope is fixed. The experimental data are standardized to reduce the calculation error. The standardized difference method is used to take the difference between the two groups of adjacent experimental data under the same experimental conditions.

**Calculation methods**

The water height $H_1$ and $H_2$ in the triangular and rectangular weir on the reflux channel are obtained respectively by needle reading in the experiment. Based on the triangular turbulent flow calculation formula (Eq. (1)), the crack water discharge $Q_1$, $Q_2$, and $Q$ are calculated. Based on the rectangular turbulent flow calculation formula (Eq. (2)), the water volume in return channel $Q_2$ is calculated. Then, the total water volume $Q_3$ in the leakage can be calculated according to equation 3.

\[
Q_1 = \frac{8}{15} \tan \alpha \frac{1}{2} \sqrt{2gH_1^2} \\
Q_2 = \frac{2}{3} B \sqrt{2gH_2^2} \\
Q_3 = Q_1 + Q_2
\]

Where $\alpha$ is the angle of the top of the triangle weir; $H_1$ is the water depth in triangular weir; $B$ is the width of the backflow channel; $H_2$ is the water depth in a rectangular weir; $g$ is the gravitational acceleration.

The experimental data of channel crack water volume under the experimental conditions of slope angle, water flow and crack width, and the crack water discharge has a linear correlation with water flow when the crack width and slope angle value are fixed.

The experimental data are standardized to reduce the calculation error. The standardized difference method is used to take the difference value between the two groups of adjacent experimental data under the same experimental conditions. The standardized experiment value can be expressed as

\[
\lambda = \frac{m(b-\delta) + n}{1 + \frac{b-\delta}{\delta-a}}
\]

Where $(\alpha,m)$ and $(b,n)$ are coordinate of two separated experimental value; $(\delta,\lambda)$ is the coordinate on the line of $(\alpha,m)$ and $(b,n)$.

The standardized experiment results are shown in table 1.

The standardized data of crack water discharge has a linear relationship with its influenced factors as shown in Fig.6. Therefore, we can use the crack water discharge $(Q)$ data and the water flow discharge $(x)$ with different crack width in the channel to establish a one-dimensional linear relationship:

<table>
<thead>
<tr>
<th>Channel slope</th>
<th>Crack width (m, 10^{-2})</th>
<th>Water flow (m³/s, 10^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>5‰</td>
<td>0.5</td>
<td>0.453</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.964</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.709</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.392</td>
</tr>
<tr>
<td>5‰</td>
<td>0.5</td>
<td>0.241</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.376</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.582</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.778</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.894</td>
</tr>
</tbody>
</table>
correlation equation sets respectively which can be expressed as \( Q = a_0 + a_1x \), then \( a_0 \) and \( a_1 \) can be expressed as

\[
\begin{align*}
\frac{\partial s}{\partial a_0} &= -2 \sum_{i=1}^{m} (y_i - a_0 - a_1x_i) = 0 \\
\frac{\partial s}{\partial a_1} &= -2 \sum_{i=1}^{m} (y_i - a_0 - a_1x_i)x_i = 0
\end{align*}
\]

(5)

Then the equation can be simplified as

\[
a_1 = \frac{\sum_{i=1}^{m} x_i y_i - \sum_{i=1}^{m} x_i \sum_{i=1}^{m} y_i}{m \sum_{i=1}^{m} x_i^2 - \left( \sum_{i=1}^{m} x_i \right)^2}
\]

\[
a_0 = \frac{1}{m} \sum_{i=1}^{m} y_i - \frac{a_1}{m} \sum_{i=1}^{m} x_i
\]

(6)

By the same way, the relationship between crack water volume and crack width can be calculated. Then combining the equation (6), the crack water discharge can be expressed as a binary linear equation with variables of crack width and water flow volume.

The relationship between crack water volume and its influenced factors can be divided into two types, according to the crack water volume in the field. When water flow discharge is small in the channel, we assume that crack water volume is equal to water flow discharge in the channel. The crack water volume can be expressed as

\[
Q = x
\]

(7)

Whereas, when water flow discharge is larger than that water volume in the crack, the relationship between crack water discharge and water flow discharge and crack width can be expressed as following equations:

\[
Q_{5\%} = f(x, y) = (3x + 0.3)y + 0.02x
\]

(8)

\[
Q_{5\‰} = f(x, y) = (12x + 0.3)y + 0.03x
\]

(9)

Where, \( Q \) is crack water discharge, \( Q_{5\%} \) and \( Q_{5\‰} \) is the discharge when slope angle is 5% and 5‰ respectively, \( x \) is the water flow discharge, \( y \) is the crack width.

Matlab stands for matrix laboratory, it is a technical computing environment for high-performance numeric computation and visualization. In the paper, it is used to verify the accuracy of the fitting formula. When the slope angle is 5% degree, the fitting coefficient is 0.986 indicating that water leakage volume has an obviously nonlinear relationship with channel water volume and cracks width, as shown in Fig.7(a). As shown in Fig.7(b), it can be concluded that when the slope angle is 5‰ degree, the fitting coefficient is 0.956
indicating that water leakage volume has an obviously nonlinear relationship with channel water volume and cracks width.

**Conclusions**

In this paper, we qualitatively conclude that the main influenced factors of the crack water break are channel rock types, channel slope, channel width and channel water volume, etc. Experiments are carried out by means of the control variable method. The crack water volume in the channel cracks is negatively correlated with the slope of the channel whereas it is positively correlated with the crack width and flow volume at the bottom of the channel. The functional relationship between channel flow volume (x), channel crack width (y) and crack water discharge (Q) are obtained. When the channel slope angle are 5% and 5‰, crack water volume are expressed as:

\[ Q_{5\%} = f(x, y) = (3x + 0.3)y + 0.02x \]

\[ Q_{5\,\text{‰}} = f(x, y) = (12x + 0.3)y + 0.03x \]

**Acknowledgements**

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**References**


Abstract.

The problem of forecasting of geodynamic dangerous zones at early stage of potash deposits development is very important for providing safe mining operation. In result of insufficient geological studies and/or improper mine planning more than 80 potash mines have been flooded over the past 150 years in the world. The author and others have developed special techniques for assessing geodynamic (neotectonic) activity of territories - morphoneotectonic, lineament-geodynamic and landscape-geodynamic analyzes based on remote sensing, which allow to reliably establish geactive zones of various levels - from regional (with areas of hundreds and thousands km²) to local (with areas less than 1 km²). The used methodology includes analysis of the remote sensing data at different scale and defining the spatial distribution of the neotectonic indicators, the most important of which is a density of lineaments. The results of the analysis of modern tectonics and geodynamics in the area of the Verkhnekamskoye potassium salt deposit (Russia, Perm Territory) - the largest in the world and best studied by various geological and geophysical methods, as well as Zhilyanskoe (Kazakhstan) and Tyubegatanskoye (Uzbekistan, Turkmenistan) potassium salt deposits.

Keywords: neotectonics, geodynamic active zones, potash mines, remote sensing, photo-interpretation.

Introduction

Evaluation of the geodynamic activity of the of mine lands in the development of any mineral deposits, including - potassium salts is an essential element of their geological safety.

The problem of forecasting geodynamic hazardous zones at an early stage of potash mining is very important to ensure the safe mining of mineral resources. As a result of insufficient geological research and/or inadequate mine planning in the world over the past 150 years, more than 80 potash mines have been flooded (of which over 30 in Germany, 6 in Canada, 2 in Russia). It was established that the overwhelming majority of accidents in mines occur under conditions of high geodynamic activity of mountain ranges, complicated by high fracturing of rocks [1, 3, 5].

The newest tectonics and modern geodynamics, pronounced geodynamic active zones, discontinuous dislocations and other structures, objects, manifestations, together with the salt karst, determine the main factors of engineering-geological and mining-geological conditions (especially the strength properties of the water-resistant strata of rocks, due to the increased degree of fracture) conducting mining operations in the potash mines. Most accidents at potash mines occur at the boundaries of neotectonic blocks of different levels, where, under conditions of high geodynamic activity, areas with a high degree of fracture of rocks are formed.

In recent years, remote sensing methods, interpretation of satellite images for studying regional interblock faults [2], environmental problems of mining in karst areas [1] and geodynamic zoning of mine lands [5, 6, 7 have been widely used to assess the geodynamic activity of territories of various objects. In this article, we present an example of successful use of remote sensing data to solve the problems of the geological safety of mines.
Methodology for assessing geodynamic activity

Geodynamic active zones (or simply geoactive zones) are areas of the earth’s crust that are active at the present stage of neotectonic development, characterized by increased fracturing, permeability, manifestations of discontinuous tectonics, seismicity and other processes. They are a powerful factor in the formation and alteration of the ecological, hydrogeological, and geological conditions of the territories of the development of mineral resources, and often lead to accidents in mines.

The basis of the methodology for studying and evaluating geodynamic hazards (geodynamic active zones) in areas of existing and projected potash mines can be a systemic lineament-geodynamic analysis based on remote aerospace geological methods in combination with geophysical, structural geomorphological, hydrogeological and geochemical methods.

The author and others have developed special methods for assessing the geodynamic (neotectonic) activity of territories - morphoneotectonic, lineament-geodynamic and landscape-geodynamic analyzes based on remote sensing, which allow to reliably establish geoactive zones of various levels - from regional (with areas of hundreds and thousands km2) to local (with areas less than 1 km2). Lineament analysis based on remote sensing studies in combination with geological and geophysical data proved to be a useful tool for characterizing the regional and local geodynamic field [5, 6, 7].

Criteria for assessing geodynamic (neotectonic) activity are various calculated indicators. One of the most important indicators of geoactive zones is the increased density of tectonic disturbances (lineaments), expressed in their total length per unit area. The ranking of geodynamic activity by this indicator is carried out according to the gradations, taking into account the classes of statistical distribution according to their intensity (usually 6 grades are distinguished taking into account the arithmetic mean – «x» and the standard deviation – «s»): 1 class <(x-s); 2 class (x-s) ÷ x; 3 class x ÷ (x + s); 4 class (x + s) ÷ (x + 2s); 5 class (x + 2s) ÷ (x + 3s); 6 class > (x + 3s). It is quite confident that they reflect, respectively, various degrees of geodynamic activity (from conditionally stable to conditionally extremely high activity). In this case, geoactive zones include areas with very high and extremely high fracturing, and in some cases - areas with high fracturing, characterized by high contrast relative to the background. The author identifies 9 ranks of geoactive zones by dimension: 1 - planetary zones (several hundred thousand km²), 2 - subplanetary zones (tens of thousand km²), 3 - geozones (first tens of thousand km²), 4 - megazones (first thousand). km²), 5 - macrozones (several hundreds of km²), 6 - mezozones (up to 100 km²), 7 - local I order zones (several tens of km²), 8 - local II order zones (several km²), 9 - local III order zones (shares and units km²). As a rule, large geo-active zones have a complex mosaic structure and upon more detailed study, they are divided into lower-level zones with different degrees of activity. The analysis consists in obtaining a lineament-block model by interpreting satellite images, ranking the territory according to the degree of geodynamic activity and building its cartographic evaluation models, comparing it with geophysical fields. Decoding of digital space images, data processing, geographic information cartographic modeling is carried out using GIS technologies in Arc GIS and ArcView GIS.

Below are some examples of identifying geodynamic active zones based on the analysis of modern tectonics and geodynamics based on aerospace research in various salt-bearing regions: in the Verkhnekkamskoye potassium salt deposit (Russia, Perm region), the largest and best studied in the world by various geological and geophysical methods and also Zhilyansky (Kazakhstan) and Tubegatansky (Uzbekistan and Turkmenistan) deposits of potassium salts. In areas poorly studied by aerospace methods, deciphering was carried out over several (5-8) levels of generalization, ranging from survey and regional 1:10 000 000-1: 1 000 000 over large areas (hundreds of thousands of km²) to detailed work 1:50 000 and 1:25 000 in the mining allotment areas.
Research results and discussion

The Verkhnekamskoye potassium-magnesium salt deposit (VPMSD) is the world’s largest deposit of potassium and potassium-magnesium salts. After its discovery in 1925, over 1000 works were published, highlighting its geological structure and genesis, several large monographs were published, a large number of maps and schemes of discontinuous tectonics and faults were compiled (e.g. R.N Valeev, 1974; M.I. Denisov, 1980; G.G. Kassin, 1985, 1991; N.M. Dzhinoridze, 1987; V.P. Belyaev, 1989; L. Noyaksova, 1990; T.V. Kharitonov, 1992; I.A. Sanfirov, G.G. Kassin, 1993; B.M. Golubev, 1998; A.I. Kudryashov, 2001, 2004, 2013; I.A. Sanfirov, S.G. Bychkov, 2009; V.P. Kolesnikov, 2010; V V. Belkin, 2010; G.G Kassin, V.V. Filatov, 2011).

The Verkhnekamskoye field is characterized by increased seismicity, anomalously high values of the velocities of modern vertical movements of the surface, and is limited by deep faults active at the present stage of tectogenesis. The newest tectonics and geodynamics (geodynamic active zones, discontinuous dislocations and structures) together with salt karst determine the main factors of engineering-geological and mining-geological conditions (especially the strength properties of the water-resistant strata of rocks, due to the increased degree of fracturing) of mining operations in potash mines VPMSD [6, 8]. Powerful complex technogenesis leads to the technogenic transformation of the geological environment of the Verkhnekamskoye field. Within the limits of the geodynamic active zones, earthquake-prone sites are located, the main anomalies coincide with the regional zone of the north-west strike of the possible occurrence of earthquakes. Within their limits, the epicenters of earthquakes were recorded with an intensity of 3-6 points of the MSK-64 scale. All of them are potentially dangerous with the possible presence of weakened sections of water protection strata. Known catastrophic failures at the Berezniki mines – №. 3 (1986) and №. 1 (2006), which led to their complete flooding, as well as failure on the railway tracks in the city of Berezniki in 2010, failure at the Solikamsky mine No. 2 (2014) occurred precisely in the geodynamic active zones.

In 2010, special work was carried out to compile a map of the geodynamic active zones of the Perm Territory at a scale of 1: 500,000 and at the Verkhnekamskoye field at a scale of 1: 100,000 (I.S. Kopylov, V.Z. Khursik). According to the results of the interpretation of digital spectral space images on the territory of VPMSD, more than 1,800 straight lineaments identified with tectonic basement and sedimentary cover disturbances were identified.

According to the regional geodynamic estimate of a scale of 1: 500,000, it was established that the territory of VPMSD is within geo-active zones of the regional level with an area of more than 1,000 km². According to the zoning scale of 1: 100,000, over 50 geoactive zones ranging in size from 1-2 to 5-15 km are allocated within its limits. Detailed aerospace geological studies of a scale of 1:25 000, in which the interpretation of digital satellite images was applied, data processing using GIS technologies made it possible to further detail the geodynamic structure – geo-active zones with sizes up to 1 km were identified. Some of them had good spatial convergence with decompression zones by gravimetry (Sanfirov, 2009) and with strong permeability zones for electrical exploration (Kolesnikov, 2010), as well as for GPR studies [4]. Based on a set of geodynamic assessment criteria, geoinformation modeling was conducted and a map of the geodynamic state anomaly was compiled, the data of which were taken into account later when designing mining operations at new sites (for example, Talitsky section) [6].

Zhilyanskoe deposit of potassium and polyhalite salts, located in the Aktyubinsk region of the Republic of Kazakhstan, 10 km east southeast of Aktobe; represented by deposits of polyhalite and sylvinitite. It is characterized by a large extent, disunity in plans of and heights of ore bodies, sharp fluctuations in the conditions of occurrence, capacities of ore bodies and the content of useful components. By geodynamic conditions, the Zhilyanskoe deposit area is located in difficult tectonic conditions, being at the junction of the Caspian syncline (from
the west and directly on the square), the Pre-Urals regional (from the north) trough and the Ural folded system (from the east). The block-thrust interaction of these large tectonic structures is complicated by the salt-dome tectonics, forming a complex modern geodynamic setting. The main geodynamic activity is associated with the system of meridional tectonic disturbance, passing through the field from south to north. It is crossed by numerous local sublatitudinal and diagonal lineaments, which in turn are fledged with short lineaments.

According to the results of aerospace geological research at the Zhilyanskoe deposit, its geological and neotectonic structure was specified. Lineamental-geodynamic analysis and geodynamic zoning were carried out at the level of detail of 1:50 000 and 1:25 000 scale [7]. In the contours of the mining allotment of the deposit, 8 local geoactive zones with very high lineament density are established, their dimensions are 0.7-4.0 km long, 0.3-0.8 km wide. Within their boundaries, 13 sections (with an extremely high density of lineaments), with sizes ranging from 0.1 × 0.2 to 0.6 × 1.5 km, are set. They must be taken into account in the design, construction of the mining and processing plant and in the further development of the field.

Tyubegatanskoye potash salt deposit, located: the northern part - in the Dekhkanabad district of the Kashkadarya region of the Republic of Uzbekistan; the southern part - within the Republic of Turkmenistan. The length of the field from the southwest to the northeast is 24 km with a width of up to 7 km (within the Uzbek part, respectively, 14 and 1.5-3 km). In the contour of the calculation of reserves the area is 69.6 km2. By geodynamic conditions, the region is located in complex tectonic and seismic conditions, being at the junction of the planetary (Eurasian and Indian plates) and subplanetary (Turan plate and Tien Shan orogen) tectonic structures. The block-thrust interaction of these large tectonic structures is complicated by local shear and salt-dome tectonics and karst (Figure 1).

![Figure 1. Landscapes and Geodynamic Manifestations in the Tyubegatanskoye potash salt deposit: a - tectonic fractures, b - karst, c - temporary watercourses, d - brine inflow in the mine](image)

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
The main geodynamic activity is associated with the system of the northeastern tectonic disturbance, which passes through the Tyubegatan structure from south-west to northeast. It is crossed by numerous local sublatitudinal and diagonal lineaments, which in turn are fledged with short lineaments. For the field under development, the study of modern tectonics and modern geodynamics is particularly important, since at the end of 2012 there was a strong emergency inflow of brines into the mine shafts at the mine, which with great difficulty was eliminated. It was necessary to establish unfavorable and more favorable areas for the penetration of the shaft.

Remote sensing and interpretation of satellite images were carried out on 8 levels of study - from a survey within the whole of Southern Uzbekistan and Northern Turkmenistan, to a large-scale on the Tyubegatan field and a detailed one - on a section of mine fields with analysis of the latest tectonics and modern geodynamics. According to the results of regional aerospace geological studies of 1: 1 000 000 - 1: 100 000 scales, large lineament zones of alleged tectonic basement and sedimentary cover disturbances were identified. More than 2,150 rectilinear tectonic lineaments of various ranks with prevailing northeastern and northwestern directions, as well as arc-shaped lineaments and ring structures were distinguished in large-scale decoding of satellite images of 1:50 000 - 1: 10 000 scales in the field and the adjacent territory.

Neotectonic zoning was carried out on the basis of lineament-block analysis with the allocation of neotectonic block structures. In

Figure 2. Maps of geodynamic activity of the Dekhkanabad mine territory in scales of 1:10 000 (A) and 1: 5 000 (B)
the central part of the field, 2 mesoblocks, 6 local blocks of the first order and 22 local blocks of the second order, characterized by varying degrees of neotectonic activity, are distinguished. Lineamental-geodynamic analysis and geodynamic zoning were performed at the level of detail scales of 1:50 000, 1:25 000 and 1:10 000. 10 geodynamic zones were identified in the area of the field (Figure 2).

The largest of them is the Tulesh geoactive zone in the northern part of the central part of the field, isometric in shape, with an area of 4.3 km$^2$; in detailing, it is differentiated into 11 zones with areas of 0.01–0.06 km$^2$ [5]. Taking into account the available geological material in the mine area of the mine, a comprehensive analysis of geological and aerospace geological materials was carried out with the construction of a comprehensive analysis map and methodological recommendations were made for conducting geological and geophysical studies for the safe conduct of mining and industrial development.

**Conclusion**

Detailed remote sensing studies conducted at the operating mines of the Verkhnekamsk and Tyubegatang deposits show that the results of various remote sensing and geophysics methods are well convergent. This ensures the reliability of prediction of areas of increased fracturing of rocks and brines in mining, knowledge of which is necessary for making operational decisions on the sinking of shafts. In these areas, the most active geodynamic zones are predicted, which represent the greatest danger to mining. In the areas of the mine fields of the Dekhkanobad mine, they were confirmed by field observations and geophysical survey data.

The established anomalous geodynamic active zones (zones of very high and extremely high geodynamic risk) must be taken into account when mining and industrial development of potash deposits. Probably, local areas within geodynamic active zones with an extremely high degree of fracturing should be excluded from the field development, leaving the pillars. So, in the Tyubegatang field, it is necessary to assign reserves in the area of 2, 4, 6 panels to the temporarily preserved ones, which will be worked out at the final stage of mining operations.

According to the results of aerospace geological studies in all the regions we studied, high spatial and correlation convergence of geodynamic active zones with geophysical, geochemical and hydrogeological anomalies with areas of unfavorable geological processes and phenomena and soil conditions, increasing the intensity of dangerous natural and man-made processes was established. The provision on the leading role of geodynamic active zones in the formation of geological, hydrogeological, engineering-geological and geoeological conditions is confirmed.

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Assessment of the Prospective Water Inflow Hazards Using Georadar: Case Study of Upper Kama Potash Deposit

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Abstract

The problem of prevention of the water influx in the potash mines is vital for proper planning of the safe ore extraction and timely collapse hazard mitigation action. Geophysical methods provide with the effective tools for studying the fractures, which are the possible water passageways into the mine. Previous works showed that usage of georadar might be a valuable solution for fracturing investigation in salt rock. The investigations were conducted in the Solikamsk Mine #3 (former JSC Silvinit), where the wide fracture zone was encountered during ore extraction. This study allowed delineation of single fractures and their systems including the hidden features inside the surrounding rock mass.

Keywords: potash mines, water inflow, fracture delineation, georadar.

Introduction

The Upper Kama (Verkhnekamskoye) potash deposit is situated to the west of the Urals Mountains in the northern part of the Perm krai (Russia) at about 250 km north of Perm (Figure 1). The stratabound salts of about 500 m thick were deposited in the Late Carboniferous at the centre of Solikamskaya Depression of the Pre-Urals Foreland Basin. The Upper Kama is the second currently mined after the Prairie Evaporite Deposit (Canada) in size. Mining is conducted with room-and-pillars mode.

The problem of ground water influx is principal for the potash mines because salt is very soluble material. Dissolution of the water protective salt beds leads to flooding the mines, losses of reserves, catastrophic surface subsidence, collapse features, and consequent contamination of ground water, and damage of the buildings or different infrastructure objects (Figure 2).

As a rule, some portion of salt rock is left above the potash mines to provide the water protective cover. In mines of the Upper Kama Deposit, the impermeable strata composed of thick carnallite, and overlaying interbedded halite, marl, anhydrite, gypsum, and carbonate beds of total thickness of 70-90 m is used to prevent the water inflow into the workings.

Because of salt high plasticity and healing capability, the natural open fractures have been rarely encountered in the mine workings. A few number of stand-alone...
natural fractures and fracture systems of various scales have been observed during mining operation, especially, in a central part of deposit. Most fractures within the salts are healed and visually are observed only in the clay/anhydrite layers. However, the open fractures are of the most concern for miners. In contrast to the stress relief cracks around the openings, natural fractures usually are related to the large zones of strata failure that may affect the whole water protective cover. The increased attention must be paid to vertical and subvertical fractures as the primarily possible pathways for water influx.

The largest set of open fractures discovered in the Upper Kama potash deposit was eventually exposed at the eastern edge of mining field of the Solikamsk mine #3 at the sylvinite beds level (Figure 3). Upward exploration boreholes and visual observation of the roof showed that the fractures die out within overlying carnallite layer or interlayer clay seams (Figure 4).

To determine the spatial extent of the fractured rock, the special exploration drift of about 200 m length was made. The extensive drilling is limited in the salt mines due to the safety of the impermeable strata and economic reasons. Therefore, non-invasive and economic geophysical methods are used currently for investigation of the anomalous geological features (Thoma 2003). Georadar (ground penetrating radar, GPR) method has proven by previous research to be an effective geophysical tool providing with detail images of the salt rock structure (Annan 1988) and was chosen for study. Presented in the paper experimental works were conducted in 2003 and 2005 in order to delineate fractures and estimate their extent outward the mine workings.

**Method**

Method georadar is based on emitting the short high frequency electromagnetic impulse and receiving the signal reflected on the subsurface interfaces between materials with different electrical properties (Utsi 2017). The electromagnetic properties of medium (mainly dielectric constant or relative permittivity) control the georadar signal parameters such as velocity and attenuation. The velocity \( v \) and dielectric constant \( \varepsilon \) are connected by following relationship:

\[
    v = c/\sqrt{\varepsilon} \quad (1)
\]

where \( c \) is a light velocity in vacuum. Knowing the velocity, one can obtained the distance \( h \) to the reflection object as:

\[
    h = \frac{vt}{2} \quad (2)
\]
where \( t \) is a signal travel time to the interface and backward. The amplitude of the recorded signal from the target depends on the reflection coefficient \( R \):

\[
R = \frac{\sqrt{\varepsilon_1} - \sqrt{\varepsilon_2}}{\sqrt{\varepsilon_1} + \sqrt{\varepsilon_2}} \quad (3)
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are dielectric constants of two contacting media.

The signal attenuation is frequency dependent parameter. The higher frequency, the higher signal attenuation and, consequently, the lower penetration depth. Critical parameter for signal ability to resolve the reflections from both walls of the fracture is a resolution \( \Delta r \):

\[
\Delta r \geq \frac{\lambda}{4} = \frac{v}{4f} \quad (4)
\]

where \( \lambda \) – wave length, \( f \) – central frequency of antenna. Therefore, selection of proper operation frequency providing with most details about certain object is trade off between spatial resolution and depth of penetration of the signal. Previously, it was shown that the detection (not resolution) is available for fractures of thickness under threshold of resolution depending on their geometry and properties of filling material (Kovin 2011, 2017). Reflections in the uniform salt rocks strata relate mainly to the clay/anhydrite thin (centimeter scale) layers having the contrast electrical properties against the contacting rocks.

The Ramac (Mala GeoScience AB, Sweden) and OKO (Logical Systems, Russia) georadar systems with 250 and 400 MHz antennas were employed for data acquisition. Operating frequencies were chosen according the results of previous tests as showed the optimal relationship between resolution and penetration depth. Radargrams were recorded using continuous common offset mode. Data were acquired sounding into the back, walls, and floor of exploration drift. The main attention was paid to the subvertical (especially upward) direction of investigation.

Reflexw (Sandmeier Geophysical Research) software was used for processing and interpretation of obtained radargrams. Common processing flow applied to all the GPR data included start time correction, “dewow” filtering, background or “ringing” noise removal, and gain correction for visualization of weak signals.

Results and discussion
Orthogonal orientation regard the traverse line make challenging obtaining the prominent reflections from the fractures plane. The radargrams recorded on the roof and floor of exploration drift are shown in Figures 5 and 6 respectively. Sounding in the
wall (in horizontal plane), when the fractures cross the observation line under relatively small angle (Figure 3), the clear reflections could be easily identified (Figure 7). In contrast, the subvertical fracture plane does not produce reflections when the common antennas configuration is implemented. However, the fractures were traced by the series of diffraction patterns that could be generated at the plane irregularities or in case of plane rotation to a favorable reflection angle (Figure 5, 6).

Analysis of radargram in the Figure 5 shows that failure concentration is observed at the fracture intersection with the bedding interface presented usually by weak clay or anhydrite thin layers. In addition, it was established that a coalescence fracture and interface is observed in place of intersection (Zhang 2007) and the fracture plane changes the trajectory and rotates to the favourable for reflection angle.

Results of georadar study shown that extent of fractures does not exceed 4-5 m
above the mine level and 7–8 m in underlying beds, thus suggesting that the observed fractures do not form the crosscutting pathway for ground water. However, the further mining at this area was stopped and workings were backfilled.

**Conclusions**

The results of this study demonstrate that georadar might be a useful tool for investigation of the mine hazardous features such as fractures and possible ground water pathways they may provide. Georadar allowed studying a substantial area in non-invasive, cost and time effective manner, and obtaining the most detail information provided by geophysical methods. The study revealed the problem of imaging the subvertical fractures that require the development of new instrumentation and methodology of the field work.

**Acknowledgements**

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Sustainable salt management in mine affected surface waters

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Abstract

Water treatment is a key process during and after the remediation of the tailings ponds at the former uranium processing site Seelingstädt and the flooding of the former uranium mine Ronneburg. For that reason Wismut GmbH operates water treatment plants at each site in the eastern part of Thuringia.

The plants were designed for the removal of uranium, manganese, arsenic and metals from the mine water by using lime precipitation. Beside these contaminants, the mine water contains high concentrations of sulphate, chloride, calcium and magnesium. These compounds cannot be separated by the established technology.

Treatment plant flow rates need to be managed according to the respective flow situations in the receiving creeks and the river Weiße Elster influencing the flooding level in the Ronneburg mine and the hydrological situation at Seelingstädt TMF site. Especially in dry season, the local water management is a very challenging task.

The availability of water is a limiting factor and does not allow lower salt concentrations especially in the Culmitzsch creek. Other alternative technologies are currently under investigation in various lab and pilot scale experiments aiming for a technical solution fulfilling the main criteria for long-term suitability. At the moment, membrane techniques seem to be favourable. But there are still a number of open questions concerning the implementation of this technology at the site. The problem of handling residues is not resolve at the moment. So it is still necessary to proceed with R&D activities.

Keywords: salt management, water treatment, sulphate, chloride, hardness

Introduction

Water collection and treatment are key processes during and after the remediation of the tailings ponds at the former uranium processing site Seelingstädt and the flooding of the former uranium mine Ronneburg. For that reason, Wismut GmbH operates water treatment plants (WTP) at both sites.

The WTPs were designed to remove uranium, manganese, arsenic and metals from the mine water by lime precipitation. In the Seelingstädt WTP, lime precipitation is used in combination with a stripping pre-treatment step to remove carbon dioxide. Beside these constituents, the mine waters contain high concentrations of sulphate, chloride, calcium and magnesium. These compounds cannot be separated by the applied technology. In case of chloride, even a concentration increase occurs due to the stripping technology.

The recipients of the outflow from the treatment plants are small creeks. At all sites, the water quantity and quality in the creeks is dominated by the output of the respective treatment plant. Both receiving creeks are tributaries of the river Weiße Elster. Treatment plant flow rates need to be managed according to the respective flow conditions in the receiving creeks and the river Weiße Elster. The resulting management of water discharge influences the flooding level in the Ronneburg mine, which is managed by mine water discharge into a drainage system and mine water release from an artesian well. At the Seelingstädt site, limitations of the water discharge may lead to a delay of the TMF remediation. The geotechnical stabilisation of the tailings ponds depends on tailings consolidation by continuous release of highly mineralised pore waters. Especially in dry season, the local water management is a very
The necessary quantity of river water from the Weiße Elster to be released into the respective creek is permanently adapted. The results of this stepwise adaption are shown in figure 1. The diagram shows two different situations. The first half of 2018 is considered a typical meteorological situation. An addition of river water from the Weiße Elster was only necessary occasionally. In the second half of the year, Thuringia was afflicted by a prolonged drought. Without addition of the riverwater, discharge from water treatment would not have been possible at Seelingstädt site.

At the Seelingstädt site contaminated water can be stored for 10 days. A stop of water treatment for more than 10 days would lead to a stop of other remediation activities because working areas would be flooded. In times with a low natural flow, the maximum water treatment capacity is reduced from 330 m$^3$/h to 200 m$^3$/h. This is due to the limited availability of river water (max. 250 m$^3$/h) and the high salt concentrations in the released waters from the WTP.

At the Ronneburg mine site a permanent discharge of contaminated mine water occurs into a drainage system in the Gessental valley. Therefore, a permanent treatment is necessary. A stop of water treatment for longer than a week is difficult to handle. The focus for the salt management is sulphate at this site.

General data characterising the amendment of the natural discharge in the receiving creek compared to the quantity of mine waters treated are given in table 2 for the year 2018. They show how essential the adding of river-water is for the operation of the two treatment plants. Only with this

<table>
<thead>
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<th>Site</th>
<th>parameter</th>
<th>average (max. Conc.)</th>
<th>limit</th>
<th>ratio average (max) conc/limit</th>
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<td>Seelingstädt</td>
<td>Cl in g/L</td>
<td>1.2 (1.7)</td>
<td>0.9</td>
<td>1.4 (1.9)</td>
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<tr>
<td>(Culmitzsch creek)</td>
<td>SO$_4$ in g/L</td>
<td>6.3 (10.0)</td>
<td>5.0</td>
<td>1.3 (2.0)</td>
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<tr>
<td></td>
<td>Hardness in ‘dH</td>
<td>245 (398)</td>
<td>180</td>
<td>1.4 (2.2)</td>
</tr>
<tr>
<td>Ronneburg (Wipse</td>
<td>Cl in g/L</td>
<td>0.01 (0.18)</td>
<td>0.5</td>
<td>0.1 (0.4)</td>
</tr>
<tr>
<td>creek)</td>
<td>SO$_4$ in g/L</td>
<td>2.3 (3.1)</td>
<td>3.0</td>
<td>0.8 (1.0)</td>
</tr>
<tr>
<td></td>
<td>Hardness in ‘dH</td>
<td>143 (193)</td>
<td>230</td>
<td>0.6 (0.8)</td>
</tr>
</tbody>
</table>
measure the prescribed limits in the receiving creeks are to be met. Cost driving factor is the power supply for the pumping of the water, maintenance of the supply pipeline, sampling and analytics.

Management of compliance with limits in the Weiße-Elster

The receiving creeks Culmitzsch and Wipse are tributaries of the river Weiße Elster. In addition to the limits in the two creeks, there are prescribed limits for chloride, sulphate and hardness in the Weiße Elster, too. The limits of hardness vary depending on the flow conditions and water temperature.

Especially during dry season the natural flow in the river Weiße Elster can be critical in respect to the water discharge from the remediation sites. To prevent an interruption of water treatment and as consequence of the remediation works Wismut contracted the management of the storage reservoir Pöhl situated upstream of the remediation sites in the catchment area of the Weiße Elster river. This storage reservoir has multiple functions. It is used for flood prevention, recreation as well as regulation of minimum discharges downstream. These management objectives partly contradict especially during the dry season. The total storage volume of the reservoir is about 62 Mio m$^3$, with about 32 Mio m$^3$ available for the low flow management. Based on the Wismut contract the operator has to stabilize the flow in the river Weiße Elster upstream of the water discharges and thereby to ensure a minimum discharge in the river of 3.5 m$^3$/s at the gauging station Greiz. Nevertheless, it is the task of Wismut to harmonize the output of the WTPs Seelingstädt and Ronneburg taking

![Scheme 1 Mixture of the water flow in the creek Culmitzsch in 2018](image)

<table>
<thead>
<tr>
<th>Site</th>
<th>treatment WE-Water</th>
<th>Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seelingstädt</td>
<td>1.51 Mio m$^3$</td>
<td>0.75 Mio m$^3$</td>
</tr>
<tr>
<td>Ronneburg</td>
<td>1.90 Mio m$^3$</td>
<td>0.46 Mio m$^3$</td>
</tr>
<tr>
<td>sum</td>
<td>3.41 Mio m$^3$</td>
<td>1.21 Mio m$^3$</td>
</tr>
</tbody>
</table>

Table 2 Data of the current salt management
into account the discharge condition in the river and the water inflow at the remediation sites. The level of 3.5 m$^3$/s does not allow a simultaneous output at the maximum treatment capacity at both WTPs. In addition to the management of the discharge from the Pöhl reservoir the much smaller Weida reservoir allows an additional amendment of surface water to the river Weiße Elster as another temporary measure but with just limited effect.

Basis for the discharge management are a daily sampling in the river Weiße Elster, observing the present water flow, evaluating the accruing mine water quantities and qualities taking into account the past and present weather conditions as well as the progress of the remediation works. Based on this analysis priorities are set which have implications on the remediation works. Based on these priorities the discharges are adapted where the site with higher priority is allowed a higher discharge, while at the other site the treatment capacity is reduced. 

Another important boundary condition for the discharge management is the lag time for the water flow between the discharge points as well as the gauging station and the monitoring point where the limits have to be met. This lag time is pretty similar for both flow between 7 and 8 hours. That means that the whole system shows sluggish reactions, which is a challenge for discharge management.

A crucial factor for the discharge management is the availability of stored water in the storage reservoir Pöhl over the whole year. In 2018 the lower limit of the storage water level was reached for the first time. The discharge of water had to be remarkably reduced from 3.5 m$^3$/s to 2.3 m$^3$/s. As a consequence the discharge from the sites had to be more stringently managed using all available storage volumes at the sites.

### Further Development

Despite the presently implemented management of salt concentrations in the receiving creeks and the river Weiße Elster additional R&D activities are conducted to further reduce the discharge of salt from the remediation sites as it is required also by the permitting authorities. According to a permitting with a stepwise reduction of limit values the limit for sulphate in the Wipse creek will be as low as 800 mg/L by 2020. The current technical system is limited by the capacity of pipelines and pumping stations which are necessary for transportation of river water to be added into the receiving creeks.

Therefore, technology development for salt removal from mine and seepage waters is underway. Different treatment technologies (nanofiltration, reverse osmosis, addition of Barium chloride, evaporation) are assessed. Economic constraints are important for the comparison of the current solution discharge management with the implementation of the new technologies.

In our understanding in terms of water treatment a sustainable solution includes the following 5 criteria:

<table>
<thead>
<tr>
<th>Table 2 Comparison of different technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>technology</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Feed of WE-Water (current technology)</td>
</tr>
<tr>
<td>Evaporation</td>
</tr>
<tr>
<td>Ionexchange [Ruhland]</td>
</tr>
<tr>
<td>Reverse osmosis [GEOS]</td>
</tr>
<tr>
<td>Nanofiltration</td>
</tr>
<tr>
<td>Membranelektrolyse [Friedrich]</td>
</tr>
<tr>
<td>Bipolar elektrodialysis</td>
</tr>
<tr>
<td>Bariumchlorid [GEOS]</td>
</tr>
<tr>
<td>Precipitation of ettringit [GEOS]</td>
</tr>
</tbody>
</table>
1. Predominant use of renewable natural resources
2. Restricted carbon dioxide footprint
3. Aiming to get marketable products instead of a considerable amount of residues to be disposed of
4. No need for long term supervision, self containing systems
5. Negligible effect on ecosystems and future generations

None of the salt management technologies performs well in terms of the 5 criteria defined. The current technology benefits from the existence of a water resource upstream, the storage reservoirs. It is clear that construction of additional water storage capacity would cause more than a negligible effect on nature.

Different studies showed that it is very difficult to produce marketable products from the residual brines at acceptable conditions due to the nature of the treated waters originating from former uranium mining and processing sites. The last step is mostly a precipitation of salts (for example gypsum). One critical point is that a nearly uranium (and decay products) free solution is needed to avoid enrichment of uranium, radium and other radioactive isotopes in such a product. This is still an unsolved problem. In a pilot plant we want to investigate this point in more detail. The test will start in summer of this year. The currently used lime precipitation technology allows to reduce the uranium concentrations reliably to about 0.1 mg/L and less depending on the site conditions. If it is not possible to produce marketable products, a dumping of treatment residues is necessary. The deposit of wastes may lead to higher expenses for long term supervision and deposits have to be insoluble to avoid later mobilisation. This is especially in case of salts difficult to achieve and contradicts the 4th criterion for sustainable technologies.

Conclusions
Water treatment is a key process during and after the remediation of the tailings ponds at the former uranium processing site Seelingstädt and for the flooding of the former uranium mine Ronneburg. The current system of salt management ensures a stable water treatment at both sites, since it allows WTP’s discharge into receiving creeks in compliance with salt regulation limits. The use of river water to dilute salt concentrations and the use of upstream water storage reservoirs to allow a sufficient flow are considered sustainable solutions. At the moment, this technology is state of the art, allows a stable process of water treatment and thereby, remediation of the former uranium mining and milling sites. Nevertheless, even with all regulatory limits are met, it constitutes a remarkable effect on surface water quality. The availability of water is a limiting factor and does not allow lower salt concentrations especially in the Culmitzsch creek. Other alternative technologies are currently under investigation in various lab and pilot scale experiments aiming for a technical solution fulfilling the main criteria for long-term suitability. At the moment, membrane techniques seem to be favourable. But there are still a number of open questions concerning the implementation of this technology at the site. The problem of handling residues is not resolve at the moment. So it is still necessary to proceed with R&D activities.

Acknowledgements
The site remediation activities are part of the Wismut mining and environmental rehabilitation project. It is financed by the Federal Government of Germany. The project’s success is based on the work of many colleagues, external contractors and local authorities. We wish to thank all those who contributed with their excellent expertise and cooperation.

References
Prediction Of Mining-induced Fracture In North China Coal Field Based On Orthogonal Test

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Abstract
The floor failure depth has an important influence on the mining of Carboniferous-Permian coal seam. In view of the characteristics of the above-mentioned seam floor, this paper analyses the main controlling factors affecting the floor failure depth, and design orthogonal experiment to simulate fracture development under mining conditions. Through the analysis of the experimental results, the influence of different floor lithology combination and floor shear strength on the failure depth of coal seam floor is determined, and the mathematical model for predicting the failure depth of coal seam floor is established. The model is proved to be reliable by the measured data.

Keywords: floor failure depth, orthogonal test, lithological combination, numerical simulation, linear regression model

Introduction
In the process of coal seam mining, the destruction of seam floor will produce fracturing, and we call it 'floor failure depth'(Shi 2000). If the floor failure depth reaches to communicate with underlying aquifer, water inrush from floor will easily occur, causing serious safety accidents.

Coal in North China type coalfields was mainly produced in the late Carboniferous-early Permian coal-accumulating period (Qiu 2017). Most of the coal was formed in a marine sedimentary environment. Therefore, the north China coal field has a remarkable feature that coal measure strata are mainly composed of sandstone, mudstone and carbonate rock. Under the same mining conditions, different mechanical properties of floor rocks and different combinations of fracture mechanism among different rocks have a decisive influence on floor failure depth. For this reason, it is necessary to make a reasonable prediction of the floor damage depth of North China type coal field according to the characteristics of North China type coal, so as to ensure the safety of coal production.

Analysis of the Main Control Factors of Mining Floor Failure Depth
There are many factors affecting the floor failure depth, which mainly depend on the influence of two major factors: one is the damage resistance ability of underlying strata, the other is the force that causes floor failure. In this paper, 6 major factors, such as mining thickness, mining depth, slope length of working face, coal seam inclination, lithological association of floor and shear strength of floor, are selected to model and analyze the main control factors affecting the floor failure depth. The changes of six main controlling factors have a strong influence on the failure depth of the floor. The mining thickness, the mining depth, the slope length of the working face and the inclination angle of the coal seam together determine the mine pressure, the lithologic combination of the second floor and the shear strength of the floor(Wei 2018). The lithological association of floor and shear strength of floor affects the damage resistance ability of the floor rock mass.

Orthogonal test design
Considering the general characteristics of
coal production in China and the process and characteristics of floor rock mass failure, in the simulation test, six factors including the thickness of stope, floor lithology combination, floor shear strength, mining depth, working face inclined length and coal seam inclined Angle were selected as the test parameters, as shown in table 1.

Establishment of computational models

In order to determine the influence of lithologic difference of floor on the floor failure depth, the finite element difference method is used to set different parameters for numerical simulation. The parameters of the whole model, such as size, mining thickness, dip angle, thickness of coal seam and lithological association, are determined respectively according to orthogonal test schedule. Taking into account the larger range of calculations, horizontal and vertical displacements are constrained by lateral and lower boundaries on both sides of the model, and the vertical load (where, above, the gravity of the rock mass on the surface) is applied. (0.025 MN/m$^3$ is the average bulk density of overlying strata, H is mining depth and p/13MPa is stress). There are 69782 elements and 64800 nodes in the model. The 3-D numerical model is shown in figure 1.

Orthogonal test scheme design

In order to study the sensitivity of the factors determining the floor failure depth, the orthogonal experimental design method was adopted, this method can effectively reduce

---

**Table 1 The level values of the main control factors of floor failure depth**

<table>
<thead>
<tr>
<th>Main control factors</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
<th>Level 4</th>
<th>Level 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear strength</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Mining thickness/m</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Lithologic combination of floor</td>
<td>4:0</td>
<td>3:1</td>
<td>2:2</td>
<td>1:3</td>
<td>0:4</td>
</tr>
<tr>
<td>Mining depth/m</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>Slope length of working face/m</td>
<td>80</td>
<td>100</td>
<td>120</td>
<td>140</td>
<td>160</td>
</tr>
<tr>
<td>Dip angle of coal seam/(°)</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>

Remarks: Floor lithology assemblage is expressed by sand-mud ratio
the amount of calculation. The orthogonal design method was used to design the orthogonal test table of 6 factors and 5 horizontal values, as shown in Table 2.

According to this design scheme, the 3D numerical model is simulated and tested, and the failure depth of the floor under different experimental schemes is obtained.

**Analysis of Simulation results of orthogonal experiment**

Based on the orthogonal test theory, the failure depth of the simulated floor was analyzed by variance and range analysis. Variance analysis and range analysis was used to determine the sensitivity of each main controlling factor and the influence of the main control factors on the experimental results.

According to the variance analysis and range Analysis, it can be concluded that the sensitivity of the main factors affecting the failure depth of the floor from $R_e > R_p > R_c > R_s > R_d > R_a > R_b > R_f$ is the slope length of the working face, the mining depth, the lithologic combination of the floor, the shear strength of the strata, the mining thickness and the dip angle of the coal seam in the order of strong to weak.

Comparing the average deviation of each factor, it can be seen that the shear strength

<table>
<thead>
<tr>
<th>Test number</th>
<th>Shear strength</th>
<th>Mining thickness/m</th>
<th>Lithologic combination of floor</th>
<th>Mining depth/m</th>
<th>Working face slanting length/m</th>
<th>Coal seam dip angle (°)</th>
<th>Floor failure depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1(5)</td>
<td>1(1)</td>
<td>1(40)</td>
<td>1(200)</td>
<td>1(80)</td>
<td>1(5)</td>
<td>2.42</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>2(3)</td>
<td>2(3:1)</td>
<td>2(300)</td>
<td>2(100)</td>
<td>2(10)</td>
<td>5.31</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>3(5)</td>
<td>3(2:2)</td>
<td>3(400)</td>
<td>3(120)</td>
<td>3(15)</td>
<td>9.62</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>4(7)</td>
<td>4(1:3)</td>
<td>4(500)</td>
<td>4(140)</td>
<td>4(20)</td>
<td>10.14</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5(9)</td>
<td>5(0:4)</td>
<td>5(600)</td>
<td>5(160)</td>
<td>5(25)</td>
<td>19.28</td>
</tr>
<tr>
<td>6</td>
<td>2(4)</td>
<td>1</td>
<td>3:1</td>
<td>400</td>
<td>140</td>
<td>25</td>
<td>10.81</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>3</td>
<td>2:2</td>
<td>500</td>
<td>160</td>
<td>5</td>
<td>11.73</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>5</td>
<td>1:3</td>
<td>600</td>
<td>80</td>
<td>10</td>
<td>9.96</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>7</td>
<td>0:4</td>
<td>200</td>
<td>100</td>
<td>15</td>
<td>4.08</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>9</td>
<td>4:0</td>
<td>300</td>
<td>120</td>
<td>20</td>
<td>10.63</td>
</tr>
<tr>
<td>11</td>
<td>3(3)</td>
<td>1</td>
<td>2:2</td>
<td>600</td>
<td>100</td>
<td>20</td>
<td>8.35</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>3</td>
<td>1:3</td>
<td>200</td>
<td>120</td>
<td>25</td>
<td>5.36</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>5</td>
<td>0:4</td>
<td>300</td>
<td>140</td>
<td>5</td>
<td>10.83</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>7</td>
<td>4:0</td>
<td>400</td>
<td>160</td>
<td>10</td>
<td>14.7</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>9</td>
<td>3:1</td>
<td>500</td>
<td>80</td>
<td>15</td>
<td>8.23</td>
</tr>
<tr>
<td>16</td>
<td>4(2)</td>
<td>1</td>
<td>1:3</td>
<td>300</td>
<td>160</td>
<td>15</td>
<td>8.86</td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>3</td>
<td>0:4</td>
<td>400</td>
<td>80</td>
<td>20</td>
<td>7.7</td>
</tr>
<tr>
<td>18</td>
<td>2</td>
<td>5</td>
<td>4:0</td>
<td>500</td>
<td>100</td>
<td>25</td>
<td>8.2</td>
</tr>
<tr>
<td>19</td>
<td>2</td>
<td>7</td>
<td>3:1</td>
<td>600</td>
<td>120</td>
<td>5</td>
<td>12.94</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>9</td>
<td>2:2</td>
<td>200</td>
<td>140</td>
<td>10</td>
<td>4.72</td>
</tr>
<tr>
<td>21</td>
<td>5(1)</td>
<td>1</td>
<td>0:4</td>
<td>500</td>
<td>120</td>
<td>10</td>
<td>11.61</td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>3</td>
<td>4:0</td>
<td>600</td>
<td>140</td>
<td>15</td>
<td>17.75</td>
</tr>
<tr>
<td>23</td>
<td>1</td>
<td>5</td>
<td>3:1</td>
<td>200</td>
<td>160</td>
<td>20</td>
<td>14.74</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>7</td>
<td>2:2</td>
<td>300</td>
<td>80</td>
<td>25</td>
<td>4.5</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>9</td>
<td>1:3</td>
<td>400</td>
<td>100</td>
<td>5</td>
<td>6.73</td>
</tr>
</tbody>
</table>
of the strata increases, the failure depth of the floor decreases first and then increases, which is closely related to the lithology of the floor. When the lithologic combination of coal seam floor is sand-mudstone interaction, the floor failure depth is the smallest; when the floor is a single lithology, the failure depth is larger; when the floor is sandstone, the floor failure depth is the largest(figure 2).

**SPSS linear regression analysis**

Based on the above-mentioned simulation tests, it can be found that the lithologic combination and shear strength of coal floor have obvious influence on the failure depth of coal floor except for the slope length and mining depth of the coal seam, which accord with the characteristics of North China coalfield. Therefore, in this paper, the linear

---

**Table 4 Orthogonal Test Variance Analysis Table of influencing factors of floor failure depth**

<table>
<thead>
<tr>
<th>Main control factor</th>
<th>Deviation squared sum</th>
<th>Free degree</th>
<th>F ratio</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock shear strength (A)</td>
<td>27.431</td>
<td>4</td>
<td>5.748</td>
<td>medium</td>
</tr>
<tr>
<td>Mining thickness (B)</td>
<td>13.827</td>
<td>4</td>
<td>2.973</td>
<td></td>
</tr>
<tr>
<td>Lithologic combination of floor (C)</td>
<td>41.920</td>
<td>4</td>
<td>9.013</td>
<td>medium</td>
</tr>
<tr>
<td>Mining depth (D)</td>
<td>151.478</td>
<td>4</td>
<td>32.567</td>
<td>high</td>
</tr>
<tr>
<td>Face slope length (E)</td>
<td>192.692</td>
<td>4</td>
<td>41.428</td>
<td>high</td>
</tr>
<tr>
<td>Coal bed pitch (F)</td>
<td>5.394</td>
<td>4</td>
<td>1.411</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5 Range Analysis Table of orthogonal Test for influencing factors of floor failure depth**

<table>
<thead>
<tr>
<th>Main control factor</th>
<th>Average deviation</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock shear strength (A)</td>
<td>K₁ 10.866</td>
<td>1.982</td>
</tr>
<tr>
<td>Mining thickness (B)</td>
<td>K₂ 9.694</td>
<td>2.06</td>
</tr>
<tr>
<td>Lithologic combination of floor (C)</td>
<td>K₃ 7.884</td>
<td>3.556</td>
</tr>
<tr>
<td>Mining depth (D)</td>
<td>K₄ 9.442</td>
<td>6.392</td>
</tr>
<tr>
<td>Face slope length (E)</td>
<td>K₅ 10.154</td>
<td>7.3</td>
</tr>
<tr>
<td>Coal bed pitch (F)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remarks: K₁-K₅ are the average deviation

**Figure 2** Trend chart of influence of rock shear strength and floor lithology combination on failure depth
regression method is used to analyze the test results, and a reasonable prediction model for the failure depth of the coal floor in North China type coalfield is established.

**Construction of the model**

Based on the above-mentioned orthogonal numerical simulation test results and correlation analysis, the linear regression analysis method is adopted by using SPSS software. The prediction model of failure depth of mining floor is established:

\[
h = x_0 + a_1 x + a_2 y + a_3 z + a_4 w + a_5 f
\]

(1)

H is the failure depth of the mining floor, x is the constant term of the regression equation, \( a_0, a_1, a_2, a_3, a_4, a_5 \) are the regression coefficients.

**Regression significance test**

Regression analysis is carried out on the prediction model of floor failure depth, and the results are shown in Table 6.

Check the F distribution table: \( F_{0.100}^{(4,4)} = 2.28, F_{0.010}^{(4,4)} = 4.46, F_{0.001}^{(4,4)} = 7.44 \). It can be seen from the F values in Table 6 that for the linear equation, \( F_{0.100}^{(4,4)} < F < F_{0.010}^{(4,4)} \), the regression is highly significant.

Based on the results of significance test, it can be concluded that the regression calculation results obtained from orthogonal test simulation and linear analysis are more reliable. Get the formula:

\[
h = -5.338 + 0.156 A + 0.19 B + 0.087 C + 0.02 D + 0.07 E + 0.01 F
\]

(2)

**Analysis and inspection**

Formula (2) is obtained by analyzing 25 orthogonal tests. In order to verify whether the model is feasible in practical application, verification analysis is carried out through the actual measured case data of 8 groups of north China type coal mines (Table 7). Table 8 shows the comparison between the measured and calculated failure depths of the floor of each working face.

According to the analysis of calculation results in Table 7, the maximum error of the failure depth of coal seam floor calculated by the model is 0.92. The prediction result of the model is close to the reality, with high precision and small error, which can basically meet the engineering needs. It is proved that the model is feasible to predict the failure depth of coal seam floor in north China type coalfield.

**Conclusions**

1. Through orthogonal test simulation, it is concluded that floor lithology combination and rock shear strength have great influence on floor failure depth,
especially in the north China type coal field, the roof and floor lithology of coal seam should be paid attention to.

2. Through the analysis of the experimental results, it is known that the shear strength of rock strata increases, and the failure depth of floor decreases first and then increases; When the lithological combination of floor is sand-mudstone interaction, the failure depth of floor is the minimum, while the failure depth of single lithological floor is large. When the coal floor is sandstone, the failure depth of floor is the maximum.

3. By establishing a linear model, a relatively reliable prediction formula of floor failure depth was obtained, and the calculated value of the model was compared with the calculated value and measured value of the three procedures to analyze its accuracy, proving that the prediction model has applicability.

**Acknowledgements**

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**References:**


Abstract

Based on their physicochemical properties, water bodies can differentiate, resulting in stratification. Where stratification occurs, water with better quality is usually closer to the surface than higher mineralized water. The authors investigated if stratification in flooded underground mines can be used as a passive in-situ remediation method. After reviewing research results about stratification, it will be possible to give an overview about the state of knowledge, usage of terms as well as scenarios in which stratification occurs and breaks down. New approaches how to evaluate existing data as well as new research methods and further research ideas are described.

Keywords: stratification, underground mines, layering, mine water

Introduction

In mine water research, stratification is mainly considered in relation to pit lakes. Yet, this phenomenon also occurs in flooded underground ore, salt or coal mines (Geller et al. 2013; Wolkersdorfer 2008). Earliest observations of stratification in flooded underground mines have been described by Stuart and Simpson (1961). Ladwig et al. (1984) first described the topic in detail, for example the use of downhole probes and water sampling, and a recent review article was published by Mugova and Wolkersdorfer (2018). In all mines where stratification occurs, water with better quality is located in the upper part of the mine and due to higher mineralisation, the water closer to the sump is of worse quality (Ladwig et al. 1984; Nuttall and Younger 2004; Wolkersdorfer 2008). Although the same scenario is described, different terms are used in literature. For instance, stratification can be specified as mine water stratification (Rapantova et al. 2013), mine pool stratification (Engineers 1975) or density stratification (Melchers et al. 2015). Fresh water, meteoric water or shaft water (Melchers et al. 2015; Rosner 2011; Rüterkamp 2001; Wolkersdorfer 2008) are terms used for the upper water body, while saline water or sump water are terms used for the lower water body (Henkel and Melchers 2017; Wolkersdorfer 1996). The layer in-between has been described as intermediate layer (Wolkersdorfer 2008), transition layer (Wieber et al. 2016), boundary layer (Kories et al. 2004) or tranquillizing zone (Czolbe et al. 1992).

Methods

One of the most common methods to investigate stratification in flooded shafts is the application of down-hole probes and dippers, hence parameters such as temperature and electrical conductivity are measured. Rapid physico-chemical changes within a small distance indicate a boundary between two different water bodies. Additional, depth related water samples also help to identify a stratified system (Wolkersdorfer 2008). Shaft cameras are another tool used for investigating changes in visibility or the water's colour, indicating stratification (Snyder 2012; Stemke et al. 2018). Usually, layering in a shaft is detected only once on a single measuring campaign, however, in case of multiple campaigns, occurrence of stratification over a longer timespan or break down can be observed (Coldewey et al. 1999;
Wieber et al. 2016). Most research focuses on one single location. The authors of this paper compare worldwide existing depth logging data and create a database to find causal relationships between stratification and set up of mines. Different criteria like the geometry of the shafts and galleries, location of onset stations or distinction between single shaft and multiple shaft mines are considered. An additional measurement method in flooded mines is the application of tracers, for example fluorescent dyes. Tracer tests help to understand the velocities and flow pattern in the mine, which is important to explain the stratified system. Wolkersdorfer (2008) describes several worldwide tracer tests associated with stratification. Rüterkamp (2001) worked with a small-scale testing facility with two shafts and interconnected galleries to generate artificial stratification. Eckart et al. (2010) described the combination of experiments with small-scale testing facilities and numerical modelling. Tests about stratification are being carried out at an analogue mine water model in South Africa (Mugova and Wolkersdorfer 2018). The first numerical modelling about stratified systems in flooded underground mines was conducted in the early 1990’s by Czolbe et al. (1992). Later Eckart et al. (2010) used CFD modelling. Within the project described here, onsetting stations will be numerically modelled with the program COMSOL Multiphysics (COMSOL 2018), as the onsetting stations seem to be the location for most of the observed stratifications.

Results and Discussion

Stratification in flooded underground mines has been described in more than 40 publications over the past 5 decades (Mugova and Wolkersdorfer 2018). After comparing existing publications, it can be concluded that stratification occurs in different states of the mine. During the mine water rebound, after flooding and during ongoing pumping activities (Johnson and Younger 2002; Melchers et al. 2015; Nuttall and Younger 2004; Rapantova et al. 2013; Wieber et al. 2016; Wolkersdorfer 1996). In general, an intermediate layer divides different water bodies due to chemical changes (e.g. sulphate concentration), physical changes (e.g. temperature) or turbidity, whereby the density difference is the decisive factor (Coldewey et al. 1999; König and Blömer 1999; Ladwig et al. 1984; Nuttall et al. 2002; Nuttall and Younger 2004; Rüterkamp 2001; Wolkersdorfer 1996; Wolkersdorfer 2008). According to Wolkersdorfer (2008) “ [...] temperature differences above 10 K (Δρ > 2 kg/m³), total dissolved solid differences of more than 3% (Δρ > 20 kg/m³) or large differences in turbidity (Δρ > 200 kg/m³) can cause stable stratification”. Moreover, the geothermal gradient is a driving force. Water is heated in the deeper sections of a shaft, rises along the shaft walls and stops at an anomaly, for instance a connected gallery. From there, the water flows down in the middle of the shaft towards the sump. Czolbe et al. (1992) and Kories et al. (2004) describe this movement as the occurrence of convection cells, though there are probably several cells named “bales”. The intermediate layer is located at the boundaries of the convection cells, only minor exchange of heat and particles due to molecular diffusion is assumed in this area (Rüterkamp 2001). Occurrence of stratification in shafts is always in conjunction with inflow or outflow of water. The water may be of different origins (fig. 1). During the mine flooding, water can reach a connected gallery and therefore an anomaly at the shaft wall as described above (Nuttall and Younger 2004). Meteoric or infiltration water can enter the mine directly via the shaft or flow through the overburden (Coldewey et al. 1999). Wieber et al. (2016) use the term “surface water cap”. Inflow from adjacent mine voids is another possible scenario how stratification can form, as well as the change of shaft properties such as shaft lining (Mugova and Wolkersdorfer 2018; Rüterkamp 2001). Whether a stratified system develops or not always depends on the mine set-up. A mine with multiple interconnected shafts can act as a thermosiphon, described by Bau and Torrance (1981), the concept first being adopted for flooded underground mines by Wolkersdorfer (1996). The prevention of convection loops allows stratification. If convection loops develop, an existing stratified system breaks down.
If the infiltrating surface water minimizes the density differences between the layers too much, stratification also breaks down (Wieber et al. 2016). Manmade interference like shaft measurements, pumping or tracer tests as well as natural interference like earthquakes or storm events can result in a stratification break-down (Nuttall and Younger 2004; Wolkersdorfer 2008). Wolkersdorfer (2008) mentions horizontal jet stream-like inflow as another reason for a stratification break-down. There are no clear statements in the literature about the time spans, stratified systems remain stable. Kories et al. (2004) repeated measurements nine years after a first measurement, only to find still a stable stratified system. Based on the current knowledge, it can be assumed that under certain conditions the intermediate layer might be stable for decades.

There is currently no known publication regarding the intentional use of stratification in flooded underground mines as an in-situ remediation measure. Wolkersdorfer (1996) describes the potential prevention of convection loops given the optimal flooding levels and relevant manmade barriers; however, the concept was never applied in a mine. For the planning stage of treatment plants, stratification plays an important role. If a stratified system develops or exists, the discharge water quality is better, hence less effort for treatment is necessary. On the other hand, if stratification breaks down, but the treatment facility is only designed for better quality water, the treatment will result in the desired results. Consequently, a tool is necessary to predict occurrence, stability and break down of stratification in flooded underground mines. Causal relationships between stratification and the set-up of the mines will help to define criteria for prediction. If a mine fulfils certain criteria, predictions could be made about the potential for stratification to occur, where the intermediate layer will arise and which flooding level will facilitate the process. Furthermore, manmade barriers like dams could prevent convection loops and favour stratification. More depth logging data, repeated measurements and tracer tests are necessary to extend the database, as well as numerical modelling to support the findings. The predication of stratification might perhaps only work for small mines with just a few shafts and galleries. For a system of
interconnected mines with many shafts and galleries there might be too many factors that have to be considered.

**Conclusion**

Although stratification in flooded underground mines has been well observed over the last decades, most research focuses on local measurements. Development and break down scenarios are known, but a detailed understanding is not yet present. Furthermore, it is not yet possible to predict mine water stratification. A database might help to find causal relationships between the underground structure and stratified systems. With such knowledge, predictions could help to apply stratification as a passive in-situ remediation method, plan suitable mine water treatment facilities and, finally, reduce costs.

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**References**


Abstract
In the process of coal seam mining, the water-resisting strata under coal seam floor deform, and then produce floor heave and cracks, which makes the underground water stored in aquifers under the coal seam floor pour into the mine, causing water inrush accidents. Therefore, the depth of damaged floor is the key data to evaluate the water resistance performance of rock strata under coal seam floor. Aimed at the influences of various complicated factors for damaged floor during coal mining, the prediction for the depth of damaged floor in working area is regarded as a pattern recognition problem with nonlinear, multi dimensions and finite samples. A bivariate multivariate non-linear model for predicting the depth of damaged floor based on MATLAB was constructed. Six factors were selected as indices to evaluate the depth of damaged floor. Based on factor analysis theory, three exogenous latent variables of structural equation model were determined by dimensionality reduction. On this basis, MLP neural network and Deng's grey correlation were used to calculate weights of main controlling factors, then the combined weights of three exogenous latent variables were solved by conflicting evidence fusion. Structure optimal bivariate multivariate nonlinear regression modified model. Taking the No. 2, coal seam mining of Shanxi Formation in Gahanshan coal mine as an example, predict its depth of damaged floor, then auxiliary prove the accuracy of the bivariate multivariate nonlinear regression modified model by Flac3D numerical simulation. The results show that the bivariate prediction model has higher accuracy rate, providing theoretical basis for preventing water inrush from coal seam floor.

Keywords: depth of damaged floor; bi-variable; multivariate nonlinear prediction

Introduction
In China’s coal industry, North China is an important coal-producing area in China. It has complex geological and hydrogeological conditions. Especially in the process of coal seam mining, the water-resisting strata under coal seam floor deform, and then produce floor heave and cracks, which makes the underground water stored in aquifers under the coal seam floor pour into the mine, causing water inrush accidents. Therefore, the depth of damaged floor is the key data to evaluate the water resistance performance of rock strata under coal seam floor. In the past, empirical formulas in regulations were usually used to calculate the depth of damaged floor, however, in these formulas, only mining depth, dip angle and facing length were considered. In practical situation, there are many factors affecting the depth of damaged floor. Thus, the author comprehensively considered the factors which have direct influence on the depth of damaged floor, including, mining thickness, dip angle, mining depth, facing length and destruction resistance of the floor strata, improving the traditional empirical formulas and providing theoretical and field basis for preventing water inrush from coal seam floor (Shi et al. 2004; Xu et al. 2012).
Study Area

The Guhanshan coal mine is located in the centre of the Jiaozuo coal field, about 25 km apart from Jiaozuo city, Shandong province, in eastern China. The mine is irregularly developed, covering an area of around 17.00 km$^2$. The mine is found in a monocline dipping gently SE, (<25º), with mainly SSE and NNW striking faults that are well developed in this area (Fig 1). According to the borehole data, the lithology in the study area consists of Tertiary (R), Quaternary (Q), Permian (P), Carboniferous (C), and Ordovician (O) strata from top to bottom (Zhang et al. 2017; Gong et al. 2012).

Water-inrush mechanism caused by damaged floor

With the advancing of the working face, there are four layer-belts existing in rock formations below coal seam floor (Fig 2), i.e. broken zone caused by mine pressure, the new damaged zone, the original damaged zone and the original water flowing crevice zone. Under the condition of long-term tectonic movement, minor faults and joint fissures well-developed in damaged zone extend continually. The continuity of rock formations in broken zone caused by mine pressure was completely destroyed, and the rock formations lost their water-resisting property entirely. Therefore, once the broken zone caused by mine pressure connected with cracks well-developed in damaged zone, floor water will gush along these layer-belts, causing mine water inrush accidents. The pattern of water inrush is shown in Fig 2. Therefore, accurate prediction for depth of damaged floor is of great significance for preventing water inrush from coal seam floor.

Factor Analysis

Using SPSS factor analysis modeling, 28 groups of measured data of the depth of damaged floor were analyzed by factor analysis, as shown in Fig 3. As can be seen from Fig 3, the fault influencing factors (E) and the dip angle ( ) have higher load values on the first principal component, which are described as Factor 1. The facing length (L) and the destruction resistance of the floor strata (D) have higher load values on the second principal component, which are described as Factor 2. The mining thickness (M) and the mining depth (H) have higher load values on the third principal component, which are described as Factor 3 (Wang et al. 2019). In other words, that is to determine the three major exogenous latent variables of the structural equation model, as shown in Fig 4. Based on Matlab programming, the correlations between the three major exogenous latent variables and their internal factors were determined, as shown in Fig 5.

Weights of Main Controlling Factors

Determining Weights of Main Controlling Factors by MLP Neural Network

The following indicators were used to describe the results, as shown in Table 1, the standardized weight distribution of main controlling factors was obtained as shown in Fig 6 (Sun et al. 2001).
1) Relevant prominence coefficient:
\[
\rho_i = \frac{\sum_{j} w_{ik}(1-e^{-r})}{\sum_{j} w_{ik}}
\]
2) Correlation index:
\[
\rho_j = \frac{1}{\sum_{i} R_{ij}}
\]
3) Absolute influence coefficient:
\[
S_{ij} = R_{ij}/\sum_{k} R_{ij}
\]

Where \( i \) is the input unit; \( j \) is the output unit; \( k \) is the hidden unit; \( w_{ik} \) is the weight coefficients between \( i \) and \( k \); \( w_{jk} \) is the weight coefficients between \( j \) and \( k \).

### Determining Weights of Main Controlling Factors by Deng’s Grey Relation

Determine the grey association set \( X \) of the nondimensionalized parent sequence and subsequence as follows (Qiu et al. 2016).

\[
X = (X_1, X_2, \ldots, X_n) = \begin{pmatrix}
x_1(1) & x_1(2) & \ldots & x_1(n) \\
x_2(1) & x_2(2) & \ldots & x_2(n) \\
\vdots & \vdots & \ddots & \vdots \\
x_n(1) & x_n(2) & \ldots & x_n(n)
\end{pmatrix}
\]

### Table 1 Weights of main controlling factors determined by MLP neural network

<table>
<thead>
<tr>
<th>Main controlling factors</th>
<th>E</th>
<th>D</th>
<th>L</th>
<th>M</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weights ( W )</td>
<td>0.571</td>
<td>0.032</td>
<td>0.103</td>
<td>0.022</td>
<td>0.031</td>
</tr>
</tbody>
</table>
Then we can define the correlation coefficient of the $x_0$ and $x_i$ at the point $k$ as follows (Qiu et al. 2016):

$$
\xi(k) = \frac{\min_j \min_i [x_0(k) - x_i(k)] + \rho \cdot \max_j \max_i [x_0(k) - x_i(k)]}{\max_j \max_i [x_0(k) - x_i(k)] + \rho \cdot \max_j \max_i [x_0(k) - x_i(k)]}
$$

Where $\rho$ is the resolution ratio, normally $\rho = 0.5$. According to $\frac{\omega_j}{n} = \frac{1}{n} \sum_{i=1}^{n} \xi_j (j=1,2,...,n)$, the weights $W_2$ of each evaluation index we determined as shown in Table 2.

### Coupling Weights of Main Controlling Factors by Conflicting Evidence Theory

Determine the initial weight matrix $A$ of main controlling factors as follows (Zhang et al. 2018):

$$
A = \begin{pmatrix}
0.571 & 0.032 & 0.103 & 0.022 & 0.031 & 0.241 \\
0.191 & 0.169 & 0.182 & 0.159 & 0.143 & 0.156
\end{pmatrix}
$$

The matrix $\rho = (0.381 \ 0.1005 \ 0.1425 \ 0.0905 \ 0.087 \ 0.1985)$ was obtained, and then the mean matrix $B$ was obtained as follows.

$$
B = \begin{pmatrix}
0.476 & 0.066 & 0.123 & 0.056 & 0.059 & 0.220 \\
0.286 & 0.135 & 0.162 & 0.125 & 0.115 & 0.177
\end{pmatrix}
$$

Solve D-value matrix

$$
\lambda = \begin{pmatrix}
0.499 & 0.682 & 0.277 & 0.757 & 0.644 & 0.214 \\
0.499 & 0.682 & 0.277 & 0.757 & 0.644 & 0.214
\end{pmatrix}
$$

according to formula $\lambda_j = \frac{[a_j - p_j]}{p_j}$.

Then the unauthentic vector $C$ and credibility vector were gained (Zhang et al. 2018).

$C = (0.5 \ 0.5) C^\prime - (0.5 \ 0.5)$

Based on this, we can determine the initial weight credible matrix $A^\prime$ and weight unauthentic matrix $A^\prime\prime$. Ultimately, we can get the comprehensive weight matrix $I$ and optimization weight matrix $I^\prime$ as follows.

$$
A^\prime = \begin{pmatrix}
0.286 & 0.016 & 0.052 & 0.011 & 0.016 & 0.121 \\
0.096 & 0.085 & 0.091 & 0.080 & 0.072 & 0.078
\end{pmatrix}
$$

$$
A^\prime\prime = \begin{pmatrix}
0.238 & 0.033 & 0.061 & 0.028 & 0.030 & 0.110 \\
0.143 & 0.067 & 0.081 & 0.062 & 0.058 & 0.089
\end{pmatrix}
$$

$$
I = \begin{pmatrix}
0.524 & 0.049 & 0.113 & 0.039 & 0.045 & 0.230 \\
0.239 & 0.152 & 0.172 & 0.142 & 0.129 & 0.167
\end{pmatrix}
$$

$$
I^\prime = \begin{pmatrix}
0.729 & 0.018 & 0.059 & 0.013 & 0.014 & 0.167 \\
0.484 & 0.081 & 0.131 & 0.068 & 0.060 & 0.176
\end{pmatrix}
$$

The optimal weights were fused according to the formula

$$
\omega_j = \frac{\sum_{i=1}^{n} w_{ij}}{1 - \sum_{i=1}^{n} w_{ij}}
$$

as shown in Table 3.

### Nonlinear prediction model for the depth of damaged floor based on bi-variables

Based on MATLAB programming, three groups of relationships in Fig 5 were fitted, and the correlativity surfaces and residual analysis diagrams were obtained as shown in Fig 7, 8 and 9. The optimum surface equations between measured depth of damaged floor and bi-variables were determined as follows:

$$
De = a_1 + a_2 E + a_3 D; De = b_1 + b_2 L + b_3 D + b_4 L^2 + b_5 LD
$$

$$
De = c_1 + c_2 L + c_3 H + c_4 M^2 + c_5 MH + c_6 H^2 + c_7 M^2 + c_8 M^2 H + c_9 MH^2
$$

On the basis of considering combined weights of principal factors, the established bivariant optimal surface equations were substituted into the SPSS statistical analysis software for bivariant multiple nonlinear

---

**Table 2** Weights of main controlling factors determined by Deng's grey relation

<table>
<thead>
<tr>
<th>Main controlling factors</th>
<th>E</th>
<th>α</th>
<th>L</th>
<th>D</th>
<th>M</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weights $W_1$</td>
<td>0.191</td>
<td>0.169</td>
<td>0.182</td>
<td>0.159</td>
<td>0.143</td>
<td>0.156</td>
</tr>
</tbody>
</table>
Table 3 Index weights fused by conflicting evidence theory

<table>
<thead>
<tr>
<th>Main controlling factors</th>
<th>Optimized Weights</th>
<th>Deng’s grey correlation</th>
<th>Weights fused by conflicting evidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0.571</td>
<td>0.191</td>
<td>0.527</td>
</tr>
<tr>
<td>L</td>
<td>0.032</td>
<td>0.169</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.022</td>
<td>0.159</td>
<td>0.274</td>
</tr>
<tr>
<td>M</td>
<td>0.031</td>
<td>0.143</td>
<td>0.199</td>
</tr>
<tr>
<td>H</td>
<td>0.241</td>
<td>0.156</td>
<td></td>
</tr>
</tbody>
</table>
regression analysis. The coefficients of each variable were recalculated to determine the bi-variables multiple nonlinear regression modified model for predicting depth of damaged floor as follows:

$$De = 22.83E - 0.004L + 0.057D - 2.05D + 0.005L^2 + 2.76M - 0.05H - 0.42M^2 + 0.031MH + 0.12M^3 - 0.003M^2 + 8.37$$

Based on the above formula, the depth of damaged floor of 15031, 15051, 15071 and 15091 working faces in Guhanshan Coal Mine was predicted, as shown in Table 4.

In order to further illustrate the feasibility of the bivariate multivariate nonlinear regression modified model for predicting depth of damaged floor, now, Flac3D three-dimensional program was adopted to simulate the depth of damaged floor of 15031 working face in Guhanshan Mine, as shown in Fig. 10. From the figure, it can be seen that the numerical simulation results are similar to the prediction results of the model established in this paper, which auxiliarily confirms the accuracy of the bivariate multivariate nonlinear regression modified model for predicting the depth of damaged floor.

**Conclusions**

(1) Considering six factors affecting depth of damaged floor comprehensively, we determined weights of main controlling factors based on MLP neural network and Deng's grey relation, and then coupled these weights by conflicting evidence theory, ensuring the effective evaluation of the relative importance of each indicator for the dynamic model.

(2) Based on the bivariate multivariate nonlinear regression theory, a prediction model for the depth of damaged floor was established, and applied to the prediction of the depth of damaged floor in Guhanshan Coal Mine. Compared with the outcomes of Flac3D numerical simulation, the results show that the bivariant multiple regression equation have higher prediction accuracy, providing theoretical and field basis for preventing water inrush from coal seam floor.

**Acknowledgments**

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**Table 4 Prediction of depth of damaged floor in Guhanshan Mine**

<table>
<thead>
<tr>
<th>Working faces</th>
<th>E</th>
<th>α</th>
<th>L</th>
<th>D</th>
<th>M</th>
<th>H</th>
<th>Predicted values</th>
</tr>
</thead>
<tbody>
<tr>
<td>15031</td>
<td>0.40</td>
<td>11.3</td>
<td>120</td>
<td>0.3</td>
<td>2.3</td>
<td>435</td>
<td>14.79</td>
</tr>
<tr>
<td>15051</td>
<td>0.38</td>
<td>11.3</td>
<td>120</td>
<td>0.3</td>
<td>2.3</td>
<td>455</td>
<td>14.45</td>
</tr>
<tr>
<td>15071</td>
<td>0.42</td>
<td>11.3</td>
<td>120</td>
<td>0.3</td>
<td>2.3</td>
<td>475</td>
<td>15.47</td>
</tr>
<tr>
<td>15091</td>
<td>0.40</td>
<td>11.3</td>
<td>120</td>
<td>0.3</td>
<td>2.3</td>
<td>495</td>
<td>14.12</td>
</tr>
</tbody>
</table>
Figure 10 The numerical simulation of the depth of damaged floor

Prediction of the Confined Water Rising Zone in a Coal Floor Based on Fuzzy Theory (Fuzzy) – Gray Relation Analysis (GRA) – Particle Swarm Optimization (PSO) – Support Vector Regression (SVR)

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²National Engineering Laboratory for Coalmine Backfilling Mining, Shandong University of Science and Technology, Tai’an 271019, China
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Abstract
The confined water rising zone and water inrush from the floor are closely related. In this paper, based on the collected samples of North-China-type coalfields, after the nondimensional disposal of the influencing indices by Fuzzy Theory (Fuzzy), four main indices were selected by the Gray Relation Analysis (GRA): aquifuge index, water pressure index, permeability index and structural index. The (Particle Swarm Optimization) PSO was used to optimize the parameters of the (Support Vector Regression) SVR; then, the nonlinear regression model was established by the SVR to predict the confined water rising zone based on MATLAB. Compared with other methods, the Fuzzy-GRA-PSO-SVR model has good generalization and can be applied to field prediction.

Keywords: Fuzzy-GRA-PSO-SVR model, confined water rising zone, water inrush from floor, Ordovician limestone aquifer

Introduction
In China, the karst of Ordovician limestone aquifer is abnormally developed (Qiu 2017) with the characteristics of strong supply, high water pressure and big water content. When the water resistance ability of the coal seam floor is weak, the water in the Ordovician limestone aquifer will directly pour into the working face under the action of high static water pressure and easily cause a mine water disaster. The confined water rising zone (Fig. 1) (Shi 2000) refers to the elevation of confined water in the Ordovician limestone aquifer along the split or fault fracture zone of a lower aquifer under the action of high water pressure, which is a key factor to evaluate the safety of coal seam mining above the confined aquifer. A higher confined water rising zone has a greater possibility of water inrush from the floor. Its characteristics are that the rock is in an elastic-plastic behavior, the fissure has become a channel of water inrush, and the continuity of the rock is poor.

In the current technology, there are few records about the prediction method of the confined water rising zone. Xiaoge Yu predicted the confined water rising zone for the first time based on the BP neural network model (Yu 2014). However, this method requires a large quantity of measured data as training samples and has the problems of slow convergence rate and local minimization. In this paper, we establish a Fuzzy-GRA-PSO-SVR model to accurately predict the confined water rising zone, which can provide the theory gist for the prediction of the Ordovician limestone water inrush and precise mining of coal mines.

Influencing Indices
Workface index (W): The inclined length of the working face reflects the strength of the coal seam mining. Generally, a wider working
face corresponds to a greater mining intensity of the coal seam, and a more unstable stress environment of the strata is more conducive to the development of cracks in the confined water rising zone.

Aquifuge index (M): The aquifuge refers to the rock and soil layer with poor permeability. A thicker aquifuge has lower possibility of water inrush from the floor, which is more unfavorable to the development of the confined water rising zone.

Water pressure index (P): The water pressure of the Ordovician limestone aquifer provides the driving force for its development. The data are obtained by the underground water level conversion of the Ordovician hydrogeological hole.

Depth index (D): The buried depth of the coal seam is the vertical distance from the earth's surface to the middle of the roof and floor of the coal seam. It affects the surrounding pressure environment, mining way, mining intensity, etc.

Permeability index (K): A larger permeability coefficient corresponds to a smaller resistance that the confined water must overcome along the way, which is more conducive to the development of the confined water rising zone.

Structural index (F): The fault intensity index (FII) is the sum of the products of the extension length of all faults in the unit area and their drop height. This index can comprehensively reflect the fault complexity in one general area. The faults provide space for the development of the confined water rising zone, reduce the resistance along the channel and directly affect the development of the confined water rising zone.

Data
In this paper, 25 samples from North China-type coalfields were collected (tab. 1), of which the first 20 were used as training samples, and the last 5 were used as testing samples. The distance between the initial water levels of the Ordovician injection grouting drill hole and the maximum normal of the top surface of the Ordovician limestone aquifer is set as the practically measured value of the original confined water rising zone.

Model Establishment
The GRA refers to the level of similarity between two sequences. A closer relational degree to 1 indicates a better relativity. The indices with the gray relational degree greater than 0.8 were taken as the main influencing indices. We programmed by using MATLAB software and calculated the relational degrees as follows (tab. 2).

The 4 main influence indices $(P/MPa; K/10^{-13}m^2(Pa\cdot s)^{-1}; F; M/m)$ and the confined water rising zone of the 20 training samples in tab. 1 were normalized using MATLAB.

SVR (Zhang 2018) has functions of nonlinear modeling, nonlinear prediction, and optimization control. Let the data samples be an n-dimensional vector, the training data set is $\{(x_1, y_1), \ldots, (x_i, y_i)\}$, $x_i \in \mathbb{R}^n, y_i \in \mathbb{R}, i = 1, 2, 3, \ldots, I$; then, the regression function used to fit the function of sample data is:

$$f(x) = \omega \times \Phi(x) + b$$

where the undetermined parameters $\omega$ and $b$ are the weight vectors and offset value, respectively. A punitive factor $C (C>0)$ is
introduced, and equation 1 can be expressed as the following constrained optimization problem:

$$\text{Min} : \frac{1}{2} \sigma^2 + C \sum \xi_i (\xi_i + \xi_i^*)$$ \hspace{1cm} (2)

where $\xi_i$ is the relaxation factor.

The Lagrange multiplier is used to transform equation 2 into its dual problem:

$$\text{Max} : W(\alpha, \alpha^*) = -\frac{1}{2} \sum_{(i,j) \in \mathcal{S}} (\alpha_i - \alpha_i^*) (\alpha_j - \alpha_j^*) K(x_i, x_j) + \sum_{i=1}^l (\alpha_i + \alpha_i^*) y_i - \sum_{i=1}^l (\alpha_i + \alpha_i^*) \xi_i$$ \hspace{1cm} (3)

$$k(x_i, x_j) = \exp \left\{ -\frac{|x_i - x_j|^2}{2\sigma^2} \right\}, \quad 1/\sigma^2 = g$$ \hspace{1cm} (4)

where $K(x_i, x_j) = [\Phi(x_i), \Phi(x_j)]$ is called the kernel function, and $\alpha$ and $\alpha^*$ are the corresponding support vectors. After solving equation 3 and obtaining the corresponding

### Table 1 Measured Data of North China-type Coalfields

<table>
<thead>
<tr>
<th>number</th>
<th>W/m</th>
<th>M/m</th>
<th>P/MPa</th>
<th>D/m</th>
<th>K/10^–4m³/(Pa·s)</th>
<th>F</th>
<th>H/m</th>
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### Table 2 Relational degree with the confined water rising zone

<table>
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<tr>
<th>W/m</th>
<th>M/m</th>
<th>P/MPa</th>
<th>D/m</th>
<th>K/10^–4m³/(Pa·s)</th>
<th>F</th>
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<td>0.7926</td>
<td>0.8563</td>
<td>0.9750</td>
<td>0.3640</td>
<td>0.9678</td>
<td>0.9614</td>
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</table>
a and b, the optimal fitting function can be determined as:

\[ f(x) = \sum_{i=1}^{l} (\alpha_i - \alpha_i^*) K(x_i, x) + b \]  

(5)

The PSO is used to select the support vector regression parameters, which can avoid the blindness and randomness of artificial selection, and improve the efficiency and accuracy of the parameter selection. C controls the error of the training samples. A larger C corresponds to a better training effect but also a lower generalization ability. Width coefficient g reflects the degree of correlation between support vectors. A larger g indicates a looser relation among the support vectors. Therefore, the selection of appropriate C and g is the key to ensure the regression of the SVR.

Based on the MATLAB platform, the initial population parameters were set by the PSO; then, the learning sample fitting graph (Fig. 2) was obtained by sample mapping calculation and linear fitting training. The learning effect was evaluated according to the relative error of the fitting degree. If the average relative error is smaller, then the learning effect is good. If the average relative error is larger, the original population generates a new population through iteration, and the second step is to reoptimize the SVR parameters using the PSO. Finally, after many studies, the optimal parameters c and g are found.

**Establishment of the multiple linear regression formula**

In this paper, the weight function of the MATLAB software is used to calculate the weight of the main influence indices. The weights of the aquifuge index, water pressure index, permeability index, and structural index are 0.0964, 0.1907, 0.3386, and 0.3743, respectively.

![Figure 2 Fitting Chart of the Training Samples of the Fuzzy-GRA-PSO-SVR model](image)

![Figure 3 Fitting curve between the confined water rising zone and each influence index](image)
According to the fitting curve of Fig. 3, the linear fitting formulas between the main influence index and the development height of the confined water rising zone are as follows:

\[ H_a = 0.0843M + 8.7225 \]  \hspace{1cm} (6)
\[ H_b = 1.595P + 5.8787 \]  \hspace{1cm} (7)
\[ H_c = 2.5225K + 7.5132 \]  \hspace{1cm} (8)
\[ H_d = 20.434F + 5.9956 \]  \hspace{1cm} (9)

Based on the linear fitting formula and entropy weight of each influence index, a formula to predict the development height of the confined water rising zone is obtained:

\[
H' = W_1H_a + W_2H_b + W_3H_c + W_4H_d
\]
\[
= 0.0964(0.0843M + 8.7225) + 0.1907(1.595P + 5.8787) + 0.3386(2.5225K + 7.5132) + 0.3743(20.434F + 5.9956)
\]
\[
= 0.0081M + 0.304P + 0.854K + 7.65F + 6.745
\]  \hspace{1cm} (10)

**Discussion**

The SVR parameters obtained by the PSO optimization are: \(c = 13.7913\); \(g (1/\sigma^2) = 0.01\); the termination generation is 100; the mean square error (MSE) of the test sample is 0.052728 and tends to be 0, which shows that the model has good generalization. The curve diagram of the fitting result of the confined water rising zone is shown in Fig. 4. The minimum relative error of the fitting results is 2.68%, the maximum relative error of the fitting results is 21.6%, and the average relative error is 11.83%. Thus, its fitting effect is preferable.

The predicted relative error of the zone of pressure water, which induces the height by using the multiple linear regression formula, was 2.61-49.2%, and the average relative error was 21.19%. The SVR was 6.65%-32.87%, and the average relative error was 16.5% (tab. 3). Compared with other methods, the predicted results of the Fuzzy-GRA-PSO-SVR model have good generalization and can be applied to field prediction.

**Table 3 Comparison of the relative error of each method**

<table>
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<th>test data</th>
<th>H/m</th>
<th>linear formula/m</th>
<th>relative error/%</th>
<th>Fuzzy-GRA-SVM/m</th>
<th>relative error/%</th>
<th>Fuzzy-GRA-PSO-SVR/m</th>
<th>relative error/%</th>
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</thead>
<tbody>
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<td>21</td>
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<td>16.5</td>
<td>11.83</td>
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Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
Conclusion
The higher correlative degrees among the aquifuge index, aquifer water pressure index, permeability index, structural index and original confined water rising zone are 0.8563, 0.9750, 0.9678 and 0.9614, respectively. The SVR parameters obtained by the PSO optimization are $c=13.7913$, $g=0.01$, $CV_{mse}=0.052728$. The predicted relative error of the zone of pressure water inducing height using Fuzzy-GRA-PSO-SVR was 2.68-21.6%, and the average relative error was 11.83%. By comparing other methods, the predicted results of Fuzzy-GRA-PSO-SVR have good generalization and can be applied to field prediction.

Acknowledgements
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Yu XG A Prediction Method for Primitive Height Conduction Zone of Floor, CN 104239738 A[P]. 2014-12-24
Mine Water Monitoring in Abandoned Mines at RAG Aktiengesellschaft

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Abstract

The shutdown of hard coal production in 2018 implicates a challenge in deriving physical and chemical parameters of mine water in situ. This report describes an application of underground probes in the abandoned coal mine Auguste Victoria. Four probes are dedicated to deliver information about the water rebound process in the mine. Beside a short description of the installation and local parameters of the probes the expected rebound process is figured out. Two years after installation and closing of the mine production some first results can be analysed. The whole rebound process will go on for more than 15 years.

Key words: Mine closure, underground probes, monitoring

Introduction

German hardcoal mining was shut down in Germany in the year 2018. The former production company RAG Aktiengesellschaft is responsible for future consequences of the mining activities. Mine water management is a long term task to fulfill beside regulation of damages caused by subsidence and management of groundwater. The regional concept of RAG Company includes a controlled rebound of mine water level, a reduction of pumping stations and installation of well pumps in shafts instead of underground pumps. The mine water will be controlled permanently on a level below the ground water reservoir, which is used for drinking water abstraction. Individual concepts had been developed also for other mining districts in the Saar area and Ibbenbüren.

In practice the concept includes a closure of the pumping station at the Auguste Victoria mine. Instead of heaving the mine water at this place, the water goes via underground connection to the Lohberg pumping station 35 kilometers away. At Lohberg station the mine water can be drained away to the Rhine river and so the load of mine water in the smaller Lippe river is reduced. In addition there is no need for a mine water preparation plant at the Auguste Victoria mine.

Monitoring of abandoned mines

Observation of abandoned mines includes several measures of monitoring, including observation measures before underground closure. This report will not describe the total range completely. All measures are aiming at supervision of safety, avoidance of risks and environmental protection.

An underground monitoring system was developed in the frame of a research project between Technical University Georg Agricola and RAG company (1). This system allows to gather additional information from abandoned mine districts. The pilot application has been installed at Auguste Victoria mine since 2017. The system includes probes with different sensors, electrical supply and data transfer units for the collection above ground. The complete system is intrinsically safe and approved by the mining authority in Germany. Following parameters are observed:

- Pressure
- Temperature
- Electrical conductivity
- Direction of velocity
- Flow rate

4 Probes are located on the levels of -1100 mNN (6th floor) and -990 mNN (5th floor). In addition 2 sensors at the level -885 mNN
(4th floor) collect data of barometric pressure and methane content of the atmosphere (figure 1).

Parameters of the lower levels are very important to proof the functioning of the planned water flow, therefore the probes are located in the main water gateways. In minimum the measurement system should deliver data about rebound between level -1110 mNN and -600 mNN. This process is prognosed with a duration of appr. 15 years.

Fundamental data for the interpretation of probe parameter are:
- Chemical and physical parameter of mine water analysis
- Amount of mine water inflow to the mine
- Geometrical data of mine infrastructure
- Prediction of mine water rebound process and mine water quality parameter
- Results of barometrical measurements and probe sensors

More than 13 Million data per year are collected by the system. Some 100 thousand data of geometry and prediction, which are extracted from specific data systems at RAG, are also part of the interpretation.

**Basic elements of trial at Auguste Victoria mine**

Figure 1 gives an overview to the underground mine Auguste Victoria in 2016. At that time production areas had been abandoned yet and only the main roadway system was still in use.

The analysis and interpretation are based on the information of the roadway profile on the level of floor 6 (figure 2). Three probes (1W, 3W, 4W) are located on the level in a depth of approximately -1110 mNN. A detailed analysis of the height profile clarifies local trough structure (figure 2). In addition there are junctions to the North and the South connecting to the levels of the upper and lower mine districts. These connections allow inflow and outflow from the 6th level. The picture also shows the measured level of mine water (dated from December 2018) at the probes.

The interpretation of sensor data also has to consider the detailed geometry of the installed probe. A schematic overview is given in Figure 3. The figure shows different sensors at a height of 0,4 meter to 0,6 meter above the floor and an additional mechanical

![Figure 1: Perspective view of Auguste Victoria – level 4, 5 and 6 – and probe locations (2016).](image-url)
indicator to proof a water level at 0.2 meter above the roadway floor.

**Prediction of mine water rebound**

Water rebound of the former mines Auguste Victoria and the neighbour mine Lippe is planned as a process in different phases. In the figures 4 a to c these phases are explained by schematic vertical shape views between the shafts Fürst Leopold 1/2 in the West and Auguste Victoria 3/7 in the East. At the end of the year 2017 the mine water level in the East reached the level of appr. -860 m NN. At this level the connection to the eastern area was flooded and the water can flow to the former Auguste Victoria mine. The mine water level on that side was below -1110 mNN at that time. (figure 4a)

Rebound of mine water in the area of Auguste Victoria up to the level of 6st floor is characterising the second phase. This phase should have a duration of 9 months according to the simulation model results and will be finished by leaving and closing of the underground area Auguste Victoria. (figure 4b)

In phase 3 the rebound process from the 6st up to the 5th floor in the eastern area
**Figure 4a:** Schematic shape and mine water level in 2017.

**Figure 4b:** Schematic shape and mine water level 9 month after shutdown.

**Figure 4c:** Schematic shape and mine water level appr. 5 years after shutdown.
takes place and reaches up to a level of -990 mNN. At the end of this phase the mine water level will reach -860 m NN. At this height the connection point to the western part is flooded within a duration of 5 years according to simulation results (figure 4c). After achieving a common water level in the western and eastern part, the level will rise up to the connection point with the Zollverein water district (-598 m NN). After that, the mine water can flow to the pumping station of Lohberg through the network of roadways and former panels in the underground.

The process in total, up to a water level of -598 m NN, will take a time of appr. 15 years between the stop of pumping at Auguste Victoria mine until reaching the connecting level.

Prognosis is done by using a special planning tool of DMT GmbH company. This model is covering the whole district of mining in the Ruhr area. Figure 5 shows a description in the form of a diagram and timetable. Each line is representing the development of the water level in different parts (mined districts) of the former mine. Dots within the diagram show the results of additional measurements (e.g. water level of a shaft), which are used to proof the calculations. Beside prognosis and additional measurement of water levels the basics of the trial are the fundamental data of mine water chemistry and the parameter of sensor results.

Specific weight and electrical conductivity

For interpretation of the sensor data the context between electrical conductivity and specific weight of the mine water plays an important role. The results of different mine water samples, derived before leaving the underground areas, are shown in the diagram of figure 6. The mathematical analysis shows a linear function with a 98 % - coefficient of determination.

As a conclusion, from the measurement of electrical conductivity a quantification of specific mine water weight is possible. This is important for the interpretation of pressure results in a situation of higher water levels. Taking into account the exact specific weight allows the calculation of local water level above the probe.

Measurement results

Figure 7 gives an overview on the results of
stress measurements by the water probes. This figure show the results of daily mean values calculated from each 1440 single data of the probe exemplarily.

Probe 2W (5th floor, ~ 990 m NN) is located above the mine water level and gives an example of barometric influence to the stress level with a mean value of 1.0 dbar. Very similar is the measurement result at probe 3W on the 6th floor (~1.110 mNN). This indicates a water level below the sensor at that location 3W. Probe 1W is installed in a local trough close to a leaky dam with inflow of mine water from the 5th level. This probe was 2.5 meter below the water level immediately after the installation. Obviously an outflow to lower areas occurs in a level 2.5 meter above. Probe 4W shows a time row with substantial increasing stress after October 2017. Considering the geometry of the roadway according to figure 2, the result of probe 4W can be interpreted. The next outflow to the lower mine areas must be appr. 1.5 meter above the probe.

Beside the exemplarily figured results, the temperature is measured. The probes below mine water level (1W and 4W) indicate a level of temperature between 38°C and 42°C. Probe 2W, which is proved to be above the water level, shows a lower level of temperature between 30°C and 37°C and a substantially more intensive change day by day. Probe 3W seems to be influenced by mine water, because the daily changes show a similar structure to probe 1W and 4W and a high level of appr. 40°C.

The range of electrical conductivity of mine water was expected to be > 100 mS/cm up to 180 mS/cm at maximum and the measurement of conductivity does prove the interpretation of local water level at the position of each probe. In addition, a detailed analysis of time row development at probe 4W shows, that the probe was temporary flooded twice in August and October 2017. The probe was under the water level for a time of up to 49 hours, before the water level did sink below the sensor again. This kind of result is typical for obstacles in the water way. In front of an obstacle the water level rises and at a level of sufficient water pressure, the release of water way is achieved.

In addition to water probes, the barometric pressure is collected at the 4th floor (~885 mNN). This probe should later give information about barometric conditions in the closed mine, up to now the shaft is still open. The results of 19 months of measurement are included in the data interpretation. The mean value is at 1110 mbar and changes include a bandwidth of 20 mbar.

**Correlation of pressure and atmosphere**

Time rows of barometric pressure and pressure measurement at probe 2W indicate a direct barometric influence to the probe at the 5th level. In figure 8 the time row of probe 3W and barometric pressure is shown. There
is no direct connection between both sensors and the distance between them is about 7,000 meter. For several months probe 3W was isolated from ventilated mine sections. It seems to be a delayed reaction of pressure at probe 3W to barometric changes. For elimination of sough signals at probe 3W, the light green dots mark the mean values of every 1 hour for an exemplary chosen time between January 1st and 31st 2019.

The linear dependency between barometric changes and stress at probe 2W can be determined by analysis of changes between the data of the time row. The correlation of differences at probe 2W and barometric changes have a coefficient of determination with 97.5 % (figure 9). The analysis today does prove the current reliability of the measurement system.

**Current interpretation**

Data collection of underground probes form the basic information about the water level. Density of water and barometric pressure have a proved influence on measured stress below the water level. These parameters can be quantified by the results of the trial at Auguste Victoria mine and the level of mine water can be estimated accurately because basic information about the correlation
between electrical conductivity and water density could be derived from former tests. The fully encapsulated sensors of the water probes indicate a basic stress level, which must be considered for interpretation as well. The barometric influence within a range of less than 0.1 meter is not calibrated in current mathematical interpretation. Figure 10 represents the time row and actual mine water level of the 6th floor of the closed mine Auguste Victoria considering the quantified parameter of influence. In fact the probes 1W and 4W are substantially more than 1 meter below the water level. Probe 3W gives currently not a clear combination of signals – it seems to be very close to the water level, but there is no substantial indication up to now. The results of probes also show a very low level of flow rates at the 6th floor of the former mine. Ongoing measurement is focussing on higher flow rates in later phases of mine water rebound for interpretation of erosion processes within the flooded roadways. Up to now, the different probes below the mine water level show different temperature at points of installation. Continuous
measurement will indicate mixing process, because the resolution of data collection fits to a difference of less than 1°C.

The electrical conductivity can be used as a fingerprint of water origin. The comparison of results indicates, that probe 1W is influenced by the mine water inflow from the north of the mine. Probe 4W is influenced by inflow from the upper level (5th floor).

**Future Application**

RAG is preparing additional applications of the underground monitoring system at Prosper- Haniel and Ibbenbüren mines, as well as at pumping stations of the former Saar mine, Zollverein and Heinrich.

According to the planned water flow geometry and the planned rebound process, the number and locations of probes were defined. Data collection will be managed at the new central control room of RAG at the location in Herne. Data processing and visualisation of every probe will be centralized. The duration of usage is planned for the next 2 or 3 decades, so the total rebound process in all former hardcoal mines will be covered by this monitoring.

**References**

(1) Final report “Grubenwassermonitoring” project, RAG 2017, not published
2

MINE CLOSURE
AND REMEDIATION
Irrigation with mine affected waters: A demonstration with untreated colliery water in South Africa

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Abstract
There is renewed interest in the use of mine water for irrigation as a means to reduce mine impacted water treatment costs and to create sustainable livelihoods as mines reach closure and communities need to diversify away from mining. Large volumes of mine waters are affected, and many mine waters are suitable for irrigation.

A 19 ha demonstration centre pivot has been erected on previously un-mined land in Middelburg, Mpumalanga, South Africa. Maize (summer) and stooling rye (winter) have been irrigated with an untreated, circum-neutral, calcium and magnesium sulphate dominated mine water since September 2017. Crops grew exceptionally well under irrigation with this particular mine water, far out producing rain fed crop production, and proving more profitable.

Currently, no off-site effect of irrigation have been detected, and grain produced is safe to consume. A newly developed irrigation water quality assessment tool indicates that Mn and B may be of some concern over time. We advocate regular testing for food or fodder safety, specifically for elements of potential concern, in order to assess if published soil thresholds are robust indicators of the suitability of poor quality waters for irrigation.

Keywords: Irrigation water quality, gypsum precipitation, mine closure, food safety, Decision Support System

Introduction
There is much interest in the beneficial use of mine water for agricultural irrigation. Irrigation is often a cost-effective means for operating mines to manage surplus water. Upon closure, irrigation may present a sustainable means for communities to diversify away from mining, by producing food and fibre sustainably, and creating employment. Large savings in water treatment costs are also likely to follow. However, not all mine waters are suitable for irrigation, and support is necessary to make informed decisions on suitability.

An irrigation water quality Decision Support System (DSS) has recently been developed (du Plessis et al. 2017). Fitness-for-use of water is presented as being ‘ideal’, ‘acceptable’, ‘tolerable’ or ‘unacceptable’. The DSS is novel in a number of ways. Firstly, it is risk based, enabling the user to assess the implications of irrigating with a range of waters, including mining impacted waters on soil and crop resources, as well as on irrigation equipment. Secondly, the guidelines are structured in three tiers. Tier 1 provides generalised, conservative estimates of the suitability of water for irrigation. If mine waters are shown to be ideal or acceptable at this level, there may be no need to treat water or to utilise it through irrigation, and release into surface water bodies will likely be permitted and desirable. As this is unlikely with most mine-impacted waters, Tier 2 supplies more site-specific guidelines, enabling the user to design a crop production system to best accommodate the specific water quality. If there are still concerns about the usability of water for irrigation, then a Tier 3 assessment is indicated. This will require
detailed expert input to assess whether or not irrigation is at all feasible, and if concerns highlighted by the Tier 2 assessment can be mitigated. Finally, the DSS is electronic and user-friendly, with colour coding to make the suitability of waters for irrigation intuitive.

**Site description**

After a careful soil survey to select a site with irrigable soils, a 19 ha demonstration centre pivot has been erected on previously un-mined land in the Middelburg District of Mpumalanga, South Africa. This experimental site (25°48'25"S, 29°45'48"E, 1670 m.a.s.l.), has been planted to maize (summer) and stooling rye (winter), and has been irrigated with an untreated, slightly alkaline, calcium sulphate dominated coalmine water since September 2017. Soil water and salt balances were monitored in-field, as were potential off-site effects through surface and groundwater monitoring. The trial site, as well as the location of surface and groundwater monitoring stations is presented in Figure 1.

**Agronomic practices**

A local, large-scale, commercial farmer from the area, who leases the land from the mining house, is growing the crops for his own account. The centre pivot was erected by the colliery, which supplies mine water to the field under pressure. A white maize variety PHB 32B07BR was planted in early October 2017 at a seeding rate of 80 000 per hectare. Around the irrigated area, maize is also planted under rain-fed conditions at a lower seeding density of 50 000 per hectare. When this first irrigated maize crop was harvested in June 2018, stooling rye, a fodder crop was planted to demonstrate that irrigation could also be successful in winter. Due to logistical reasons, this crop was planted late and harvested early, to make way for the following maize crop. Ideally, from a water utilisation point of view, it is desirable to have a green transpiring canopy for as many months of the year as possible. Taking maize off early for silage, would enable the winter crop to be planted earlier, thereby maximising production. The winter crop in this trial will not be discussed in detail, but it was evident that this salt and cold tolerant crop could be successfully produced in the cooler winter months.

The maize was well fertilised (290 kg ha\(^{-1}\) nitrogen (N), 40 kg ha\(^{-1}\) phosphorus

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**Figure 1.** A Google Earth image of the experimental site showing the location of the centre pivot (yellow circle), the monitoring boreholes (BH1 to BH4) surrounding the irrigated field, as well as piezometers (P1 to P3). The discard dump monitoring boreholes (DBH8 to DBH11), and Beestepan Dam, where surface water quality is monitored, are also indicated.
(P), 64 kg ha⁻¹ potassium (K), and 10 kg ha⁻¹ sulphur (S)), with nutrient supply depending on expected yields and soil analyses. Crop protection also received attention, with spray programmes followed to minimise disease and insect damage, and to control weeds. All input costs were recorded to estimate profitability at the end of the season.

Irrigation water quality

The mine water used was untreated, and pumped from one of the opencast voids to the field. The pH is circum-neutral (7.1), with an electrical conductivity (EC) of around 240 mS m⁻¹. The major cations were calcium (Ca) at 235 mg L⁻¹, magnesium (Mg) at 160 mg L⁻¹ and sodium (Na) 70 mg L⁻¹. Major anions were bicarbonate (HCO₃⁻) at 335 mg L⁻¹, chloride (Cl⁻) at 10 mg L⁻¹ and sulphate (SO₄²⁻) at 1130 mg L⁻¹. From a plant nutrient point of view, the water contained 3.5 mg L⁻¹ nitrogen (N) and 35 mg L⁻¹ potassium (K). Several trace elements were below detection limits and therefore not considered in this analysis. Trace elements that were present in measurable quantities were, in µg l⁻¹, aluminium (Al) 510, manganese (Mn) 390, iron (Fe) 110, zinc (Zn) 40, boron (B) 225, cobalt (Co) 3.2, vanadium (V) 7.5, and fluoride (F) 0.7.

This mine-impacted water was assessed using the Irrigation Water Quality DSS to identify options available to utilise this water and to alert the users to potential constituents of concern. No yield decline was simulated due to salinity for both maize and a cool season cereal, wheat (which would respond similarly to stooling rye), but wheat may be sensitive to boron according to the DSS. Most trace elements will only reach soil thresholds after a millennium of irrigation, but Mn reaches its threshold in half a century.

Environmental impact monitoring

A pair of boreholes, one deep (B1) and one shallow (B2) is located on the eastern side of the field and another pair, also one deep (B3) and one shallow (B4), are located on the western side of the field (Figure 1). The shallow boreholes (2 and 4 referred to as Shallow Upstream and Shallow Downstream, respectively) are about 10 m deep and the deep boreholes (1 and 3 referred to as Deep Upstream and Deep Downstream, respectively) are around 30 m deep. These boreholes are sampled and analyzed by the colliery every quarter.

Measured EC and SO₄ concentration of the downstream boreholes were quite high even before any irrigation had taken place (irrigation commenced in September 2017), thus indicating that these solute signatures are determined by an external salt source. The chemical signatures of these downstream boreholes also indicate that these waters are NaCl dominated and not Ca/Mg sulphate dominated, as is the case for the irrigation water. The most likely explanation for these observed elevated salt levels prior to irrigation is that they can be attributed to runoff from the discard dump that is located adjacent to these boreholes. Four additional boreholes have recently been drilled around the discard dump to enable groundwater monitoring closer to the discard dumps, thereby reducing uncertainty around the effect of irrigation on groundwater resources. These boreholes are marked DMBH in Figure 1. It appears that irrigation water currently has a minimal effect on groundwater, as it is not clearly accumulating SO₄ (Figure 2).

Beestepan Dam (Figure 1) was identified as a monitoring point where one could potentially observe any effect of irrigation on downstream surface water bodies. Sulphate was the selected constituent to flag such effect, and the decision taken was that if a 20% increase above the original (before irrigation) concentration, attributable to irrigation is observed, all irrigation should be stopped immediately. This, however, is somewhat complicated by the fact that a discard dump in close proximity to the field will also affect the water quality in this dam. The average sulphate concentration in Beestepan Dam for the three years prior to the commencement of irrigation (October 2014 to August 2017) was 535 mg L⁻¹. The threshold for action is therefore 642 mg L⁻¹. Average sulphate concentration in the first irrigation season stood at 309 mg L⁻¹, and is currently around 400 mg L⁻¹. This is affected by rain, with declining values in the rainy season, and increases observed in the dry season or in drought years.
Field salt and water balance

Over the three cropping seasons (18 months), around 900 mm of irrigation has been applied to the field. This roughly adds up to the addition of 2.1 t ha$^{-1}$ Ca, 1.4 t ha$^{-1}$ Mg and just over 10 t ha$^{-1}$ sulphate. In addition, 340 t ha$^{-1}$ K and 2 t ha$^{-1}$ B was added through the irrigation water. It is clear that the irrigator needs to take into account what is being added with the irrigation water and adjust fertilisation programmes accordingly. In addition, it would be prudent to take regular soil samples to identify any nutrient imbalances that may develop.

The DSS simulated over 45 years that around 1000 mm of irrigation would be applied per year on average. This would add 886 t ha$^{-1}$ salt, of which 324 t ha$^{-1}$ is leached, and 175 t ha$^{-1}$ is predicted to precipitate as gypsum, about 20% of the salt added. It appears that Ca limits gypsum precipitation so there may be opportunities with the fertilisation programme to increase precipitation, which does the soil no harm, but keeps solutes out of water bodies. The balance (387 t ha$^{-1}$) is stored in the soil profile.

The DSS also predicts that soil saturated paste electrical conductivity (ECe), a measure of salinity, will increase upon commencement of irrigation, but will soon stabilise around a level below 200 mS m$^{-1}$, a clear sign that gypsum is precipitating and excess salts are leaching, thereby preventing the profile from becoming too saline for the production of most crops. This is depicted in Figure 3, where 45 years of maize wheat production is simulated. The salinity threshold levels for maize, wheat and soybeans (Maas and Hoffman, 1977), are also indicated in this figure. It is clear that maize may not be the best crop choice for summer production, especially if water quality deteriorates, but soybean should do well in summer, and cool season cereal crops like wheat, should show no yield decrease due to salinity.

Crop yield and profitability of production

The summer rainfall region of South Africa often experiences mid-summer droughts that can drastically reduce dryland yields. The advantage of having irrigation available, even with relatively poor quality mine water, is evident in Table 1. Yields more than doubled under irrigation compared to rainfed production, and although input costs of irrigated systems are higher, it appears that in most years, production under irrigation will be more stable and profitable than traditional dryland farming, even if the grower has to pay for pumping costs.

Food safety

Although mine waters contain a range of metals including iron, aluminium, and manganese, the main elements of concern...
were identified as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb) and mercury (Hg). International guidelines for these elements are presented in Table 2, together with the levels measured in the grain from the 2017/18 season.

It is clear that the grain produced is safe for human consumption and levels of constituents of concern are at least an order of magnitude lower than the recommended

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**Table 1** Maize yields and profitability in 2017/18 and 2018/19. Typical exchange rate 14 South African Rand (R) to 1 US$

<table>
<thead>
<tr>
<th>Season</th>
<th>2017/18</th>
<th></th>
<th>2018/19</th>
<th></th>
</tr>
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<td>Field</td>
<td>Elevated</td>
<td>Dryland</td>
<td>Elevated</td>
<td>Dryland</td>
</tr>
<tr>
<td>Yield (t/ha)</td>
<td>13</td>
<td>5,4</td>
<td>14,7</td>
<td>5,6</td>
</tr>
<tr>
<td>Cost (R/ha)</td>
<td>17859</td>
<td>15980</td>
<td>17092</td>
<td>14586</td>
</tr>
<tr>
<td>Cost (R/t)</td>
<td>1374</td>
<td>2959</td>
<td>1163</td>
<td>2605</td>
</tr>
<tr>
<td>Avg SAFEX Price (R/t) (May - July)</td>
<td>2070</td>
<td>2998</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Earnings (R/ha)</td>
<td>26910</td>
<td>11178</td>
<td>44071</td>
<td>16789</td>
</tr>
<tr>
<td>Profit/Loss (R/ha) (excl pumping costs)</td>
<td>9051</td>
<td>-4802</td>
<td>26979</td>
<td>2203</td>
</tr>
<tr>
<td>Profit/Loss (R/ha) (incl pumping costs of R5000/ha)</td>
<td>4051</td>
<td>-</td>
<td>21979</td>
<td>-</td>
</tr>
</tbody>
</table>

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**Table 2** International grain food safety thresholds for human consumption adapted from Codex Alimentarius Commission 2011, 2013, South African Department of Health 2016. The measured values for the 2017/18 season are also presented.

<table>
<thead>
<tr>
<th></th>
<th>China</th>
<th>EU/SA</th>
<th>Ireland</th>
<th>Irrigated</th>
<th>Dryland</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>0.003</td>
<td>0.004</td>
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<tr>
<td>Cd</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Pb</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.006</td>
<td>0.005</td>
</tr>
<tr>
<td>Hg</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

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Image: Figure 3. Soil profile salinity (ECe in mS m⁻¹) predicted by the DSS for 45 years of irrigation of a maize-wheat rotation with the water quality used in this demonstration. Salinity thresholds for three crops are also indicated.
safety thresholds. At the time of writing, the analyses for the second maize season were not yet available, but are also likely to be of no concern.

Acknowledgements
The authors thank the Water Research Commission for funding the development of the Irrigation Water Quality DSS, as well as the mine water irrigation project.

Conclusions
Not all mine waters are suitable for irrigation. However, the user-friendly DSS is able to assess site-specific factors that influence the suitability of mine waters for irrigation. It is clear from this study, that it is possible to profitably utilise some mine affected waters. This has important implications for sustainable mine closure, and diversification of communities away from mining post closure. Currently, no off-site effects of irrigation have been detected, and grain produced is safe to consume. We advocate that food and forage safety be assessed when using mine waters for irrigation, in order to ascertain if trace element thresholds commonly published in irrigation water quality guidelines are robust. This is especially important for elements that are naturally abundant in soil, and many mine waters, like Fe, Al and Mn, and are likely to become unavailable for plant uptake over time.

References
Comparative study of two biggest mineral wastes in South Africa for mine reclamation: A geotechnical study 🏗️

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Abstract
Laboratory investigations were conducted on two mineral wastes to assess their geotechnical properties for mine backfilling. Coal Fly Ash (CFA) sludge recovered from CFA and acid mine drainage (AMD) reaction (ratios 1:2 and 1:3) and gold mine tailings (GMT) with 3 % cement were evaluated at varying curing ages. Both samples showed favourable characteristics for use in mine reclamation. However, solid/liquid ratios should be maintained to ensure maximum strength. The results show that CFA is recommended for mine reclamation due to its geotechnical properties. The use of GMT is possible, however blending with higher percentages of cement should be considered.

Keywords: Coal Fly Ash, gold mine waste, geotechnical characterisation, backfilling

Introduction
South Africa generates approximately 70% mineral waste annually from its mining activities (DEA 2012). Waste generated from gold mining alone accounts for 47% of the total mineral waste generated in South Africa. This percentage excludes ≈30 MT CFA that is accumulated annually from electricity generating and liquid fuel production (Du Plessis et al. 2013). Small percentages of this waste are beneficially utilized in South Africa, with huge amounts stored in tailings and ash dams (Mashifana 2018; Van der Merwe et al. 2011).

Underground mine backfilling has become an integral part of mine reclamation in most parts of the world. Backfilling provides ground support and regional stability, thus reducing subsidence and improving ore recovery (Der Verleihung 2009; Potgieter 2003). A wide range of backfilling methods has been assessed; these methods include rock backfill, hydraulic backfill, cemented backfill and silica alumina-based backfill (Sheshpari 2015; Sivakugan et al. 2015). The methods considered for backfilling often make use of mineral waste (waste rock and tailings) in conjunction with small proportions of binders such as cement to improve the properties of the backfill material (Lokhnde 2005). The use of mineral waste in mine backfilling provides an effective means of disposal due to cuts in storage costs and a reduced environmental footprint.

Previous studies on viability of using CFA and GMT in mine backfilling (Kruger and Krueger 2005; Yilmaz 2011) were encouraging and very few studies of this nature were carried out in South Africa. Realising the consequences of mineral waste disposal and the opportunity thereof for use in mine reclamation, this study aims at assessing the properties of GMT and CFA for mine backfilling purposes.

Materials
Class F CFA was collected in dry state from the hoppers of a coal fired power station in Mpumalanga. GMT used in the study was a composite sample collected from one the tailings dams of a gold mine in west rand basin, South Africa. The sample was obtained using an auger from a depth of 0.5 m to 5 m to ensure that the non-oxidised layer was represented to the best of our ability. Mine water used in the co-disposal with CFA was collected from an old abandoned coal mine located in Emalahleni, Mpumalanga.
Province. Samples were collected following the standard procedure described in DWAF (1996). Water samples were kept cooled en-route to the laboratory and subsequently stored in a refrigerator at 4 °C for analysis. Lafarge CEM II 52.5N (at 3%) was used as an additive for GMT during geotechnical testing to improve the properties of the material. During geotechnical testing samples were remoulded to 95% maximum dry density (MDD) and cured in moisture over a 7, 28 and 56 days curing period and at a room temperature of about 23 °C. The grain size analysis of CFA and GMT (without cement and curing) was determined by sieve analysis. The measure of the critical water content of the CFA and GMT (without cement and curing) was determined using Atterberg limits. The maximum dry density (MMD) and optimum moisture content (OMC) of composite samples was determined by modified proctor test. The coefficient of permeability (k) for composite CFA and GMT was measured using the falling head method. The compression characteristics of composite CFA and GMT was determined using unconfined compressive strength. Shear strength parameters cohesion (c) and angle for internal friction (φ) were determined using a direct shear test.

Results and discussions

Grain size distribution

Figures 1 and 2 show the grain size distribution curves of CFA and GMT. The ash consists of grain size fractions ranging from 0.01 mm to 0.1 mm. These range fractions, according to Das (2006), are similar to silt soils and show a potential for pozzolanic reaction as reported by Paya et al. (2001) and Jatuphon et al. (2005). The coefficient of uniformity (Cu) and the coefficient of curvature (Cc) for CFA could not be determined due to the particle size distribution of the material.

The particle size distribution obtained for GMT is composed of 52% sand, 40% silt and 8% clay fractions with ranges of 0.01 mm to 1 mm. The Cu for the tailings was 12 mm comparable to well graded sand. The Cc for the tailings was 0.5 outside the range for well-graded sands. Upon the addition of the 3% cement, the particle size composition changed to 21% sand, 67% silt and 12% clay fractions resulting in more silt fractions. The Cc value was also adjusted to 2.6 providing for categorisation under well-graded sand.

Atterberg limits

Atterberg tests revealed that both materials were non-plastic consequently, the liquid limit and plastic index could not be determined. According to Bartle (2000), non-plastic soils have an inherent shear resistance to sliding with the addition of water and can lose 50% shear strength because of water floating on top contrary to clays that lose 99.5% of their total shear resistance to sliding due to drainage.

Compaction characteristics

The compaction characteristics of CFA and GMT are given in Table 1.

Both CFA samples exhibited lower MDD and higher OMC compared to GMT. MDD values recorded for CFA, according to Geliga and Ismail (2010), Das (2011) and Sabat...
increased the fine fractions, resulting in larger inter-particle voids responsible for increased coefficient of permeability (Prashanth et al. 2001). Studies by Dungca and Jao (2017) on ash showed decreasing permeability with curing age and addition of more fines. The slight increase in permeability noted for the ash with increasing curing age was erratic; however, the permeability ranges noted were within the accepted range for embankments and backfilling (Heindel and Noyes 1997).

Compression characteristics- Unconfined compressive strength (UCS)

The measure of resistance to external loading for CFA and GMT at 0, 7, 28 and 59 days of curing is presented in Table 3. The UCS of CFA and GMT samples (without cement and curing) was low compared to the composites samples (tab. 3). The curing age together with the addition of fines appears to have substantial effects on the strength of both materials.

Early high strength recorded for the GMT could be attributed to the well grading of particles that resulted in artificial cementation. By the 56th day of curing, both materials showed improved strengths, which indicates the benefits of cement addition and curing age to the strength properties, as noted by Lee et al. (2016). Tatt and Ali (2004) made similar observations; the authors also noted that the compressive strength of soils (2015) are typical for soils with silt particle sizes. The MDD of GMT was originally 1588 kg/m³ and decreased to 1555 kg/m³ upon the addiction of cement. High OMC values recorded for CFA according to Gimhan et al. (2018) are attributed to higher air void content, which Pandian (2004) places at 5% to 15% compared to 1% and 5% of soils. Addition of cement to GMT also reduced the OMC of the material, similar to the trends noted by Al-Khafaji (2015) due to chemical reactions between the molecules of cement, clay and water. The compaction results obtained for the CFA and GMT qualifies the use of these materials in civil works, based on the Indian Road Congress (IRC) compaction specifications.

**Permeability characteristics**

Table 2 presents the values of the coefficient of permeability (k) for compacted CFA and GMT.

The coefficient of permeability for CFA and GMT increased with curing age and cement addition. The coefficient of permeability of the ash was observed to be in the range of silt material and the GMT in the range of silt sand. The coefficient of permeability range of CFA is attributed to the uniform silt particles, which form larger inter-particle voids, contributing to increased permeability. Similarly, the addition of cement to GMT increased the fine fractions, resulting in larger inter-particle voids responsible for increased coefficient of permeability (Prashanth et al. 2001). Studies by Dungca and Jao (2017) on ash showed decreasing permeability with curing age and addition of more fines. The slight increase in permeability noted for the ash with increasing curing age was erratic; however, the permeability ranges noted were within the accepted range for embankments and backfilling (Heindel and Noyes 1997).

**Table 1 Compaction characteristics of CFA and GMT.**

<table>
<thead>
<tr>
<th>Properties</th>
<th>CFA 1:2</th>
<th>CFA 1:3</th>
<th>GMT</th>
<th>GMT with 3% cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDD (kg/m³)</td>
<td>1192</td>
<td>1183</td>
<td>1588</td>
<td>1555</td>
</tr>
<tr>
<td>OMC (%)</td>
<td>34.1</td>
<td>33.3</td>
<td>14.9</td>
<td>10.4</td>
</tr>
</tbody>
</table>

**Table 2 Values of permeability at a normal stress of 100 kPa.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial void ratio (e)</th>
<th>Coefficient of permeability (m/s)</th>
<th>Dry density (kg/m³)</th>
<th>Initial degree of saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFA 1:2 (0 curing)</td>
<td>1.008</td>
<td>3.7E-08</td>
<td>1101</td>
<td>80.6</td>
</tr>
<tr>
<td>CFA 1:2 + 3% cement (7 days)</td>
<td>1.053</td>
<td>3.9E-08</td>
<td>1077</td>
<td>76.0</td>
</tr>
<tr>
<td>CFA 1:2 + 3% cement (28 days)</td>
<td>0.985</td>
<td>8.0E-08</td>
<td>1114</td>
<td>79.7</td>
</tr>
<tr>
<td>CFA 1:2 + 3% cement (56 days)</td>
<td>0.973</td>
<td>7.9E-08</td>
<td>1108</td>
<td>80.7</td>
</tr>
<tr>
<td>CFA 1:3 (0 curing)</td>
<td>1.009</td>
<td>6.2E-08</td>
<td>1100</td>
<td>79.5</td>
</tr>
<tr>
<td>CFA 1:3 + 3% cement (7 days)</td>
<td>1.032</td>
<td>9.1E-08</td>
<td>1087</td>
<td>79.1</td>
</tr>
<tr>
<td>CFA 1:3 + 3% cement (28 days)</td>
<td>1.030</td>
<td>1.2E-07</td>
<td>1088</td>
<td>78.9</td>
</tr>
<tr>
<td>CFA 1:3 + 3% cement (56 days)</td>
<td>1.022</td>
<td>1.2E-07</td>
<td>1095</td>
<td>79.3</td>
</tr>
<tr>
<td>GMT (0 curing)</td>
<td>0.933</td>
<td>3.8E-07</td>
<td>1417</td>
<td>38.8</td>
</tr>
<tr>
<td>GMT + 3% cement (7 days)</td>
<td>0.932</td>
<td>2.9E-07</td>
<td>1382</td>
<td>31.8</td>
</tr>
<tr>
<td>GMT + 3% cement (28 days)</td>
<td>0.932</td>
<td>9.0E-07</td>
<td>1382</td>
<td>27.7</td>
</tr>
<tr>
<td>GMT + 3% cement (56 days)</td>
<td>0.861</td>
<td>9.0E-07</td>
<td>1434</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
increases upon cement addition and age of curing. The strain variables achieved at these compressive strengths are an indication of the stiffness of the samples.

Shear strength characterisation - Box shear

The shear strength values for CFA and GMT are presented in Figures 3 and 4.

The values of the angle for internal friction ($\phi$) were recorded to be 34º, 26º and 29º for CFA 1:2, CFA 1:3 and GMT respectively at the initial stages of the experiment. An increase in the $\phi$ was noted until the 56th day of curing for CFA 1:2 and CFA 1:3 because of initial cementation and a long-term pozzolanic reaction. The effect of curing was observed until the 28th day for GMT due to the saturation of the samples with moisture, resulting in the loosening of particles, these observations coincide with observations made by Hasan (2012). Values of cohesion for CFA started low and improved with increasing curing age and increasing solid fractions as noted by Uchaipichat and Limsiri (2011). For both materials, an increase in cohesion was noted after 7 days of curing, followed by a slight decrease at 28 days and a substantial increase at 56 days. Studies conducted by Moayed et al. (2011) corroborate the observations made in this regard.

Based on $\phi$ and $c$ recorded for the two samples, it may be concluded that CFA composites have a higher capacity to withstand shear stress, while the tailings

![Curing Period vs Shear Stress](image)

**Figure 3** Relationship between curing period and shear stress.

**Table 3** Unconfined compressive strength for CFA and GMT.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Compressive strength (kPa)</th>
<th>Axial strain at max. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFA 1:2 (0 curing)</td>
<td>79</td>
<td>1.32</td>
</tr>
<tr>
<td>CFA 1:2 + 3% cement (7 days)</td>
<td>126</td>
<td>1.14</td>
</tr>
<tr>
<td>CFA 1:2 + 3% cement (28 days)</td>
<td>178</td>
<td>1.13</td>
</tr>
<tr>
<td>CFA 1:2 + 3% cement (56 days)</td>
<td>383</td>
<td>0.77</td>
</tr>
<tr>
<td>CFA 1:3 (0 curing)</td>
<td>111</td>
<td>1.33</td>
</tr>
<tr>
<td>CFA 1:3 + 3% cement (7 days)</td>
<td>144</td>
<td>1.76</td>
</tr>
<tr>
<td>CFA 1:3 + 3% cement (28 days)</td>
<td>155</td>
<td>1.67</td>
</tr>
<tr>
<td>CFA 1:3 + 3% cement (56 days)</td>
<td>419</td>
<td>1.21</td>
</tr>
<tr>
<td>GMT (0 curing)</td>
<td>129</td>
<td>1.96</td>
</tr>
<tr>
<td>GMT + 3% cement (7 days)</td>
<td>315</td>
<td>1.49</td>
</tr>
<tr>
<td>GMT + 3% cement (28 days)</td>
<td>386</td>
<td>1.14</td>
</tr>
<tr>
<td>GMT + 3% cement (56 days)</td>
<td>412</td>
<td>0.89</td>
</tr>
</tbody>
</table>
show moderate capacity. The ability of both materials to withstand shear stress qualifies the use of these materials in mine backfilling. However, blending with the higher percentages of cement should be explored to ensure maximum shear strength.

Conclusions

GMT and CFA composites yielded appreciable geotechnical properties suitable for application in mine backfilling; with the only drawback being the permeability properties of the material, which showed increased permeability with age of curing. It is therefore advised that the addition of a wider variety of percentages of cement be evaluated to improve the permeability properties of the material and to further ascertain its geotechnical properties.

Acknowledgements

The authors would like to thank Council for Geoscience for funding the project.

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![Figure 4 Relationship between curing period and cohesion.](image)


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Abstract

In the Coal Mining Region of Santa Catarina is located the largest pole producing ceramic floors in Brazil. Considering the large volume of alkali feldspar rich waste that is generated during the porcelain polishing step. The ceramic industry is great generator of solid waste, usually deposited in landfills, being responsible for the pollution of extensive areas. There is a great availability of this alkaline material that can potentially be used as a neutralizing agent to prevent the generation of AMD in the coal mining.

In this work the characterization of the potential of the generation of DAM through static and kinetic tests of a coal waste obtained in a beneficiation plant of the coal mining region, was characterized chemically the waste originated during the step of polishing in the production of porcelain tiles and determined the neutralization potential of the alkali feldspar waste. The results indicate that the coal mining waste presents a high potential of acidity (AP), the waste of the production of porcelanates presents as a major component of its composition silicon oxide and aluminum oxide, but also other oxides such as of potassium and has a moderate neutralization potential (NP).

The results indicate a moderate potential of use as an alkaline additive in the prevention of AMD generation. However other uses are recommended, such as the production of soil-cement with this waste.

Keywords: Porcelain; Wastes; AMD; Prevention.

Introduction

Acid Mine Drainage (DAM) comes from the natural oxidation of sulfide minerals when in contact with air and water. DAM is associated with coal mining and polymetallic sulphides, especially in the presence of iron sulphide (pyrite or marcasite — FeS₂). These sources remain active for decades and even centuries after their production (Fernandez-Rubio, 1986, Kontopoulos, 1998, Capanema and Ciminelli, 2003, Johnson and Hallberg, 2003).

The Carboniferous Region of Criciúma, in Santa Catarina, is highly affected, being considered one of the 14 most polluted areas in Brazil. The improper management of these wastes, practiced in the past, and in certain cases even in the current activities, resulted in the formation of an AMD contaminating soil and water with low pH and a high concentration of sulfate, iron (II and III), aluminum, zinc and manganese (Gomes, 2004).

It is estimated that, in the Carboniferous Basin of Southern Santa Catarina, there are about 786 km of rivers affected by DAM in the Araranguá, Tubarão and Urussanga Rivers basins. The contamination of water resources is due to 134 areas mined in the open air amounting to 2,924 ha, 115 areas with waste deposits to 2,734 ha, 77 acidic lagoons amounting to 58 ha, as well as hundreds of underground mines (de Luca, 1991; Menezes et al., 2000; Gomes, 2004).
**Prediction of the Acid Drainage Generation**

The pressure from environmental agencies, public ministry, the community at large and awareness of the Carboniferous are promoting a major joint effort to minimize the environmental problem. An important tool in this context is the need to forecast the generation of DAM by the materials handled in the mining activities and mainly by the tailings of the beneficiation. The DAM prediction through static and kinetic tests has been applied worldwide for decision-making in mining enterprises (EPA, 1994; Kontopoulos, 1998; Sobek et al., 2001). However, these methods have not been applied in the Carboniferous Region of Criciúma.

The static tests have the purpose of evaluating the potential of generation of AMD by a certain material. They are easy and fast and allow the application of specific criteria that allow the classification of the samples according to their potential for acid generation. Afterwards, the materials are subjected to a series of kinetic tests that will determine the acid generation behavior over time, as well as the expected quality of drainage (EPA, 1994).

The usual kinetic tests are performed on Soxhlet reactors, agitated flask techniques, humidity cells and column leaching tests. Although there is no standardized method, the most popular laboratory kinetic assay is that of moisture cells (ASTM D 5744-96). In-situ tests on stacks are also employed. Kinetic tests require a long time, ranging from weeks, months or even years. Based on the results of the static and kinetic tests, appropriate mathematical models can be applied in order to extrapolate the results over a period of years, decades or even centuries.

AMD is due to an autocatalytic reaction. Thus, the best method of control is not to generate it. The use of alkaline additives in mixture with pyrite wastes is a technique recognized as a preventive method for the generation of DAM and little (or none) has been applied in the coal region of southern Brazil.

Sintered porcelain ceramics, known as porcelain tiles, are a class of ceramic products used for coatings. The porcelain stoneware is the ceramic for coatings that presents the best technical and aesthetic characteristics when compared with the others found in the market. Due to its properties this material has increased its participation in the market of ceramic material. The ceramic mass of porcelain tiles requires a proportion of feldspar up to 50% of the ceramic mass (Azevedo et al., 2007).

**Methods**

The methodology of the work within the context of the prediction of DAM was initially restricted to the static test of determination of the ABA Neutralization Potential by the SOBEK and modified SOBEK method, to the kinetic test with moist cells.

**Samples of coal tailings**

The materials studied were collected directly from coal beneficiation plants of the Carboniferous Region of Santa Catarina. Samples of coal generated in beneficiation operations were sampled. The samples were conditioned, transported and prepared for the static and kinetic tests.

**Samples of alkaline residues**

The alkali feldspar rich was supplied by Cerâmica Eliane S / A. Only this company produces approximately 1000 tons of this waste per month, and is currently destined for grounding. The samples were conditioned, transported and prepared for the static and kinetic tests.

**Static Tests – “Acid Basic-Accounting (ABA)”**

The static tests to be implemented were the acid and base accounting procedure developed by Sobek (Sobek et al., 1978). It is an essay that aims to determine the balance between acidity production and acidity consumption (neutralization) by the mineral components of a sample. The test involves calculating the sample’s acidity potential (AP) from measurements of sulfur concentration and the measurement of neutralization potential (NP) (EPA, 1994).

From this data will be calculated:
- net neutralization potential (NNP) = NP – AP
- neutralization potential ratio (NPR) = NP/AP
- where AP, NP and NNP are generally expressed in kg CaCO3 / t sample.
The procedure for the determination of the acidity potential (AP) will be from the total sulfur content (Sobek) or pyritic – FeS\(_2\) (Modek Sobek). Stoichiometrically, one mole of CaCO\(_3\) is required per mole of S:

\[
\text{AP (kg CaCO}_3/\text{t sample)} = \left(\frac{1000}{32}\right) \times \text{weight}\% \text{ S}
\]

The Neutralization Potential Determination was performed by attacking the sample with acid heated at 90 °C to consume the neutralizing minerals and titration with NaOH to pH 7.0.

\[
\text{NP (kg CaCO}_3/\text{t sample)} = (\text{HCl cons. G/g sample}) \times \left(\frac{50}{36.5}\right) \times 1000
\]

The ABA criteria for identifying the acidity potential of the materials are (NNP and NPR):

- NNP values less than -20 will form acid
- NNP values above +20 will not form acid
- NNP values between -20 and +20 are difficult to verify potential.
- NPR values less than 1:1 indicate the likely generation of AMD
- NPR values between 1:1 and 2:1 indicate the possible generation of AMD
- NPR values between 2:1 and 4:1 indicate that AMD is not expected
- NPR values greater than 4:1 indicate that DAM was not generated.

**Characterization and Neutralization of a Acid Mine Drainage (AMD)**

The treatment of a sample of acid mine drainage (DAM) was carried out by the addition of porcelainate powder under mechanical agitation in jar test equipment. The DAM used in the tests was collected at the same mine that provided the coal mining tailings for the experiments.

To characterize the acid mine drainage sample, the pH and concentration of iron, manganese, zinc, aluminum and sulfate were analyzed. The metals were analyzed in an Agilent brand AA-240 atomic absorption spectrometer, while the sulfate was determined by the turbidimetric method using a Hach turbidimeter. These analyzes were carried out at the Environmental Studies Laboratory for Metallurgy and followed the procedures of the Standard Methods for Water and Wastewater Analysis (APHA, 2015).

**Results and Discussion**

The following results were presented in the characterization tests of the materials, coal mining tailings and porcelain powder. As well as the neutralization potential (NP) of the porcelainate powder residue, aiming to evaluate its applicability in the treatment of AMD or in the prevention of its generation. It was also evaluated the potential of generation of AMD by the mining tailings used in the work.

**Mineralogical Characterization of Materials**

Initially the characterization of the materials used in this work, mining tailings and porcelain powder was carried out. For mineralogical characterization, the X-ray diffraction technique was used. The analyzes were performed on a Siemens D5000 X-ray diffractometer. The following are the diffractograms.

The results show that the majority phases are the silicon and silicon oxides, also showing a peak for a potassium feldspar. The results indicate that the material may present a potential for alkalinity generation. Then, the X-ray diffraction analysis of the coal mining material was carried out. Below we can observe the diffractogram.

The results obtained show the presence of silicon and aluminum oxides, but also a large amount of pyrite. This indicates that the material has the potential to generate acidity.

**Determination of Net Neutralization Potential**

Table 3 presents the results obtained in the tests to determine the neutralization potential of the material originating from the porcelain tile production. Performed according to the ABA methodology.

The results obtained in the step of determining the neutralization potential of the analyzed samples, demonstrates that the material has a relative capacity of neutralization. Featuring reasonable potential for use with the alkaline agent in preventing the generation of AMD. Also, the tailings produced during the process of concentrating the coal from the Barro Branco layer of the State of Santa Catarina were analyzed. The results obtained are shown in table 4.
The results obtained demonstrate that the material has a very high acidity potential. This indicates potential for generation of AMD. The NNP value is equal to -304, which according to the ABA criteria indicates potential for the generation of AMD.

**Kinetic Generation Assays of AMD**

Kinetic prediction of the generation of AMD was carried out using the materials used in this work. From the results obtained in the analyzes of the Liquid Neutralization
Table 3 Results of the Tests of Determination of the Neutralization Potential of Porcelanate Powder.

<table>
<thead>
<tr>
<th>Static Test</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>In Paste pH</td>
<td>8,57</td>
</tr>
<tr>
<td>Total Sulfur (%)</td>
<td>0</td>
</tr>
<tr>
<td>AP (kg CaCO₃/t)</td>
<td>0</td>
</tr>
<tr>
<td>NP (kg CaCO₃/t)</td>
<td>30,70</td>
</tr>
<tr>
<td>NNP</td>
<td>30,70</td>
</tr>
<tr>
<td>NPR</td>
<td>30,70</td>
</tr>
<tr>
<td>AMD formation</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 4 Results of coal wastes characterization analyzes

<table>
<thead>
<tr>
<th>Parâmetros analisados</th>
<th>Rejeito de carvão antes do processo de lixiviação</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (%)</td>
<td>80,4</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>12,4</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>7,2</td>
</tr>
<tr>
<td>S total (%)</td>
<td>9,7</td>
</tr>
<tr>
<td>S pyritic (%)</td>
<td>9,6</td>
</tr>
<tr>
<td>S sulphatic (%)</td>
<td>0,1</td>
</tr>
<tr>
<td>S organic (%)</td>
<td>ND</td>
</tr>
<tr>
<td>Pyrite(%)</td>
<td>23,0</td>
</tr>
<tr>
<td>AP (kg CaCO₃/t⁻¹)</td>
<td>304</td>
</tr>
<tr>
<td>NP (kg CaCO₃/t⁻¹)</td>
<td>0</td>
</tr>
<tr>
<td>NNP (kg CaCO₃/t⁻¹)</td>
<td>- 304</td>
</tr>
<tr>
<td>C (%)</td>
<td>5,3</td>
</tr>
<tr>
<td>H (%)</td>
<td>1,0</td>
</tr>
<tr>
<td>N (%)</td>
<td>0,1</td>
</tr>
</tbody>
</table>

Potential (NNP) of the porcelain powder and the Acid Generation Potential (AP), the mass mixing ratios were determined. The ratio obtained between the porcelain dust mass and the coal tail is approximately 10 times, then static tests were performed with the raw material, with a mixture of 10 parts of porcelain powder and one part of coal tailings, were also 15 parts of porcelain tile powder and one part of coal mining tailings were used. The results indicate what the results of the static tests pointed out, that is, if the coal mining tailings are inadequately deposited in the environment, acidity will occur. And we can classify this waste as high-power generating AMD.

Assays with one part of tailings from coal mining added to 10 parts of porcelain powder indicate that it greatly reduces the potential for acidity generation. Even so there is release of acidity by the material, which indicates that this mass ratio still produces acidity. When a higher proportion of porcelain powder material was used, the potential for acidity generation was greatly diminished, even though in a few weeks the pH became slightly acid. The obtained results indicate that this mass mixing ratio can be used to avoid the generation of AMD.

Conclusions

From the results obtained in the present work, it can be concluded that:

- Coal mining in Brazil generates millions of tons of coal tailings, rich in pyrite, that generate DAM with great environmental impact. To solve this problem, companies have invested in effluent treatment plants, with high operating costs. However, an alternative to this operational procedure is the adoption of the practice of alkaline additives in coal mining tailings, thus preventing the generation of this serious environmental problem.

- The porcelain powder was efficient in preventing the generation of DAM, however the ratio of porcelain powder / coal waste mass is quite high.

- Also the porcelain powder can be used as a source of alkalinity in the treatment of acid effluent (DAM), however the dosages should be studied aiming at a lower
generation of sludge in the treatment process of AMD.

**Acknowledgements**

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**References**


Comprehensive approach for mine water management in Vietnamese hard coal mines under transition

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**Abstract**

The R&D project WaterMiner investigates on the example of the mining area Hon Gai (Vietnam) under different spatiotemporal situations how and to what extent the existing water demand in the mines, and parts of the water demand in the surrounding area, can be covered by treated mine water. In the course of harder implementation of environmental legislation as well as transition from open pit to underground mining, there is a need for a comprehensive approach in mine water management. In addition, WaterMiner is developing a planning guidance, how to improve the mine water treatment and surface runoff management.

**Keywords:** hard coal mining, mine water management, comprehensive approach, Vietnam

**Introduction**

Hard coal mining in Northern Vietnam takes place in three different mining areas in Quang Ninh Province, one is located on Hon Gai Peninsula. Both open pit and underground mines are working in the region. They all operate under the parent company Vietnam National Coal – Mineral Industries Holding Corporation Limited (VINACOMIN).

The mine water treatment was improved throughout the last fifteen years, the mine water management is still far from a comprehensive approach (DoNRE, 2016). In the course of harder implementation of environmental legislation and the transition from open pit to underground mining further improvement of mine water management in the area is needed.

The R&D project WaterMiner, funded by the Federal German Ministry of Education and Research (BMBF), focuses on a need-based and efficient reuse and recycling concept of mine water management for current and future situations and the improvement of mine water treatment to satisfy environmental requirements.

WaterMiner consists of the following work packages: project coordination and baseline analysis (eE+E Environmental Engineering and Ecology, RUB Ruhr University of Bochum); data management (Disy Informationssysteme Ltd., Karlsruhe); monitoring information concept (ribeka Ltd., Bornheim); material flow analysis (eE+E, RUB, Ruhr University of Bochum); technical concepts for surface water, sediment and coal sludge management (DGFZ Dresden Groundwater Research Centre, LUG Engineering Ltd., Cottbus; VINACOMIN, Vietnam National Coal and Mineral Industries Holding Corporation Ltd.); economic concepts (Environmental Economics, University of Koblenz-Landau).

**Comprehensive approach for current and future situations**

For current and future situations, the project provides suggestions how to improve the operation of the existing mine water treatment and mine water management by the following steps:

- Temporal analysis – understanding the transition of the mining system
- System analysis – understanding the mine water system
- Spatial analysis – definition of drainage units (DUs)
- Material flow analysis (MFA) – calculating the internal water connections and water flows in the Drainage Units
- Recommendations for improvement
a) Temporal Analysis: Understanding the transition of the mining system
In 2016 (existing situation), 11 mines (open pit (O), underground mining (U), see Figure 1) are extracting coal in Hon Gai. A large number of open pits are scheduled to be closed within the next 10 years (see Figure 1). On the other hand, coal extraction from deep seams by underground mining will increase. As a result, the amount of mine drainage water changes according to location, quality and quantity. This transition has consequences for the whole mining system. The relevant temporal situations of transition are defined as follows:

Existing situation (year 2016-2021), intermediate situation (year 2021-2026) and final situation (after year 2026) (see Figure 2).

The existing situation is divided into phase 1 and phase 2, the other situations have one phase each (phase 3 and phase 4). For all phases a short analysis of the situation is given according to mine water drainage amount, mine water treatment, mine water reuse (internal use and external use) (see Figure 2).

In phase 4 one of the former open pits will be transformed to a pit lake with reservoir and sedimentation function (rainwater, surface runoff).

b) System Analysis: Understanding the mine water system of Hon Gai
The mine water flows consist of groundwater, surface runoff, imported (QUAWACO public water supply) and exported flows (discharge Mine Water Treatment Plant (MWTP)), as well as in-situ rainfall and evaporation. There is no capture of mine waters in the surrounding of the mines (see Figure 3).

Each mine operates at least one mine water treatment plant (MWTP) (see Figure 3). The mine water flows via regulating basins to the MWTPs. In the rainy season and especially during heavy rainfall events mine water is only partially treated (Ulbricht, 2018).

The treated mine water is partially reused inside the mines (internal uses). Additionally, there is a large water demand in the surrounding urban area of Ha Long City, especially during dry season (external uses).

Large storage water entities are not available to reserve surplus water in rainy season, resulting in water deficits in dry season. The surface water runoff is not managed properly due to the lack of a...
comprehensive approach, hydrologic monitoring stations and technology.

c) Spatial Analysis: Mine water Drainage Units
To facilitate an improved mine water management, drainage units (see Figure 4) were defined. They are distinguished by their different topography, hydrology features, mine operation and ownership.

d) Material flow analysis (MFA): Calculating the internal water connections and water flows within the Drainage Units
The Umberto NXT Efficiency software is applied to identify, quantify and assess the potential for the reuse of mine water and to improve the mine water management regarding the different situations of spatial and temporal development of the mining area.

According to the particular situation of the mine water system, the MFA considers the following elements:

a) Mine water sources (pumped water from open pits and underground mines, surface runoff, etc.)

Figure 2 Phases in mining transition in Hon Gai area (eE+E)
Figure 3 Elements of the mine water system in Hon Gai (eE+E)

Figure 4 Drainage Units in Hon Gai (eE+E)
the water consumption for mining purposes will be reduced or decline. At the same time, along with the expansion of industry, urban areas and tourism, water extraction will increase to provide adequate water and satisfy higher water demands.

Therefore, a material flow analysis is a very suitable instrument to combine the results from the temporal, the spatial and the system analysis and the management of mine impacted water flows. The MFA is focusing on the water flows, but also includes other relevant material flows like energy, supplies and sludge.

Furthermore, it also supports economic analyses, which are usually the most important factors for decision makers.

The lack in dynamic modelling can be solved through the use of several models for small time periods in succession.

b) Mine water treatment (regulating basins, MWTP, etc.)

c) Internal use (water for drinking, canteen kitchens, wet coal screening, irrigation of recultivated areas, dust control, industrial cleaning, truck washing)

d) External use (irrigation of public parks, urban greens and golf courses, agricultural areas, industrial users, etc.)

Discussion

Mining operations and their water management underlie spatial and temporal changes. Changes in mine water sources, water treatment facilities, internal uses and external uses are substantial factors controlling mine water management.

As mining sites are closed, mine drainage water will decrease, mine water treatment plants will reduce or stop their operation and the water consumption for mining purposes will be reduced or decline. At the same time, along with the expansion of industry, urban areas and tourism, water extraction will increase to provide adequate water and satisfy higher water demands.

Therefore, a material flow analysis is a very suitable instrument to combine the results from the temporal, the spatial and the system analysis and the management of mine impacted water flows. The MFA is focusing on the water flows, but also includes other relevant material flows like energy, supplies and sludge.

Furthermore, it also supports economic analyses, which are usually the most important factors for decision makers.

The lack in dynamic modelling can be solved through the use of several models for small time periods in succession.
Conclusions

There is high demand for mine water reuse and recirculation in the Hon Gai coal mining area.

Therefore, a comprehensive view at all mines, which are operating in Hon Gai peninsula, is necessary to analyse and compare different temporal situations and develop recommendations for both current and future situation.

A MFA, as the central tool of the developed comprehensive approach, is a suitable instrument for the mine water management. Through variations of the water allocation, worst case analyses etc., improved spatiotemporal situations are generated, which are the basis for management and investment decisions.

Both quality and quantity features of mine water are equally considered for proposing measures for reuse and recirculation.

Acknowledgements

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References


Effects Of Deep Karst Water On The Release Of Potentially Toxic Metal Ions From Coal Gangue In Abandoned Coal Mine Region

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Abstract

A great amount of coal gangue was left out in mine goaf after the mines closed or abandoned, and they underwent the soaking of the groundwater from the underlying aquifers with the release of potentially toxic metals. A series of large-capacity immersion test was conducted to study the metal Mn and its leaching behaviour of coal gangue under different leaching solutions including site Ordovician limestone karst as opposed to three solution pH levels. We obtained the results including XRF, pH, ORP, EC, and the concentration of Mn, which showed a big difference between site karst water and lab solutions with different pH levels. All results may provide reference for security theory and contamination control technology of deep karst water in abandoned coal mines.

Keywords: immersion test, XRF, site karst water

Introduction

Potentially toxic metal ions from coal gangue in abandoned coal mines substantially affect the quality and uses of water supplies in mining area all over the world [Iii CAC 2008; Azam S and Li Q, 2010]. The mining activity of coal mines in Shandong province of China has experienced across the whole century. With the closure and integration of numerous coal mines, safety and environmental issues induced by closed mines have become increasingly prominent, including surface subsidence or landslides, unstable foundations of high buildings or buildings rupture, poor-quality mine water, and surface water or ground water contamination, etc [Hasheela I et al., 2014; Wang LG et al., 2008]. The effect of closed mines on the surrounding environment involves so many aspects, but relatively speaking, groundwater pollution pose more serious threats to human survival [Atanackovic et al., 2016; Xia Z et al., 2007]. After the closure of coal mines, a large amount of solid waste such as the abandoned coal, coal gangue and waste structures are left in the goaf [Zhou HY 2012; Peng B et al., 2018]. When ground water rebound, toxic potentially toxic metals contained in solid waste, such as chromium (Cr), cadmium (Cd), copper (Cu), manganese (Mn), lead (Pb), zinc (Zn) and arsenic (As) are continuously released into the water and cause water pollution [Zheng L et al., 2016; Tang Q et al., 2018]. In recent years, many researches related to potentially toxic metals release or migration focus on the effects of pH levels of leaching solutions, grain sizes of different solid waste, mineral structure, chemical compositions, solid–liquid ratios, temperatures, etc on solid waste during the process of static and dynamic leaching tests [Lin H et al., 2017; Roessler JG et al., 2015; Othmani MA et al., 2013]. In China, especially in North China, a great majority of coal-bearing strata overlay the Ordovician limestone karstic aquifers, which are deeply buried. These coal mines almost have special karst groundwater and large mining depth, whose greater liquidity and hydrochemistry environment sensibility further aggravated the crisis of site karst water contamination in abandoned coal mines. However, very detailed studies of site karst water on the release of potentially toxic metal ions from coal gangue under this special conditions have been reported.

The main objective of this research was to investigate the effect of site karst water using coal gangue as experimental material with regard to potentially toxic metals, and compare its difference from other pH levels of leaching.
solutions. A series of large-capacity immersion test was performed to study the potentially toxic metals and leaching behaviour of coal gangue under different leaching solutions including site Ordovician limestone karst as opposed to three solution pH levels. The release mechanism of potentially toxic metal Mn was investigated, and the relevant influencing factors were analysed and discussed during the leaching process, covering liquid-solid ratio, contact time and temperature, pH changes, oxidation reduction potential (ORP), electrical conductivity (EC), etc. The results are supposed to serve as a reference for the evaluation of potentially toxic metals pollution of Ordovician limestone water occurring in abandoned or closed coal mines and the forecast of the ecological risks induced by coal gangue, and examine the safety for applying coal gangue to the goaf.

Methods
In this paper the study area is Baizhuang coal mine, which is located in the west wing of Taishan Mountain and at the southern foot of famous Taoshan Mountain (seen in Fig 1). It lies in Midwest of Feicheng coal field, located in Feicheng, Shandong Province, east of China. The range of coal mine is west to fault F\textsubscript{7} and adjacent to Chazhunag coal mine and Guozhuang coal mine, north to fault F\textsubscript{1-1} and fault F\textsubscript{1-2}, east to fault F\textsubscript{21} and adjacent to Taoyang coal mine, south to fault F\textsubscript{3-1} and adjacent to fault BF\textsubscript{5} along with Xinglong coal mine. Baizhuang coal mine has its strike of about 4 km long, inclination of about 3.9 km wide, and area of 15.6708 km\textsuperscript{2}. The regional stratigraphic classification of Baizhuang coal mine belongs to stratigraphic subregion of western Shandong in North China, and the whole area has steady deposition. Its strata thickness, lithology, and stratigraphic contacts are essentially the same as for stratigraphic subregion of western Shandong. And its strata correspond to Quaternary, Permian, Carboniferous, Ordovician and Cambrian from above to below respectively. Baizhuang coal mine is surrounded by faults, and its northern part is influenced by the traction of boundary F\textsubscript{1} fault to form an accompanying asymmetric syncline along the F\textsubscript{1} fault group. In this area there has quite a few aquifers such as Quaternary sandstone aquifer, first, second and fourth limestone aquifers of Taiyuan Formation, fifth and sixth limestone aquifers of Benxi Formation and Ordovician limestone aquifer. Moreover, Ordovician limestone aquifer has strong water yield property, adequate recharge water and close hydraulic relationship with the fifth limestone aquifer. For karst coal mines in North China, the strong Ordovician limestone aquifer often poses a huge threat to coal seam floor, especially for the closed or abandoned mines, Ordovician water always flow into the goaf and react with the leftover coal gangue.

Fresh coal gangue exactly mined out from Baizhuang coal mine were collected as the main experimental samples. After five samples (roughly 1 kg each one) gathered in the tunnel of the buried depth of 430 m and stored in clean polypropylene bags, a process of sample pooling and crushing was conducted, and then the coal gangue with 3–8 mm in diameter was sieved to homogenize for subsequent analysis by use of classifying (seen in Fig.2). After that these coal gangue solutions.
samples were dried for 24 h at 105°C, which were finally placed in an airtight container as the samples of immersion test. Whereas Ordovician limestone water samples were collected from full hole of east wing belts I located in the drilling O\textsubscript{38} of 8506 working face in this coal mine, and then they were stored in polyethylene bottles and brought into the lab.

According to the experience of immersion research, this test was conducted to study the release of potentially toxic metals at the solid: liquid ratio 1:10 (g/mL). An equivalent amount of coal gangue samples was weighed and put into large beakers with the leaching solutions including site karst water, pH= 5.3, 7.3, and 9.3 (marked respectively A, B, C, and D, seen in Fig. 2). The initial pH value of three leaching solutions was selected in view of pH level of site karst water (pH=7.3), which was adjusted with diluted H\textsubscript{2}SO\textsubscript{4} or NaOH. One hundred and sixty gram of gangue sample was mixed with 1600 ml leaching solutions in large-capacity beakers, which were shook in stable temperature Horizontal shaking bath with oscillation frequency of 80 r/min and amplitude of 20 mm at 25°C. After a certain shaking time (12 h, 24 h, 36 h, 48 h, 72 h, 96 h, 144 h, and 216 h), 10 mL leaching solution was taken out from the beakers and then was kept under seal and labelled as testing solutions. Notably, the leaching solutions need to be stirred for one hour before sampling, and after that a supernatant liquid resting for half an hour was extracted and finally filtered into polyethylene bottles using a 0.45 μm aperture microporous membrane and stored at 4 °C until experimental analysis. After four testing solutions were collected, the content of potentially toxic metal Mn was determined by ICP atomic emission spectrometer (ICP-AES). The value of pH, ORP and EC was determined by Hach Hydrolab Multi-Parameter Water Quality Analyzer. 36 testing solutions were obtained for this experiment.

**Results and discussion**

**XRF analysis of coal gangue**

The major elements content and potentially toxic metal elements content in the original coal gangue sample were determined using X-ray Fluorescence Spectrometry (XRF) at Shandong University of Science and Technology, which are shown in Table 2. The XRF results revealed that SiO\textsubscript{2} was major constituent. From this table, we can see that the main potentially toxic metal was Mn (0.217 g/kg).

**Results of immersion test**

Through Hach Hydrolab Multi-Parameter Water Quality Analyzer, we can acquire the pH, ORP and EC of coal gangue at different solutions over time displayed in Fig. 3. As we all know, pH is one of the important parameters to measure the extent to environmental degradation. From Fig.6 we can know that the changing trend of all pH curves is consistent on the whole. After 36 h
the pH changing curves of C and D samples remained stable, but that of A and B samples have a big drop down to 8.28 after 72 h and to 8.26 after 216 h respectively. Although initial pH values vary, the variation range of all pH values at four kinds of solutions has been primarily centered on pH of 8-8.7 throughout time, which maintain the weakly alkaline. It also showed the acid buffering capacity of coal gangue. Due to this capacity the pH values of four solutions including site karst water could keep constant for a long time [Lin H et al., 2017]. Moreover, every testing pH value of sample at a solution of site karst water after 24 h (A) was almost higher than that of three other immerse solutions (B, C and D), the pH values of all solutions were successively observed, A>B>D>C, which indicate the effect of site karst water on coal gangue differs considerably from lab configuration cases in terms of solution pH. Additionally, there is a substantial difference of pH variation over time at A and C samples with the same pH of 7.3. The pH at A sample over time fluctuated larger than that at C sample, the former varies from 7.3 to 8.7, mostly at pH of 8.5 above, yet the later with almost no change, mostly at pH of 8.0. Again, it confirmed that the different effect mechanism of site karst water.

It is well known that electrical conductivity (EC) reflects the activity of the electrolyte in solutions (that is, ion concentration), which can also show the interactive intensity between solid phase and liquid phase. The EC values of all solutions were observed in the following order, C>A>D>B. It can been seen from Fig.6 that the conductivity at a solution of site karst water (A) first increased up to 733 μS/cm slightly after 36 h and then fluctuated up or down from 661 μS/cm to 764 μS/cm, and finally decreased all the way up to 636.3 μS/cm after 216 h, with the EC values ranging from 1098 μS/cm to 1291 μS/cm. Compared with A, the conductivity at a solution pH of 7.3 (C) has a similar changing trend, and it fluctuated first from 1098 μS/cm to 1291 μS/cm, and then decreased to 1146 μS/cm from 96 h to 216 h, with the EC values ranging from 636.3 μS/cm to 764 μS/cm. Whereas the conductivity at a solution pH of 5.3 and 9.3 (B and D) over time had nonlinear growth, changing from 1.2 μS/cm to 76.3 μS/cm (B), from 25.4 μS/cm to 92.6 μS/cm (D), respectively. The two samples increased faster in early stage before 96 h than that in later stage. Meanwhile, there is almost a difference of 15 μS/cm between the two solutions, and the conductivity variation of the two solutions over time can be calculated by solving the fitting formula, namely, EC=-0.0016T2+0.6536T+6.7655 and EC=-0.0013T2+0.5829T+25.178, where EC is the conductivity value, and T is the immerse time. And the correlation coefficient is 0.983 and 0.993, respectively. From the above results, we can also know site karst water (A) has a relatively higher ion concentration except C.

As we can see from the above, the pH and EC of all solutions nearly reach unchanged after 96 h, thus reflecting that the dissolution and precipitation of minerals in coal gangue maintaining a dynamic balance. Additionally, the pH changing curve of A sample has a drop after 72 h, and yet with a growth in its EC value at the same time, indicating the minerals in coal gangue dissolved in growth and thus hydrogen ions in growth. Though the ORP values of all solutions in a relatively low level, presenting a weaker redox environment [Lin H et al., 2017], the ORP value of A sample remarkably increased to that close to

![Figure 3 pH, ORP, EC, TDS and DO of coal gangue at different solutions over time.](image-url)
the maximum after 72 h with highest level in ORP values of four solutions, which showed a relatively higher degree of redox reaction and consisted with the former analysis. All ORP curves fluctuated greatly and decreased overall with a similar variation tendency, and the ORP values of all solutions were observed in the following order, C>A>B>D. There is a higher redox environment after 24 h and 72 h among the four solutions. Moreover, A and C samples curves developed more alike except initial ORP value and that after 72 h, accounting for similar redox environment.

Through ICP atomic emission spectrometer (ICP-AES), we can obtain the concentrations of Mn of coal gangue at different solutions over time depicted in Fig.4. From Fig. 4 we can know that the dissolved quantities of potentially toxic metal elements in coal gangue at different solutions present a approximately similar trends. The dissolved process can be divided into three phases: earlier phase (0-24 h), medium phase (24-144 h) and later phase(after 144 h). The release rate of Mn in earlier immerse phase was very fast and fluctuated greatly, mainly due to the sufficient contact between immerse solutions and the particles of coal gangue with an instable process, causing the quick and instable dissolving of the potentially toxic metals in samples. Then the release rate of Mn in medium phase got relatively slow, mainly because of the blocking of contact channel between immerse solutions and the particles of coal gangue induced by the dissolution of minerals. After that the release rate of Mn in the later phase got more slow and more dispersed than that in medium phase, and later immerse. In addition, compared with the other three samples (B, C and D), the release rate of Mn in sample A was the lowest, but the highest after 24-36 h, and then decreased to a minimum towards the end of immersion, resulting in lower release rate of Mn at the solution of site karst water than that at different pH solution in the lab, perhaps due to more superior self purification capacity, except transient peak in medium phase. However, the curve in sample D (pH=9.3) maintained the highest point during the medium and later phases, indicating the more easily released ability of Mn in slightly alkaline condition than other three conditions.

Conclusions

A series of large-capacity immersion test was conducted to study the Mn and its leaching behaviour of coal gangue under different leaching solutions including site Ordovician limestone karst as opposed to three solution pH levels, the results of XRF, pH, ORP, EC and concentrations of Mn was obtained and analysed. It can be founded that (1) SiO$_2$ was major constituent and Mn was almost the highest content of potentially toxic metal from coal gangue. (2) although initial pH values vary, the effect of site karst water on coal gangue differs considerably from lab configuration cases in terms of solution pH. From EC values, site karst water (A) has a relatively higher ion concentration except C. From ORP values, A and C samples curves developed more alike except initial ORP value and that after 72 h, accounting for similar redox environment. (3) there was a lower release rate of Mn at the solution of site karst water than that at different pH solution in the lab, perhaps due to more superior self purification capacity. All results may provide reference for security theory and contamination control technology of deep karst water in abandoned coal mines.

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References


Pre-treatment of coal dump leachate with MgO for pigment recovery

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Abstract
Mine water rich in metals requires sustainable and cost effective treatment that leads to recovery of resources. Consequently, this investigation was aimed at identifying a process for recovering clean water and saleable products such as pigments from iron-rich acid mine water. For this, MgO was used to remove iron as Fe(OH)3, which was converted through drying at 80°C to goethite (yellow) and at 700°C to haematite (red). Na2CO3 was used for removal of the remaining metals (Mn2+ and Ca2+) as carbonates. The pre-treated water is desalinated with RO to produce a permeate (TDS = 105 mg/L) and a brine of 85 069 mg/L. The brine is further concentrated by freeze crystallization up to a TDS of 336 820 mg/L. This is concentrated enough for the recovery of MgSO4.7H2O.

Key words: Acid mine water, ROC process, Freeze crystallization, pigment, magnesium oxide, magnesium sulphate

Background
Acid mine drainage (AMD) from mining activities is a major environmental concern in South Africa as it requires neutralisation and desalination. Sludges generated during neutralisation are rich in metals such as Fe2+, Fe3+, Al3+, Mn2+, Co2+ and Ni2+ and needs to be handled as toxic waste. Furthermore, the sludge generated during desalination is often rich in CaSO4.2H2O and Mg(OH)2. Legislation requires that mine water should be treated to drinking water quality and ideally, there should be zero-waste. These requirements imply that both neutralization and desalination are to be implemented and that any waste needs to be transported to a registered and approved toxic waste disposal site. Near zero-waste processes have a further benefit in that they allow for the recycling of a large portion of the treatment chemicals. This recycling has the benefit of generating income through the recovery of saleable by-products, thereby reducing operational costs of treatment.

In the reverse osmosis/cooling (ROC) process (see Figure 1), acidic or neutral mine water is treated with Na2CO3 and/or NaOH and/or MgO in the pre-treatment stage to allow selective precipitation of metals (Fe(OH)3, Al(OH)3, CaCO3, MnO2 and Mg(OH)2 (Akinwekomi, et al., 2016; Maree & Mtombeni, 2018; Maree, et al., 2018; Magagane, et al., 2019). After pre-treatment, the sodium-rich water is passed through a membrane stage to produce drinking water and brine. The brine has a concentration high enough to allow Na2SO4 crystallization upon cooling. In the improved ROC process MgO is used in the pre-treatment stage with the aim to recover MgSO4 from the brine treatment stage, which can be used as raw material for fertilizer manufacturing.

Objectives
This project attempted to answer the following questions, which can also be formulated differently as objectives: (i) Can MgCO3 or MgO be used for neutralization of acid mine water?; (ii) Can pigment be recovered from iron-rich mine water when neutralized with MgO?; and (iii) can magnesium sulphate be recovered from the brine after neutralized
water is desalinated with RO and the RO brine is further treated with freeze crystallization?

Materials and Methods

Feedstock

Leachate from a waste coal disposal dump was used as iron source. Mg(OH)$_2$ (analytical grade), magnesite (MgCO$_3$) and MgO were used as magnesium alkalis. Charmotte Holdings supplied the magnesite and MgO.

Equipment

The following pieces of equipment were used: Beakers (600mL), pH meter (Ohaus, Starter3100m), mechanical stirrers (IKA, RW 20 digital), thermometer and hot plate stirrers (Heidolph MR 3001k).

Procedure

Gran titrations were carried out by titrating 5 g of a magnesium alkali salt in 100 mL water with 0.05 mol/L H$_2$SO$_4$. Beaker studies were carried out to determine the rate of neutralization with magnesium alkalis. Beakers (600 mL) were filled with acid water (500 mL) and stirred at 250 rpm. At time zero the magnesium alkali was added. Samples were taken at regular intervals (10, 30, 60 and 120 minutes), filtered, pH recorded and analysed for acidity conductivity, Fe and Mg. Further, the effects of the following parameters were investigated over the given reaction time: Mg(OH)$_2$ dosage, MgO dosage and temperature (20°C to 80°C).

Analysis

Samples were collected at various stages in the treatment process, filtered (Whatman No 1), pH recorded and analysed for, acidity and magnesium using standard procedures (APHA, 2012). Acidity was determined by titration to pH 8.3 using standard 0.1 M NaOH. The magnesium concentration was analysed using ICP.

Modelling

The OLI ESP software program was used to predict the behaviour of metals dissolved in water when treated with alkalis such as MgO and NaOH (OLI, 2015). OLI is an aqueous equilibrium chemistry estimator with an interactive and self-instructive interface for clarifying reactions, the ability to work with all kinds of common equilibrium reactions, a strong solution algorithm, expressive and easily understandable displays for results, and the ability to produce results in multiple formats according to different uses. The Stream Analyzer of OLI was used to perform single point equilibrium calculations, multiple point survey calculations for calculating a complete trend analysis for characteristics such as temperature, pressure, pH and composition effects, and simple mix and separate capability. The calculations provide liquid- and solid-phase separations for a specialized model.

The OLI Analyser 9.0 System was used to simulate the reactions by running a
simulated AMD sample with assumed values of temperature, pressure and pH. The base titrants used were Na₂CO₃, MgCO₃, Mg(OH)₂ and MgO. The effect of temperature on the solubility of MgSO₄ and Na₂SO₄ was determined for when MgO was used for neutralization to pH 3.2, followed by Na₂CO₃ to raise the pH to 8.6. Once the input values were run in the OLI Systems Chem Analyzer, a calculated summary of the simulated results would appear. This could be used to predict the actual reactions to use in the treatment methods according to the specific characteristics. Thus it was used to optimize a neutralisation-precipitation-desalination process for AMD.

Results and Discussion
Neutralization with magnesium alkalis
In the ROC process sodium or magnesium alkalis can be used during pre-treatment of sulphate-rich acidic effluents. Both Na₂SO₄ and MgSO₄ have high solubilities (Na₂SO₄: 262.4 g/L and MgSO₄: 226.1 g/L at 25 °C) and therefore no chemical scaling will form on the membrane in the subsequent RO stage. As MgSO₄ is a raw material for fertilizer manufacturing it is the preferred alkali to use. A limitation of magnesium alkalis is their low solubilities. In pure water at 25°C MgCO₃ has a solubility of 12.04 mmol/L (292.6 mg/L) (as Mg) and MgO a solubility of 0.1 mmol/L (2.43 mg/L) (as Mg). OLI software showed that MgCO₃ is converted to MgCO₃·3H₂O (nesquehonite) and Mg(OH)₂ (brucite) when contacted with water.

OLI software predicted that, according to thermodynamic data, all magnesium salts will react with H₂SO₄. Gran titrations (Figure 2) show the behaviour of 123.7 mol/L MgCO₃ (magnesite) and MgO, when reacted with H₂SO₄. Predicted values with OLI software showed that with MgO the pH gradually dropped from 10.3 to 9.2 when the H₂SO₄ dosage was increased from 0 to 123.7 mol/L. Thereafter the pH dropped rapidly to 2.2 and lower, as expected when a strong acid is reacted with a strong alkali. Figure 2 also compared the effect of MgO on pH (as predicted by OLI and when carried out experimentally). In the case of actual MgO (85%; 75μm particle size) it was determined that 62% of the mass of MgO reacted with H₂SO₄. The utilization of MgO amounted to 74% (62.9 / 85.0 × 100). Unreacted MgO particles were observed. It was concluded that fine MgO with a particle size of less than 20 μm needs to be used for neutralization.

Kinetics of neutralization
MgCO₃ has a higher solubility than MgO (12.04 mmol/L versus 0.10 mmol/L). It was expected that MgCO₃ would be the preferred magnesium alkali for neutralization of iron-rich acid water. Surprisingly, it was found that MgCO₃ did not neutralize acid water rich in iron. It was assumed that MgCO₃ reacted with Fe³⁺ and formed a layer of Fe₃(PO₄)₂ on the surface of MgCO₃ particles, to prevent further dissolution. The focus was then shifted to Mg(OH)₂ and MgO for neutralization.

Figures 3 and 4 show that both Mg(OH)₂ and MgO can be used for neutralization of acid water rich in Fe³⁺. Figure 3 shows the effect of Mg(OH)₂/H₂SO₄ mol ratio on the rate of neutralization of a mine water containing 6 000 mg/L acidity (as CaCO₃) at 25 °C. It was noted that the rate of neutralization was related to the concentration. At a mol ratio of 1.0 a long reaction time of more than 120 min was required. This can be ascribed to the low solubility of Mg(OH)₂ of 2.43 mg/L (as Mg(OH)₂). This was expected and the reason why alkalis with higher solubilities are normally used for neutralization such as Ca(OH)₂ (0.173 g/L), Na₂CO₃ (21.5 g/L) and NaOH (109 g/L). This shortcoming of Mg(OH)₂, as an alkali can be overcome at increased temperatures and extending reaction times. Complete neutralization was achieved after 1 440 min at a Mg(OH)₂/Acidity mol ratio of 1.3.

Figure 4 shows the effect of the MgO/H₂SO₄ mol ratio on the rate of neutralization of mine water at 60°C containing 6 000 mg/L acidity (as CaCO₃). The particle size of the MgO was 75μm, i.e. larger than the 20μm of the Mg(OH)₂ used as depicted in Figure 3. It was noted that the increased MgO/Acidity mol ratio resulted in an increased rate of neutralization. MgO like Mg(OH)₂ can be used for neutralization, provided that a long reaction time is provided, fine particle size is used and the temperature is increased. Figure
shows that at 60°C complete neutralization was achieved after 120 min compared to much longer times required at 25°C.

**Pigment recovery**

The Fe(OH)$_3$ was produced by adjusting the coal leachate with MgO to pH 3. After separation of the Fe(OH)$_3$ from the water, the Fe(OH)$_3$-sludge was dried and heated to various temperatures. Goethite (yellow) was produced at 80°C, haematite (red) at 650°C and magnetite at pH 10 and 100°C (Figure 6).

**Water quality**

Table 1 shows the water quality before acid mine water was treated with MgO for neutralization and pigment recovery, RO for desalination and freeze crystallization for brine treatment and MgSO$_4$ recovery. It was noted that Fe(OH)$_3$ can be recovered by raising the pH with MgO to pH 3, pure water can be recovered through RO treatment, and brine with a high TDS of 80 g/L can be produced. The brine can be further treated with freeze crystallization to produce solid MgSO$_4$.7H$_2$O (72 284 mg/L) and a brine containing 54 479 g/L Mg$^{2+}$, 21 737 mg/L Na$^+$ and 256 791 mg/L SO$_4^{2-}$.

**Conclusions**

It was found that MgO can be used for removal of iron from iron-rich mine water as Fe(OH)$_3$. Fe(OH)$_3$ can be converted to goethite (yellow pigment) by drying at 80°C and to haematite (red pigment) at 700°C. Na$_2$CO$_3$ can be used for the removal of the remaining metals (Mn$^{2+}$ and Ca$^{2+}$) as carbonates. The pre-treated water can be desalinated with RO to produce a permeate with a TDS of 104.7 mg/L and a brine with a TDS of 85 069 mg/L. The brine can be further concentrated by freeze crystallization to

![Figure 2. Gran titration when 5 g/L (123.7 mmol/L) magnesium alkali is treated with H$_2$SO$_4$](image)

![Figure 3. Effect of Mg(OH)$_2$/Acidity ratio on neutralization rate (Temp = 25°C; Mg(OH)$_2$, Particle size = 25 μm; Mg(OH)$_2$ purity = 92%)](image)
Figure 4. Effect of MgO/Acidity ratio on neutralization rate (Temp = 60°C; MgO, particle size = 75 µm; MgO, purity = 75%; MgO/Acidity ratio =1.0)

Figure 5. Effect of temperature on neutralization rate (MgO particle size = 75 µm; MgO purity = 75%; MgO/Acidity ratio =1.0)

Figure 6. A furnace was used for calcination to produce goethite (yellow pigment) and haematite (red pigment). Haematite can be produced from goethite. Magnetite is produced as shown (Akinwekomi et al. 2016)

produce a brine with a TDS of 336 820 mg/L and 72 284 mg/L MgSO₄·7H₂O (epsomite).

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## Table 1. Predicted water quality (OLI software)

<table>
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<th>Parameter</th>
<th>Feed (mg/L)</th>
<th>MgO (mg/L)</th>
<th>Na$_2$CO$_3$ (mg/L)</th>
<th>RO (mg/L)</th>
<th>Permeate (mg/L)</th>
<th>Brine (mg/L)</th>
<th>Melted ice (mg/L)</th>
<th>Brine (mg/L)</th>
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<td>4.1</td>
<td>9.3</td>
<td>6.9</td>
<td>6.9</td>
<td>7.1</td>
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<td>H$_2$O</td>
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<td>1 660</td>
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<td>SO$_4^{2-}$</td>
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<td>7 798</td>
<td>7 805</td>
<td>7 814</td>
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<td>100.0</td>
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<td>Fe(OH)$_3$ (Bernalite)</td>
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<td>FeCO$_3$ (Siderite)</td>
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<td>MnCO$_3$ (Rhodochrosite)</td>
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<td>MgSO$_4$.7H$_2$O (Epsomite)</td>
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<td></td>
<td>72 284</td>
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<td>CaSO$_4$.2H$_2$O (Gypsum)</td>
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<td>643</td>
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<td>Suspended solids</td>
<td>-</td>
<td>3 432</td>
<td>687</td>
<td>1 137</td>
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<td>-</td>
<td>72 927</td>
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<td>Osmotic pressure (bar)</td>
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<td>17.2</td>
<td>71</td>
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<td>Salt removal (%)</td>
<td>99.0</td>
<td>96.0</td>
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### References


Aquifer Rebound Investigation at a Defunct Coal Colliery in South Africa

P. J. H. Lourens¹, P. D. Vermeulen¹, A. Allwright¹

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Abstract
The Institute for Groundwater Studies at the University of the Free State has been appointed to investigate the aquifer/aquifers response at a defunct coal colliery in South Africa. The investigation was required to determine possible risks to the natural aquifer systems to enable the mining company to obtain a mine-closing certificate. A numerical groundwater model was developed using the FEFLOW software package. The pre-mining conditions suggests that the seepage areas along the tributary draining the area was naturally susceptible for seepage conditions and mine water discharge will occur if a pathway exits.

Keywords: Aquifer Rebound, Defunct Mine, Numerical Model, Seepage, Monitoring

Introduction
The Institute for Groundwater Studies at the University of the Free State has been appointed to investigate the aquifer/aquifers response at a defunct coal colliery in South Africa. The colliery includes three subsections, the Main Underground Operation, the Strip Mine Operation and the Secondary Underground Operation (Figure 1). All mining operations ceased in 2005 and rehabilitation of the Strip Mine Operation have been completed. The investigation was required to determine possible risks to the natural aquifer systems to enable the mining company to obtain a mine-closing certificate.

Hydrogeological and Hydrological Regimes
The local groundwater regime within the mining rights area comprises the following hystratigraphic subdivisions:
I. The shallow (weathered) groundwater regime associated with Quaternary deposits of the Karoo Supergroup i.e. alluvium, colluvium and weathered Karoo rocks.
II. The intermediate (fractured) groundwater regime associated with hard fractured Karoo rocks i.e. sandstone and dolerite of the Karoo Supergroup.
III. The deep groundwater regime associated with pre-Karoo rocks i.e. karst aquifer comprised of dolomitic rocks of the Transvaal Supergroup.
IV. The unnatural groundwater regime (mine groundwater regime) – resulted from mining and has changed the hydrodynamics of the coal mined areas.
V. The ashfill groundwater regime (artificial) associated with the filling of fly-ash within the Colliery’s defunct mining areas (See Figure 1 for Ashfilled areas).

The mining rights area is drained by two non-perrenal streams and their tributaries. The non-perrenal streams joins the main river draining the area north of the defunct mining operations (Figure 1).

Topography and Rainfall
The topography ranges between 1500 and 1421 mamsl, sloping towards the north. The annual mean rainfall is approximately 599 mm (last 25 years), mainly occurring in the summer season in the form of thunderstorms.

Methods
To evaluate and create a conceptual understanding of the study area, all available historical groundwater monitoring data was converted into a format that is compatible with the WISH software package. After evaluation of the historical data, down-the-hole chemical profiling was conducted on existing monitoring boreholes, using an YSI-Multi-parameter probe, to determine if there
Figure 1 Site Layout map – blue circles represent borehole locations

Figure 2 Mean Monthly Rainfall – SA Weather Station 0438784-3 (Source: SA Weather Service, 2008)
is any physical or chemical stratification in the aquifers. A numerical groundwater model was developed using the FEFLOW software package. FEFLOW uses the Finite Element Method in its modelling calculations (Wasy, 2004). The model was developed in a staged manner, initially a steady state pre-mining model was created to analyse the groundwater flow before mining took place. Building on this, a steady state model for mining conditions to analyse the groundwater flow in response to mining influences. The model for mining conditions simulates the current groundwater equilibrium and was calibrated with the latest water levels. After steady state model calibration, various scenarios was considered to assess groundwater conditions at the colliery.

Results and Discussion
The extensive groundwater level monitoring data indicates that the mining voids of the underground operations are completely filled with water (Figure 3). The volumes of water in the mine voids came from various sources which include recharge from rainfall, overlying aquifers and the underlying dolomitic aquifer system. The water levels of the shallow and intermediate groundwater regime have recovered since mining ceased (Figure 4) and the mine voids left to be flooded, that the natural groundwater level has recovered to its natural state before mining commenced.

The water quality of the groundwater regimes have a great variability within each regime (Figure 5). The water types for the shallow groundwater regime varies between Na-HCO₃ and Na-Mg-HCO₃ types. The water types for the intermediate groundwater regime varies between Na-HCO₃, Ca Mg HCO₃ and Ca-Cl types. The water types of the deep groundwater regime varies between Na-HCO₃ and Ca-Mg-HCO₃ types. The water types of the mine groundwater regime varies between Na-HCO₃, Ca-Mg-HCO₃, Ca-SO₄ and Na-SO₄ types. The water types of the ashfill groundwater regime varies between Na-HCO₃, Ca-Mg-HCO₃ and Na-SO₄ types.

The groundwater regimes all indicates a sodium enrichment. Sodium enrichment is typically related to waste water discharge, dewatering of deep mines or natural deterioration of the groundwater quality by ion exchange within a aquifer (Figure 6). Therefor the Na-HCO₃ type samples can indicate an influence from the underlying coal mine, or longer resisdence times could cause the sodium enrichment (Figure 7). However, the low sulphate concentrations of the shallow, intermediate and deep groundwater regimes provide evidence for the natural deterioration of the groundwater quality, whereas the sodium and sulphate enrichment in the mine and ashfill groundwater regimes are related to the underground coal mining and ashfilling conducted, respectively.

Down-the-hole chemical profiling was conducted at 31 boreholes and the results are summarized as follows:
I. No stratification is evident in the shallow, deep and ashfill groundwater regimes.
II. Of the six intermediate boreholes profiled, one borehole to the south indicates stratification.
III. Of the 14 mine boreholes profiled, three
Figure 5 Piper diagram plot of the water qualities of all the groundwater regimes

Figure 6 Expanded Durov diagram plot of the water qualities of all the groundwater regimes
show signs of stratification (one to the south and two to the north).

The southern-most Main Underground Operations was first to fill up, and the longer flooded period and distance from the upward groundwater flow are most likely the reason for stratification at the southern most boreholes. The majority of non-stratified boreholes indicates that mixing of water between the mine and upper aquifers is taking place.

Above zero pressurised areas, or rather where the groundwater level intersects the surface, simulated by the pre-mining model (i.e. no mining voids and dewatering) are found along the eastern non-perrenial stream. Therefore suggesting that the current discharge area was naturally susceptible for seepage conditions, but the appearance of mine water at the ground surface would only occur if a pathway existed. The model shows the discharge area was naturally susceptible for seepage conditions. This hypothesis advocates that mine water was going to discharge in this area (if a pathway existed), regardless of ash backfilling in the mining voids.

The numerical mining model was used to used for different scenarios to analyse the current and most important groundwater flow processes and influences:

I. Scenario 1 considered the contribution to the groundwater system from the underlying Pre-Karoo dolomites, which was found to be variable between areas where groundwater is moving from the underlying dolomites into the mine voids, and other areas where groundwater is moving from the mine voids into the underlying dolomite.

II. Scenario 2 incorporated subsidence into the mine model to simulate the effect of ground surface subsidence on the groundwater flow system, by increasing the hydraulic conductivity and recharge in these areas. The subsidence areas increased the recharge to the groundwater system, and potentially aids the upward flow at the current discharge areas.

III. Scenario 3 incorporated the ash-backfilling of the mining voids at Main Underground Operations to investigate the effects on the groundwater system. The incomplete ash-backfill scenario, 50% of mine height within current ash-backfill areas, was found to form a combination of the two extreme cases (complete and no ash-backfilling), where the velocities within the mine void are partially retarded by the ash-backfill, and downward flow from the mine void in the northern limits is more prominent than in the no ash-backfill scenario, yet not as dominant as in the complete ash-backfill scenario. These simulations lead to the formation of a hypothesis where completing the ash-backfilling could potentially reduce the current discharge volumes.

IV. Scenario 4 incorporated a fault into the opencast mine area to more realistically represent the groundwater system within the Strip Mine Operation. The southern final void (active water abstraction) was analysed with the numerical groundwater model and it was found that groundwater flows into the void from the south, west and east; and flows out from the void along the northern border. Considering the four additional modelled scenarios without abstraction and the fact that the measured levels in the northern final have maintained a lower water level over an extended time period, the maintained water level in the southern final void could be lifted for a trial period to observe the groundwater system response.

The Australian Groundwater Modelling Guidelines established by Barnett, et al. (2012) were utilised to define the confidence-level of a model, where Class 1 is a low confidence model, and Class 3 is a high confidence model. These criteria for model confidence were analysed, and an overall model confidence of Class 2, medium confidence, was decided for the developed numerical groundwater model for the Sigma area.

Conclusions

All the underground workings are completely flooded and mixing of water between the mine and upper aquifers is taking place. According to the water level data, it is plausible that the natural groundwater level has recovered to its natural state before mining commenced. The pre-mining conditions suggests that the seepage areas along the tributary draining
the area was naturally susceptible for seepage conditions and mine water discharge will occur if a pathway exits. Therefore, regardless of the ash-backfilling (coal power station ash-slurry) of the underground mine voids, seepage would have still occurred at these areas, however, ash-backfilling could potentially reduce the current discharge volumes, if the right methodology is followed. The risk of suspending active pumping from the southern final void for a monitoring period is low, as long as the level in the northern final void remains stable.

References

Figure 7 Over pressurised areas within the pre-mining numerical model (plan view-top) – red dashed line indicates the cross-sectional line of the cross-section
A case study of the importance of hydrogeology to mitigate environmental and technological challenges associated with mine closure options

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Abstract

Kromdraai is a coal operation in South Africa approaching closure. The most substantial closure issues relate to the lack of progressive rehabilitation affected by topsoil shortages, which exacerbate the generation of acidic metalliferous mine water. This is complicated by complex interactions between surface and groundwater associated with historic underground and adjacent open cut mining.

This paper focuses on the phased multi-disciplinary development of an integrated hydrogeological conceptual model, collation and interpretation of historical data, geophysics, hydrogeological data to develop a high confidence numerical flow and transport model to simulate various post-closure water management scenarios. The model provided more accurate discharge volumes and locations, which reduced the uncertainty associated with the initial discharge prediction, resulting in a reduction from 10 to less than 5 ML AMD/day mitigating water related closure costs substantially.

Trade-off studies with cost benefit analysis were completed and considered various improved surface rehabilitation and water treatment options to address long-term closure liabilities. Critical to closure liability reduction is ingress management in the form of optimised surface rehabilitation as this results in reduced polluted mine water generation and allows for the implementation of more cost-effective passive treatment systems.

Keywords: Hydrogeology, GIS data Collation, Geophysics, Numerical Modelling, Mine Closure, Rehabilitation, Trade-off Studies

Introduction

Kromdraai is a coal operation in South Africa that is approaching closure with mining ceasing at the end of 2018. It was determined in 2014 that water management options needed further study specifically to quantify water discharge volumes, quality of discharge and water discharge locations post closure.

The mine has substantial dispersed AMD across the footprint, which is complicated by the complex interaction between surface water and groundwater associated with historic underground and current open cast mining. The current water management strategy involves the operation of a liming plant, dosing of water with caustic soda, management of water levels in pits, and future extraction of water through bores for potential reverse osmosis (RO) treatment at the eMalahleni Water Reclamation Plant (EWRP). Previous hydrogeological estimates (Hodgson, FDI et al., 2007) indicated a post closure requirement for active treatment of 8 ML/day in perpetuity at a cost of more than ZAR2.5billion (150-year period). There are hence substantial business drivers to
reduce or eliminate this requirement for in perpetuity treatment using RO.

Key to understanding the post-closure water management risk is an understanding of the mitigation measures that will reduce rainwater infiltration and the effect it will have on discharge water volumes and quality. Hence, a robust hydrogeological conceptual model, qualifying the groundwater flow regime, recharge rates and areas as well as discharge mechanism and hydrogeological and geochemical controls influencing the groundwater flow and quality over time was developed.

The conceptual flow and transport models were translated into a calibrated numerical groundwater flow and transport model for the site and the model was used to inform possible water management scenarios at closure. The objective of this paper is to highlight how the project identified the most cost-effective long-term scenarios that will ultimately be developed into an executable long-term post-closure water management solution for the site that is cost-effective and delivers an acceptable risk profile.

Methods
The development of a long-term post closure water management solution, included the following steps, outlined in more detail below.

Collation of all existing data into a single GIS database
All existing mine plans, including historic aerial photographs, historical mine plans and the latest aerial images, were obtained from various sources and collated, ensuring all data was in the correct mine coordinate system. Due to the nature of the project, the primary focus was on where mining had taken place, when this had occurred and what rehabilitation had been done. As the information was collated, care was taken to ensure that all data was in the correct mine coordinate system; specifically, LO29, and using the Cape Datum. Once all the readily available data had been collated, it was noted that the exact location of the key historical shafts and declines was missing, and the old Blackstone Colliery, right next to Kromdraai. The above missing information and understanding the locality of discharge points were a key component in formulating a closure strategy. The corporate office aerial photography archives were accessed, and three iterations of photography were found over Kromdraai Colliery from 1971, 1972 and 1986. All the collated historical data overlays were consolidated into an ArcView data base and used to plan the geophysical surveys and subsequent hydrogeological intrusive programme. Historical mine rehabilitation data, showing the temporal, spatial and quality of mine rehabilitation are included.

Geophysical delineation of structures and intrusions
The hydrogeology of the Mpumalanga Coalfields is dominated by a sedimentary sequence of sandstones, siltstones, shales, mudstones and intercalated coal seams, intruded by dolerite sills and dykes. The dolerite intrusions influence the groundwater flow directions and water strikes and often compartmentalise groundwater flow. Understanding the location of dolerite intrusions in relation to historical mining activities are key components of the hydrogeological conceptual model.

Airborne electromagnetic (AEM) and magnetic data were collected in October 2015 over the mine site to characterise the hydrogeology and map geological structures (dykes, faults and sills) believed to act as pathways and/or barriers to water flow and contaminant pathways. Interpretation of the data mapped several dykes and faults (Figure 1), while possible pollution plumes were mapped and digitised from the processed conductivity-maps (Spectrem Air Report, 2017).

Drilling and sampling of additional monitoring boreholes
Based on the results and interpretation of the high-resolution AEM and magnetic data, 21 boreholes were drilled to characterise the water level, aquifer parameters and groundwater quality as well as to map the depth extent of possible pollution plumes. Additional geochemistry test work (Barr, J, 2017) undertaken included static Acid-base accounting (ABA) and Net Acid Generation
(NAG) tests, as well as kinetic test work on the coal seam and inter-seam lithologies. A substantial feature of the ABA dataset is the prevalence of negative neutralisation potential (NP) values. These characteristics are further reinforced by NAG test data which indicated an equilibrium pH following spontaneous oxidation of sulphide and consumption of reactive carbonate of the order of 2.4, with a residual acidity release of around 50 mg/L. Kinetic testing produced particularly poor-quality leachate, with a pH of less than 2 and extremely high concentrations of sulphate, iron, manganese and aluminium (WSP Parsons Brinkerhoff, 2017). It is hence unlikely that discharge water will improve in quality to a point which would permit direct environmental release in the short term.

The hydrogeological intrusive program successfully confirms the roles of dolerite intrusion in the groundwater flow and migration pathways. The additional aquifer parameter and water level data was used to calibrate the numerical groundwater flow model.

Building the numerical flow and transport model
All hydrogeological, geochemical, geophysical and groundwater quality data were collated to formulate a hydrogeological conceptual model, describing the dynamics of groundwater flow, infiltration, storage and contaminant movement underground. Aquifer parameters (Huisamen, 2016) and infiltration rates as well as initial concentrations for sulphate were assigned to each source area to determine the effect of different rehabilitation scenarios. The conceptual model was translated into a numerical flow and transport model, using the polygons generated with the ArcView shape files, assigning aquifer parameters in the SPRING software (Witthueser, 2017), as reflected in Figure 2 below.

Rehabilitation scenario modelling
As the geochemical work and simulations in the groundwater model indicated that little can be done to change the quality of the water in the long term, the focus was to identify possible rehabilitation scenarios, which would
Figure 2 Vertical discretisation of the groundwater model

Table 1 Rehabilitation scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Explanation</th>
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</thead>
<tbody>
<tr>
<td><strong>Base case</strong></td>
<td>The current closure plan for Kromdraai is to pump water 28 km to the EWRP and to treat through RO and sell a portion of the water to the municipality.</td>
</tr>
<tr>
<td><strong>As Is</strong></td>
<td>With no further interventions, large tracts of land will have limited land use and substantial water ingress and higher post closure discharge volumes can be expected.</td>
</tr>
<tr>
<td><strong>3BS</strong></td>
<td>Aims only to use all the available topsoil to cover the surface area at the best possible depth, but at least achieving a wilderness land capability.</td>
</tr>
<tr>
<td><strong>EMPR</strong></td>
<td>Post closure land use in compliance with existing legal commitments. Due to substantial topsoil shortage, this scenario will require import of growth material.</td>
</tr>
<tr>
<td><strong>Upside</strong></td>
<td>Improves on the EMPR scenario by increasing topsoil depths with specific focus on upscaling post closure wilderness land use to grazing.</td>
</tr>
<tr>
<td><strong>4BS</strong></td>
<td>Aims to achieve the best possible outcome in terms of soil thickness. Soil thickness is believed to be the best preventative measure for water ingress in addition to vigorous vegetation cover. Import of large amounts of growth medium to achieve a minimum soil thickness of 650mm is required (all arable land).</td>
</tr>
</tbody>
</table>
result in the reduction of infiltration and hence the ultimate volume of water that would require post closure treatment (Table 1).

The four rehabilitation scenarios (3BS, EMPR, Upside and 4BS) consisted of different percentages of arable, grazing and wilderness land, based on different growth medium depths (650mm for arable vs. 350mm for grazing vs. 250mm wilderness cover respectively), which resulted in different seepage rates and different levels of legal compliance, as demonstrated in Figure 3 and Table 2.

Furthermore, closure calculations included rehabilitation requirements as reflected in Table 3, which were added to the capex component in the closure calculation and were spread over four to five years in line with the rehabilitation process. Each scenario was costed for import of topsoil as well as for scavenging of topsoil on site to address the shortfall of topsoil.

**Simulation of variable management scenarios**

Two phases of scenario modelling were completed (Muhlbauer, 2017). The first phase included modelling of 22 different combinations whilst the second phase included modelling of only five scenarios based on the outcomes of the first phase. During phase 1, the 22 post-closure modelled scenario combinations considered the effect of various rehabilitation strategies on the

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![Figure 3](image)

**Figure 3** Environmental Management Plan Report rehabilitation scenario (left) and Upside scenario (right)

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Legal Compliance</th>
<th>Growth Medium Volume required (m³)</th>
<th>Rehabilitation Cost (ZAR)*</th>
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<td>EMPR Compliance</td>
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<td>Upside</td>
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<td>Scenario 4BS</td>
<td>Yes</td>
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<td>419,469,506</td>
</tr>
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</table>

*One USD is approximately 14.50 ZAR

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predicted post-closure recharge, leakage from dams containing ferrihydrite (FeOH$_3$ also known as Yellow Boy) and discharge volumes. Model predictions provided discharge locations and discharge rates based on certain assumptions. Therefore, only approximate percentages of discharge rates for the different discharge areas were provided as reflected in Figure 4.

Actual volumes were assigned to each discharge area to enable preliminary comparative water treatment cost calculations to be completed for the identification of scenarios which could then be further refined. In Phase 2, five scenarios (Table 3) were refined using the existing numerical hydrogeological water transport model (Witthueser, 2017). To enable water treatment cost calculations, the estimated discharge volume for each area as reflected in Table 3 was derived from the percentage apportionment of discharge rates in each area using the total estimated closure discharge volume for each scenario.

**Selection of the preferred post closure groundwater solution**

The post-closure modelled volumes were used to assess the most appropriate treatment scenario. The following criteria for treatment of affected water were applied: (1) Reactive barriers, phytoremediation and expanded wetlands would be used for flow rates of less than 0.2 ML/day. These flow rates are generally dispersed over an area resulting in diffuse seepage; (2) Biological passive treatment systems would be applicable for flow rates between 0.2 and 1.4 ML/day. These flows can be collected in dedicated ponds and gravity-fed into passive biological systems; or (3) RO treatment at the EWRP for flows of 1.4 ML/day or above.

Capital estimates and operational costs

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**Figure 4** Apportionment of discharge rates (red) within the mining areas (simulated discharge location)
were derived from the closure models used for water liability calculations for both the EWRP and passive treatment calculations. Phytoremediation information was based on planting trees at a certain density to achieve evapotranspiration based on water uptake rates for certain rainfall averages. This enabled the development of detailed cost benefit analysis for each of the various scenarios, comparing increased rehabilitation costs against the benefits of a reduction in long-term groundwater treatment. This ultimately resulted in the selection of the preferred long-term solution.

The effect of improved rehabilitation on water liability costs is evident in Figure 5. Based on the results from the financial modelling, the “Upside” scenario with onsite scavenging of topsoil aimed at upgrading the wilderness land use to grazing is the most beneficial solution in terms of long-term liabilities, and hence the selected solution.

### Conclusions

The development of a defensible hydrogeological conceptual model and calibrated numerical flow and transport model, collating historical information was used to address substantial hydrogeological gaps. This allowed for the simulation of the post closure water volumes and quality applying various rehabilitation scenarios. Improved rehabilitation practices are key to ingress management and as a result discharge volumes that need to be managed. A reduction in discharge volumes allows for the implementation of more cost-effective sustainable treatment options which ultimately reduce long term water liability costs, however this cannot be at the expense of importing topsoil.

Current closure practices tend to defer rehabilitation and mine closure to reduce costs in the short-term, however this increases our long-term financial water liabilities. These typically need to be managed in perpetuity.

---

### Table 3 Post-closure mine water balance for the rehabilitation scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Recharge backfilled and undermined areas (ML/d)</th>
<th>Predicted discharge rate (ML/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>10.5</td>
<td>7.4</td>
</tr>
<tr>
<td>As Is</td>
<td>7.0</td>
<td>4.6</td>
</tr>
<tr>
<td>3BS</td>
<td>6.4</td>
<td>4.0</td>
</tr>
<tr>
<td>EMPR</td>
<td>5.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Upside</td>
<td>5.2</td>
<td>3.1</td>
</tr>
<tr>
<td>4BS</td>
<td>4.4</td>
<td>2.5</td>
</tr>
</tbody>
</table>

---

### Figure 5 Closure costs for different rehabilitation scenarios (net present cost)
which precludes sites from obtaining closure certificates. The project clearly demonstrates that the timeous implementing of appropriate surface rehabilitation will have a substantial effect on the long-term groundwater and surface water liabilities.

The Upside scenario as the preferred long-term solution, will reduce the original estimated closure liabilities (pre-project) of more than ZAR 2.5 billion to less than ZAR 0.5 billion over a 150-year period. Even though the business case for improved and timeous surface rehabilitation has been demonstrated clearly through this project, the need for sustainable long-term use of the “post passive treatment” water is required to make the solution self-funding and truly sustainable. These requirements can be addressed by initiatives, such as the “The Green Engine” concept that is currently being developed for the Kromdraai area. The Green Engine will provide a self-funding agri-business opportunity that will contribute to the management of water ingress and ultimate reduction in discharge of polluted water, by deploying solar PV farms that can capture water run-off, vertical greenhouses and other infrastructure where storm water is captured and used as part of the agri-businesses. The benefits are that water becomes an asset to the community and the agri-businesses and results in a reduction of closure liability costs related to import of top-soil and active water treatment. Changing a perpetuity liability into a sustainable post closure opportunity.

Acknowledgements

The authors wish to thank and acknowledge the Kromdraai team, the Coal Head Office team and the team from Technical & Sustainability for working together over more than two years to complete this project and in doing so adding substantial value to the business.

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Abstract

Acid mine drainage (AMD) has long been considered a global environmental hazard due to its long-term detrimental effects on waterways and the ecosystems that reside within them. The amount of AMD produced daily as well as the high cost associated with treatment has led the United Nations to classify AMD as the second biggest problem that the Earth faces. As such, new cost-effective remediation methods are strongly needed. This research involves such a method and focuses on the operation of a waste beneficiation treatment scheme that is being tested at pilot-scale. It incorporates the use of two waste-products which are produced in many AMD-affected countries: steel slag and sugarcane bagasse. The study has confirmed the potential of these products in the treatment of AMD through a two-step, chemical and biological process. Slag eluate contacted with raw AMD is used to initially buffer the AMD solution and precipitate potentially toxic metals in a sedimentation tank. Overflow from the sedimentation tank is then passed through a packed bed containing sugarcane bagasse inoculated with sulfate reducing bacteria as a polishing step to remove sulfate, precipitate metal sulfides and elevate pH to near neutral conditions. A portion of the effluent is recycled through a packed bed of slag to create the eluate for pre-treatment of the raw AMD solution. The AMD used in these experiments was characterized by pH 2.6; 174 mg/L Al, 245 mg/L Ca, 4289 mg/L Fe, 334 mg/L Mn, 415 mg/L Mg and 16333 mg/L $SO_4^{2-}$. Operation of the pilot scale system treating 200-1000 L/day has thus far shown maximum Al, Fe, Mn and $SO_4^{2-}$ removals of 97%, 87%, 100%, and 87% respectively. The dissolution of the slag and the alkalinity generation was found to occur mainly due to CaO and MgO dissolution. The SRB functioned in the slag eluate and a maximum sulfate reduction of 76% was found in the bioreactors. If optimized correctly, this treatment scheme could be implemented at mine sites throughout the world where these waste products are regionally available and could serve as either a low-cost pre-treatment program, or as a way for mines to recycle their acid waste for use as process or agricultural water.

Keywords: BOF Slag, Sulfate reducing bacteria, dissimilatory sulfate reduction, pilot plant

Introduction

Mining is an essential global industry that gives rise to multiple downstream processes, such as extractive metallurgy, minerals processing and general metal production that are vital to almost all aspects of human life - farming, healthcare, communications, water, energy supply, transport, space technology, and construction (International Council on Mining and Metals 2018; Park et al. 2019). Mining is a large source of wealth in many areas, with countries such as Zambia, Chile, Peru, Ukraine, Uzbekistan, South Africa, Australia, and Kazakhstan all reporting that mining contributes more than 7% of their annual gross domestic product (GDP).
Despite its acknowledged economic contributions, mining also causes substantial environmental degradation and generates huge amounts of wastes that are disposed of in tailings dams or stored in impoundments. Acid mine drainage (AMD) is an example of one such mining waste. The amount of AMD produced daily as well as the high cost associated with its treatment has necessitated new, viable and cost effective remediation schemes (Moodley 2018). In this regard, waste valorization/beneficiation has potential in (i) assisting AMD remediation schemes to remain economical, as well as in (ii) contributing to the alleviation of the burden of solid waste management in countless other industries (removal of secondary pollution which has multiple social and environmental benefits) (Nayak & Bhushan 2019).

Basic oxygen furnace slag (BOFS), containing high concentrations of oxides which have the ability to substantially increase the pH and alkalinity of acidic waters (Naidu et al. 2018a; Naidu et al. 2018b) is a final waste material in the steel making process that is in need of further processing before it can be re-used in the construction and building sector (Ding et al. 2017). BOFS cannot be used directly in construction due to volume instability issues that arise because of its high oxide content (Jiang et al. 2018). The treatment of AMD using BOFS as a lime substitute could potentially result in two valorized waste products, AMD treated to reusable water standards and BOFS treated to be reused as an aggregate in the construction industry.

This research investigates AMD treatment using BOFS by assessing the extent of remediation achieved in a pilot scale (200-1000 L/day) system. Another industrial by-product, sugarcane bagasse, is also used in the study to further remediate AMD after the BOFS treatment step and the efficacy of this biological treatment step is also evaluated. The aluminium, calcium, iron, manganese, magnesium and sulfate removal efficiency as well as the pH rise of the system are determined in order to evaluate the effectiveness of the scheme. Dissolution of the BOFS in the system is also assessed to determine the reduction of free oxide content in BOFS that causes volume instability.

Methods

Following the design and successful operation of a laboratory scale process using the same concept (Naidu et al. n.d.), a plant designed to treat 200–1000 L/day of AMD was constructed at a mine tailings dam in Emalahleni, South Africa. The dam site, shown in Figure 1, comprised of two dams which are used concurrently to contain seepage from a large mine tailings dump situated at a coal mine.

The chemical composition of the water contained within the dams changes constantly due to the varying nature of the coal tailings dump (new waste is continuously added to the dump and water seeps through this, entering the dam) as well as due to climactic conditions. The pilot plant was designed to account for the varying inlet quality so as not to effect the sensitive biological systems present in the process.

The system operates as follows (referring to Table 1 and Figure 2): AMD (stream 1) is pumped into an initial sedimentation vessel (R-102A/B) where it is mixed with a slag eluate stream (stream 10) from the slag chamber (R-101A/B). The slag eluate stream has high...
pH, alkalinity and hydroxide content due to reaction between the AMD and the oxides contained within the slag. When mixed with the AMD in R-102A/B and R-103A/B, the pH of the resulting solution increases, causing (i) precipitation reactions and (ii) removal of dissolved metals and sulfate in the solution via gravitational settling. The outlet from the sedimentation section (stream 3) contains substantially less sulfate and metal ions and is at a higher pH (close to neutral). This stream enters the biological reactors (R-104, R-105, and R-106), the first two of which contain sugarcane bagasse which act as a substrate (carbon source) for sulfate reducing bacteria (SRB). SRB are sensitive to extreme pH levels and thus the neutralization of the AMD in the sedimentation vessels (R-102, R-130) allows for SRB functioning. The biological reactors are responsible for facilitating further sulfate ion removal via dissimilatory sulfate reduction (DSR). The outlet from R-106 (stream 6) enters a water reservoir (TK-101) where the treated water is stored. Water from TK-101 either overflows into the AMD dam or is recycled into R-101A where it undergoes a reaction with the BOFS. All vessels were sealed and R-107 acted as a H2S scrubber. Vessels marked B are replacement vessels.

Process control was setup to control the ratio of slag eluate (stream 10) to AMD feed (stream 1) in the system in order to maintain a pH of 5 in the sedimentation vessels (R-102A and R-103A). A pH of 5 was chosen to (i) keep the recycle flowrate at a sustainable level, (ii) allow for ideal functioning of the biological entities (namely sulfate reducing bacteria (SRB)) which function best at a pH between 4 and 7, and (iii) allow for a suitable amount of precipitation of metals in the bioreactors (metals need to be present in the bioreactors to allow for metal sulfide precipitation). A depiction of the layout of the plant is shown in Figure 3.

Data collected from the plant for a 196-day period is discussed in the Results and discussion section below.

**Results and discussion**

**Flowrate and residence time**

The total volume of the system was approximately 13 000 L. Flowrates and residence times for the period are displayed in Table 2.

From day 120 onwards, the residence time for both the slag eluent and AMD streams was 5.4 days or lower. The flowrate into the system was determined by process control operation.

**Extent of remediation**

The inlet quality of the AMD changed continuously but had average Al, Ca, Fe, Mn, Mg, SO42- and V concentrations of 174 ± 99.8, 245 ± 128.4, 4289 ± 313.3, 334 ± 136.0, 415 ± 104.2, 16333 ± 1072 and 0.06 ± 0.01 mg/L respectively. The average pH of the untreated AMD was 2.6. The pH levels changed across each vessel as well as over time, but the average pH in each vessel was 5.4 (R-101), 3.2 (R-102), 3 (R-103), 4.6 (R-104), 4.6 (R-105), 4 (R-106) and 4 (TK-101). The change in pH of the AMD is due to hydration reactions that occur between the AMD and the BOFS and

### Table 1 Description of Process flow diagram elements (Figure 2)

<table>
<thead>
<tr>
<th>Diagram Number</th>
<th>Slag reactor and replacement</th>
<th>First sedimentation vessel (and replacement)</th>
<th>Second sedimentation vessel (and replacement)</th>
<th>Biological Reactor 1</th>
<th>Biological Reactor 2</th>
<th>Biological Reactor 3</th>
<th>Hydrogen Sulfide Scrubber</th>
<th>Water reservoir</th>
<th>AMD Pump</th>
<th>Recycle pump</th>
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<tbody>
<tr>
<td>R-101A/B</td>
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<td>R-103A/B</td>
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<td>P-102</td>
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</table>

### Table 2 Flowrate and Residence Time in System

<table>
<thead>
<tr>
<th>Time Period (days)</th>
<th>Flowrate of AMD (L/day)</th>
<th>Flowrate of Slag Eluent (L/day)</th>
<th>Residence Time (AMD and Slag Eluent) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>600</td>
<td>1000</td>
<td>8.1</td>
</tr>
<tr>
<td>34-43</td>
<td>270</td>
<td>1000</td>
<td>10.2</td>
</tr>
<tr>
<td>43-76</td>
<td>270</td>
<td>1200</td>
<td>8.8</td>
</tr>
<tr>
<td>76-120</td>
<td>270</td>
<td>2000</td>
<td>5.7</td>
</tr>
<tr>
<td>120-139</td>
<td>0</td>
<td>2400</td>
<td>5.4</td>
</tr>
</tbody>
</table>
the subsequent dissociation that results in the release of hydroxide units. The fluctuation in pH across the system over time (as shown in Figure 4) is attributed to the varying amount of oxide containing BOFS particles that come into contact (and are able to react) with the AMD. This varying amount is determined by the process control over the plant. When the pH of the sedimentation vessel (R-102) is lower than 5, the flowrate of the entering slag eluate (stream 10) increases until it reaches a maximum of 2400 L/day and the flowrate of the AMD stream (stream 1) decreases until 0 in order to facilitate a higher ratio of slag eluate to AMD. For pH levels higher than 5 the opposite is true. Process control over the system became automatically effective after 120 days and thus fluctuations occurred. In addition to this, precipitation and settling in the BOFS reactor limited the release of further oxides. This was combated by removing sedimentation and allowing only treated water (with a lower ion content and thus less ability to form precipitates) to flow through the BOFS reactor. The metal and sulfate levels across the system fluctuate along with pH levels (as shown in Figure 4). Metal and sulfate concentrations are dependent on the pH levels, making pH control in the system extremely important. High pH levels allow for more precipitation reactions to occur, removing a higher quantity of sulfate and metals, and pH levels between 4 and 7 allow for optimum SRB activity.
The extent of treatment in each vessel at the end of the 196-day period is shown in Table 3 in terms of % removal of each component (based on the initial and last reading). Bold indicates an increase in concentration.

The extent of remediation changed considerably over time at site, and this was attributed to the fluctuating conditions (changing feed quality, climate and availability of electricity to run equipment). The best treatment (for a combination of components) was observed after approximately 4000 hours (167 days) of operation and showed an 84% removal of sulfate, 80% removal of dissolved Fe, 62% increase of Ca, 95% removal of Al, 20% increase of Mg and a 80% removal of Mn. The maximum removals in terms of Al, Fe, Mn and sulfate were 97%, 95%, 100% and 87% respectively (across different reactors). Vanadium did not exhibit any considerable changes and Mg and Ca concentrations consistently increase in the system.

**Dissolution of BOFS**

As shown in Table 3, the Mg and Ca concentrations increased within the system, confirming the hydration reaction between the treated AMD and the oxidic compounds within the slag. According to literature, alkalinity can be generated from BOFS via hydration followed by dissociation of calcium and magnesium oxides (Gomes et al. 2016). The BOFS contained 41.6 mass% CaO and 7.2 mass% MgO (other oxides are present, but only Ca and Mg have been considered due to the rise in their concentrations). The hydration, dissolution and dissociation reactions that bring about alkalinity from CaO and MgO components are described by Equations 1 to 4.

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{O} & \leftrightarrow \text{Ca(OH)}_2 \quad (1) \\
\text{Ca(OH)}_2 & \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (2) \\
\text{MgO} + \text{H}_2\text{O} & \leftrightarrow \text{Mg(OH)}_2 \quad (3) \\
\text{Mg(OH)}_2 & \leftrightarrow \text{Mg}^{2+} + 2\text{OH}^- \quad (4)
\end{align*}
\]

Ca in the system increased by 226% and Mg increased by 23% signifying that CaO and MgO compounds could contribute to the bulk of the pH rise and that oxidic compounds are being removed from the slag.

---

**Table 3** Extent of Remediation across each Process Vessel (% removal of components)

<table>
<thead>
<tr>
<th>Component</th>
<th>R-102A/B (%)</th>
<th>R-103A/B (%)</th>
<th>R-104 (%)</th>
<th>R-105 (%)</th>
<th>R-106 (%)</th>
<th>TK-101 (%)</th>
<th>R-101A/B (%)</th>
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<tbody>
<tr>
<td>Mn</td>
<td>69.23</td>
<td>70.50</td>
<td>76.51</td>
<td>78.32</td>
<td>77.30</td>
<td>79.90</td>
<td>83.32</td>
</tr>
<tr>
<td>Mg</td>
<td>0.79</td>
<td>4.77</td>
<td>0.34</td>
<td>16.06</td>
<td>12.44</td>
<td>19.54</td>
<td>23.31</td>
</tr>
<tr>
<td>Al</td>
<td>95.22</td>
<td>95.86</td>
<td>96.61</td>
<td>97.07</td>
<td>96.08</td>
<td>95.45</td>
<td>90.03</td>
</tr>
<tr>
<td>Ca</td>
<td>185.32</td>
<td>167.87</td>
<td>69.13</td>
<td>123.12</td>
<td>69.74</td>
<td>62.43</td>
<td>226.45</td>
</tr>
<tr>
<td>Fe</td>
<td>56.28</td>
<td>69.72</td>
<td>77.96</td>
<td>82.72</td>
<td>83.39</td>
<td>79.61</td>
<td>86.61</td>
</tr>
<tr>
<td>(\text{SO}_4^{2-})</td>
<td>55.63</td>
<td>72.52</td>
<td>80.24</td>
<td>81.95</td>
<td>83.53</td>
<td>84.69</td>
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<td>pH</td>
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<td>5.34</td>
<td>5.24</td>
<td>5.49</td>
<td>5.11</td>
<td>5.20</td>
<td>7.24</td>
</tr>
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</table>
Conclusions
The extent of treatment of AMD using a two-step, chemical and biological process at a pilot plant (200-1000 L/day) scale was evaluated successfully and determined to have a maximum removal capacity of 97% for Al, 87% for Fe, 100% for Mn and 87% for SO42-. SRB functioned well in the BOFS neutralized solution and the biological reactors exhibited a maximum sulfate removal of 76%. Some oxide compounds in BOFS underwent hydration (and subsequent dissociation) reactions with the treated AMD, potentially removing a degree of volume instability from the material. Although ideal functioning did not occur until after 4000 hours of operation, the experiment confirmed functionality of the scheme at a pilot plant scale. Issues relating to the poor performance [sedimentation in BOFS chamber (R-101)] in the first 4000 hours were identified and deemed to be easily correctable. Further work will focus on achieving successful pH control in the system in order to optimize the metal and sulfate removal as well as exploring manners through which to regenerate the sludge produced in the sedimentation vessels.

Acknowledgements
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References
Introducing a New Approach for the Stowage of Waste Brines from Potash Mines of the Werra District in Germany as a Measure to Ensure the Safe and Sustainable Continuation of Potash Extraction and Processing

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Abstract
The global fertiliser production industry has been and, considering world population development, will be vital for intensive agricultural land use. However, waste brine discharge from the production of fertilisers poses environmental challenges. The German potash deposits of the Werra District are unique resources for the production of special fertilisers. A new approach to waste brine management will need to ensure a responsible and sustainable continuation of fertiliser production in the Werra District. This approach entails the conditioning of waste brines and subsequent stowage in a former potash mine whereby eventually eliminating discharge of waste brines in rivers and/or in aquifers.

Keywords: potash mining

Introduction
The importance of global potash (i.e. Potassium with symbol K) extraction and processing has been substantial for well over a century (Darst, 1991). Potash based fertilisers will, considering the growing world population, continue to be a vital resource for intensive agricultural land use. The German potash deposits of the Werra District, high in sulphatic and magnesium containing minerals, are unique in their ability to provide resources for the production of special fertilisers, i.e. potassium sulphate and magnesium sulphate (K+S AG, 2018). Globally the production of potash fertilisers is however not without controversy due to waste brine discharges into surface and ground water and saline run-off from stockpiles for solids salt wastes (Tallin, Pufahl, & Barbour, 2011), (Ladrera, Canedo-Argüelles, & Prat, 2016), (BMUB/UBA, 2016), (Rauche, 2015).

To ensure a responsible and sustainable continuation of potash extraction and processing in the Werra District, K-UTEC AG Salt Technologies (K-UTEC), in collaboration with K+S AG and K+S KALI GmbH (K+S), has proposed a new approach which can gradually decrease, and in future even eliminate, the discharge of waste brines from the production of fertilisers in rivers and/or their injection in deep aquifers. This approach entails the conditioning of waste brines and subsequent stowage in former potash mines in the Werra district and will, after successful implementation, gradually reduce and eventually eliminate the discharge of approximately 3 million m³ waste process brine in the Werra-district into surface water and/or injection of waste brines into deep aquifers. A critical condition for stowage is the chemical composition of the waste brines in relation to the host minerals in the mines of the Werra District which must be adequately considered since the stowage process can potentially initiate dissolution processes weakening the mines’ pillars consequently leading to surface subsidence and/or seismic events.

In the newly developed approach waste process brines are conditioned by increasing the concentration of magnesium chloride. The (conditioned) brines can be stowed in the following states: as a geotechnically supporting or location-stable backfill and as a liquid (FGG Weser, 2019). The performed research has thus investigated the required chemical composition of conditioned waste brine,
evaluated the preferred state for stowage and engineered the stowage process and sequence. The resulting reports on the research comprise mainly proprietary knowledge and are not publicly available. For the purpose of this paper however the relevant research insights and results have been presented with references to all public and non-public sources included in the reference list at the end of this paper.

The Werra Potash District

In 2018 the Werra District celebrated 125 years of potash mining based on the first drilling core brought to surface, proving the presence of potash in this region, on the 5th of October 1893 (Stadt Heringen, 2018). In the years following this discovery many shafts and potash processing plants were commissioned in this region, e.g. shaft Grimberg in 1900 and shafts Hattorf and Sachsen-Weimar in 1905 (K+S Kali GmbH, 2017). Potash mining in the Werra District in combination with the mining of potash in other German regions such as Staffurt, Hannover and the southern Harz area allowed Germany to maintain a monopoly position in the production and sales of potash based fertilisers for more than 50 years until the signing of the Treaty of Versailles on the 28th of June 1919, formally ending World War I (Rauche, 2015). The several individual potash mines and processing plants were consolidated in 1997 into the current K+S Werra District comprising the sites Merkers (including Springen), Wintershall, Hattorf and Unterbreizbach. The Merkers site ceased production in 1993. The mines of the Werra Potash District are presented in Figure 1 and span approximately 30 km (East-West) by 25km (North-South).

In the Werra District approximately 19 million tons of potash bearing salt is extracted per year which constitutes to circa 45% of total potash bearing salt mining by K+S KALI GmbH (K+S Kali GmbH, 2017), (K+S AG, 2018). The extracted potash bearing salts in the Werra District originate from two horizons, i.e. the Hesse and Thuringia seams, both of Permian Zechstein age (Reinhold, 2014). The potash seams in the Werra District are relatively flat-lying deposits at a depth of approximately 500 to 1000 meters (K+S AG, 2019-1) which are mined using mainly the room-and-pillar mining method (K+S Kali GmbH, 2017).

The production of potash fertilisers in the Werra District has caused high salt concentrations in the River Werra and the subsequent Weser River for over 100 years (Braukmann & Böhme, 2011), (FGG Weser, 2018). The volume of saline wastewater originating from the production of fertilisers and other potassium- and magnesium-based products for the chemical industry has been reduced by K+S from approximately 20 million m³ per year in 1997 to approximately 7 million m³ in 2015. With the erection and commissioning of the so-called KCF-facility (i.e. Kainite Crystallization and Flotation) a further reduction of 1.5 million m³ per year has been made possible reducing the total volume of saline wastewaters to approximately 5.5 million m³ per year in 2019 (K+S AG, 2019-2). This volume comprises approximately 3.1 million m³ waste brine from the production process and another 2.3 million m³ of saline run-off from the solid waste salt heaps (FGG Weser, 2018). At this time approximately 1.5 million m³ per year of waste brine from the production is permitted to be injected into a deep aquifer while the remainder is discharged into the River Werra (K+S AG, 2018). The injection of waste brine into the deep aquifer will be discontinued from 2022 onwards (K+S AG, 2018) parallel to a gradual phasing out of the waste process brine discharge practice in the River Werra. Consequently, other responsible and sustainable disposal methods must be established. One possible disposal methods entails the stowage of waste brine in former potash mines in the Werra District (FGG Weser, 2018) of which the Springen Mine is one and most likely the first candidate for a stowage operation (K+S AG, 2018-1 (not publicly available)).

The Springen Mine has been developed in several stages, initially as two separate mines (Baumgart, 2019). Currently a total 7 shafts are still open and general gradient of the potash seams dips towards the Southwest (K+S KALI GmbH, 2018 (not publicly available)). Due to the structure of the potash seams, the mine can be sub-divided in several
Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)

mining panels which are isolated from each other through topographic depth differences. The potential isolation of mining panels have dictated the stowage sequence which is described later in this paper.

**Waste brine stowage options**

Independent from each other, K-UTEC and K+S have devised the following three options for stowing waste process brines in the former potash mines (K-UTEC AG, 2018 (not publicly available)), (K+S AG, 2018-1 (not publicly available)), (K+S AG, 2018-2 (not publicly available)).

- **Stowage as geotechnically supporting backfill:** using magnesium chloride \((\text{MgCl}_2(\text{aq.}))\) as the main component, a backfill slurry can be produced which has the ability to cure and harden which is achieved using either primary binding agents or waste materials with binder properties. To improve the strength characteristics of the cured backfill sodium chloride \((\text{NaCl})\) grains, can be added to the backfill composition. This \text{NaCl} can either be sourced from a primary resource, i.e. mined locally in the former potash mines, or from a secondary resource, i.e. solid waste from the fertiliser production. The backfill slurry can be produced at the ground surface and pumped underground or, in case curing time is short, produced underground. In both cases the final backfill mixture is transported to the stowage area by hydraulic transport using pipelines. Strength characteristics of this type of backfill mixture are such that after curing it will provide geotechnical support to the pillars and hanging wall of the mines.

- **Stowage as location-stable backfill (‘gel’):** similar to the geotechnically supporting backfill, the location-stable backfill mixture comprises \text{MgCl}_2(\text{aq.}), binding agents and potentially \text{NaCl} grains. Rather than having to reach sufficient strength to support the pillars and hanging wall, the location-stable backfill composition is only aimed at supporting its self-weight. The general binding behaviour

![Figure 1 The potash mines of the Werra District, Germany (adapted from (K+S KALI GmbH, 2018 (not publicly available)))](image-url)
of the backfill is based on the so-called ‘Sorel-reaction’ creating magnesium oxychloride phases by combining MgCl₂(aq.) with magnesium oxide (MgO(s)) (Popp, 2018). Whereas traditional Sorel concrete can reach very high strengths, K-UTEC has developed backfill compositions using alternative binding agents such as calcium oxide (CaO(s)) and calcium magnesium hydroxide (CaMg(OH)₄(s)). These mixtures reach a strength after hardening as low as 0.1 MPa (using the direct shear testing method) thus resembling a type of ‘gel’ in its appearance and mechanical deformation behaviour. The use of NaCl grains in the backfill mixture can improve its ability for self-support.

- **Brine stowage in a liquid state:** the final option for stowing waste process brine in the former potash mines of the Werra district is stowage in a liquid state. The several different waste brine types from the fertiliser production process have differentiated salt concentrations and can have a dissolution potential in relation to the host rocks. As stowage in a liquid state allows convective transport of the brines within the stowage volume, the dissolution potential must be carefully considered as stowage should not weaken the bearing capacity of pillars or support capacity of room beams. The waste brines are generally not completely saturated for all salt types in the mine and they thus need to be conditioned, i.e. increasing their salt concentration, before stowage can take place. The conditioning of waste brines is further detailed in the next paragraph.

As part of the research by K-UTEC and K+S, the three proposed options for waste brine stowage have been evaluated using both economic and non-economic criteria. Although an economic evaluation is, at first sight, straightforward, the challenge is how to address non-economic factors such as the permitting process, the opinion of stakeholders and the ease with which a stowing process can be incorporated in the existing fertiliser production processes. The factor time has also been an important criterion in the evaluation as the period in which the selected stowage process must be implemented is relatively short when considering K+S decided to discontinue the injection of waste process brines in deep aquifers from 2022 onwards. The result of the performed evaluation by K-UTEC and K+S (independently) is that stowage of waste brines in a liquid state, after conditioning to increase salt saturation, is the preferred option.

### Main boundary conditions to brine stowage in the Springen Mine

The two potash bearing seams in the Werra District comprise so-called ‘Hartsalz’ (potassium chloride (KCl) and NaCl), Carnallitite (mainly hydrated potassium magnesium chloride (K₂MgCl₂·6H₂O)) and kieseritic ‘Hartsalz’ (a mixture of Kieserite (MgSO₄·H₂O) and Sylvite (potassium chloride (KCl))) (K+S AG, 2018-1 (not publicly available)). Stowage of waste brine in the Springen Mine cannot lead to an increased subsidence and/or seismic risk. The dissolution potential of stowed brine in relation to the host rocks thus needs to be carefully considered. As the distribution of the mentioned salt types is not uniform, nor are they isolated in single mining panels, the stowage brine needs to be (largely) indifferent to all salt types. A stowage brine with a chemical composition that approximates the chemical equilibrium point in the quinary system of oceanic salts, i.e. the so-called ‘Q-Point’ with ca. 320 g/L MgCl₂, is largely indifferent to the host minerals in the mines of the Werra District (Bach, 2010), thereby enabling a safer and more sustainable stowing practice by limiting the dissolution of the host rocks, thus avoiding subsidence and seismic risk. As the waste process brines from the fertiliser production in the Werra District do not sufficiently approximate the Q-Point, lacking MgCl₂, they need to be conditioned. This is possible by mixing them with Bischofite (MgCl₂·6H₂O(s)) flakes (K+S AG, 2019-3 (not publicly available)) and/or a brine with a very high MgCl₂-concentration (K+S AG, 2018-2 (not publicly available)) or alternatively by an evaporation process (K-UTEC AG, 2018 (not publicly available)).

The second boundary condition for the stowage of waste process brines is the remediation of a limited number of water inflow locations in the Springen Mine. At these locations a mostly NaCl-saturated brine,
but not nearly approximating the Q-Point, is entering the mine from the underlying Rotliegend formation (Deppe & Pippig, 2002). The inflow system of this brine must be sealed before the mine is abandoned and the shafts are sealed as this brine will dissolve the pillars, destabilising the hanging wall and thus potentially causing severe subsidence and/or seismic events. The static pressure of the inflowing brines, when the inflow system is sealed, is above 60 bar above atmospheric (K+S AG, 2018-2 (not publicly available)). As the inflow system is a complex network of faults and fissures extending over a large area (Deppe & Pippig, 2002), installing a seal and proving its integrity for thousands of years is very challenging. K-UTEC suggests an alternative approach which uses the stowage of conditioned waste brines. By stowing a largely indifferent waste brine approximating the Q-Point and allowing this brine to reach a pressure equal to the pressure of the Rotliegend brine, a pressure equilibrium can be reached thus avoiding the need for an extensive and complex sealing system able to maintain a high differential pressure for thousands of years. The stowage of conditioned waste brine can thus also be an advantage for a sustainable and secure abandonment of the Springen Mine.

Engineering the preferred waste brine stowage option

The stowage of waste process brine in the Springen Mine Waste requires careful planning and engineering to satisfy the boundary conditions, meet the 2022 deadline, be cost efficient, comply with relevant laws and regulations, fulfil permitting conditions and be acceptable to the many stakeholders involved. Both K+S and K-UTEC have independently engineered the stowing process comprising a waste brine conditioning plant, a pipeline transport infrastructure for the stowage brine and a stowage sequence for the Springen Mine which will be detailed in the following (K+S AG, 2018-2 (not publicly available)), (K-UTEC AG, 2018 (not publicly available)).

• The options for the conditioning of the waste brines have been mentioned in previous paragraphs. Not mentioned is the fact that conditioning waste brines produces not only a stowage brine but also additional solid waste salts due to crystallisation reactions during the conditioning process. Two basic options for the disposal of these solids are possible: separation directly after the conditioning process, i.e. in an above-ground plant requiring a responsible disposal method, or transport of the solids with the stowage brine to the mine and separation in an underground sedimentation basin or a separation plant, e.g. based on hydrocyclones.

• The pipeline infrastructure comprises shaft pipelines, potential pumping stations boosting the pipeline pressure to overcome topographic height differences in the mine and a stowage brine outlet system. The shaft pipeline is a API-style steel pipe (casing) with screw connections and will be suspended from the shaft hoist structure. The pressure created in the shaft pipeline through the geodetic height difference between the shaft top and bottom can either be reduced using pressure reduction (i.e. orifice) plates installed at the shaft bottom or the pressure is used to transport the stowage brine horizontally through the mine. In the latter case the horizontal pipeline must be able to withstand high pressure (e.g. PN64) and will be laid out in (lined) steel. Alternatively, the pressure is reduced and the horizontal transport can take place through HDPE-pipes with a lower pressure class (e.g. PN16). The total horizontal pipeline length will be several dozens of kilometres to span the distance between the shaft pipelines and the stowage area in the Springen Mine. The outlet of the horizontal pipelines will need to avoid scouring of the host rock at the outlet location for which several options have been suggested.

• The sequence in which the several isolated mining panels of the Springen Mine will be flooded by the stowage brine has been devised on the basis of the following design conditions:

  o Using the topography of the mine allows stowage without the need for dams having to withstand the static
pressure of brine stowed behind them, i.e. stow brine as much as possible ‘downhill’. Stowage of waste brine will thus start in the lowest areas of the mine.

- Allow access, i.e. for maintenance and repairs, to the underground horizontal pipeline.
- Allow access to the water inflow locations as long as possible to enable the installation of flow barriers as part of the remediation works.

**Conclusions and outlook**

The extensive work performed by K+S, K-UTEC and an array of other specialised firms on devising alternative waste brine disposal options has gained a wealth of knowledge and experience which can be applied to secure the production of potash based fertilisers in the Werra District. This knowledge and experience is however also potentially applicable to other mining operations (e.g. salt, metals, coal) which involve waste waters or brines. The options for creating hardening backfill compositions are also transferable outside the potash mining industry, i.e. to lower risks connected to extensive tailing ponds (e.g. avoiding incidents such as recently in Brasil) and/or increase underground resource extraction efficiency through pillar re-mining after backfilling. K+S and K-UTEC currently work together on the preparation of an optimised Process Design and subsequent engineering documents for the waste process brine stowage plant and infrastructure. Although time is short, the parties involved are confident the deadline, i.e. an infrastructure able to stow up to 1.5 million m³/year in operation from 2022 onwards, can be met.

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Abstract
A passive biological treatment system for sulfate-rich Acid Rock Drainage has been investigated, focussing on using waste biomass such as grass cuttings and sugarcane bagasse to raise the water pH and supply organic carbon as a food source for bioremediation of sulfate by Sulfate Reducing Bacteria. The objectives of this study are to assess the pH change and soluble organics released on contact between sugarcane bagasse and ARD, and if the model treatment process can run only on waste biomass.

Keywords: Sulfate Reducing Bacteria, Bioremediation, Linear flow channel reactor

Introduction
The oxidation of sulfide minerals that occurs during the generation of Acid Rock Drainage (ARD) releases sulfate and the salinity of receiving water systems is often increased. Mine discharge from the Witwatersrand region of South Africa was found to account for 20 % of the salts in the Vaal River, despite effluent water only making up 5% of the total volume of the river system (Durand 2012).

The reduction of sulfite salinity is a priority in a water stressed country like South Africa, where dilution is not a viable option. Traditional active processes are often not feasible for low volume discharges associated with coal mining. Passive treatment options involving biological systems have been developed to remediate acid rock drainage in a less expensive and resource intensive way (Johnson and Hallberg 2005; van Hille and Mooruth 2011).

Sulfate reducing bacteria (SRB) are a group of micro-organisms often found in anaerobic sediments of rivers and dams, and around the root systems of plants found in sulfate-rich environments (Muyzer and Stams 2008). Sulfate reducing bacteria may be assimilatory or dissimilatory, oxidizing organic carbon sources such as volatile fatty acids or sugars, and reducing sulfate at the end of their electron transport chain to sulfide (Muyzer and Stams 2008). When this occurs there is a simultaneous generation of alkalinity, increasing the pH of the system (Harrison et al. 2014).

Sulfide is toxic and has an unpleasant odor so management is important for SRB systems remediation. Biologically catalyzed partial oxidation to elemental sulfur has been identified as a potential way to deal with excess sulfide. The linear flow channel reactor has been used to study the kinetics of simultaneous liquid phase sulfate reduction and partial sulfide oxidation in a biofilm layer, demonstrating the concept while supplementing the feed with acetate or molasses to act as a source of organic carbon (van Hille and Mooruth 2011, Harrison et al. 2014).

Preliminary research suggests that replenishable source of biomass can be broken down by contact with the ARD to supply organic carbon for the downstream biological remediation processes (Ramla and Sheridan 2012). Waste biomass such as grass cuttings, domestic waste and agricultural by-products near to the ARD source are of interest to these studies for economic reasons.

The objective of this work is to initial evaluation sugarcane bagasse, which is the dry, fibrous by-product of sugarcane processing, as a carbon sources for a model bioremediation process based on sulfate reduction and partial oxidation in the context of previous study of this process.

Methods
The bagasse used in this work was obtained from Illovo Sugar in Eston, South Africa. The ARD used was sourced from active coal mines in the Mpumalanga region of South Africa, and as such varies with time. The typical levels of some components are pH 2.70-2.90, 1800-2400 mg/L Sulfate, 800-1000 mg/L Iron, 200-300 mg/L Magnesium and 300-400 mg/L Manganese.

**Batch Experiments**

To investigate the effect of bagasse on ARD pH, 15g and 25g of dry bagasse was added to stirred batch vessels initiated with diluted sulfuric acid and coal mine ARD as recorded in Table 1. The objective of this experiment was to measure the pH rise in ARD upon contacting with the biomass.

To mimic possible real-world inputs into the pre-treatment section of the process, various strengths of real ARD were also used in batch vessels with sugarcane bagasse as detailed in Table 2. A commercial cellulase enzyme was added to two duplicated samples.

**Continuous Experiments**

Figure 1 is an illustration of the layout of the model process used for continuous study and the sampling points referred to in the results section.

The pre-treatment reactor contacts incoming ARD with biomass to raise pH and strip some soluble organic components from the carbon source. This more carbon-rich stream flows into an 8L model Linear Flow Channel Reactor (LFCR) with SRB inoculum and carbon fibre strands to limit microbial washout. After the LFCR, a model constructed wetland is placed to provide further remediation as well as improve clarity and smell of effluent. (i.e. tertiary treatment). The wetland performance is not reported on in this work.

To compare the pH change and rise in

### Table 1 Initial conditions for synthetic ARD batch experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Initial pH</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Real ARD</td>
<td>2.72</td>
<td>300</td>
</tr>
<tr>
<td>S1</td>
<td>Synthetic</td>
<td>2.01</td>
<td>300</td>
</tr>
<tr>
<td>S2</td>
<td>Synthetic</td>
<td>2.5</td>
<td>300</td>
</tr>
<tr>
<td>S3</td>
<td>Synthetic</td>
<td>3.01</td>
<td>300</td>
</tr>
<tr>
<td>S5</td>
<td>Synthetic</td>
<td>4</td>
<td>300</td>
</tr>
<tr>
<td>S5</td>
<td>Synthetic</td>
<td>5</td>
<td>300</td>
</tr>
</tbody>
</table>

### Table 2 Initial conditions for coal mine ARD batch experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Primary liquid</th>
<th>Dilution</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>ARD 300ml</td>
<td>None</td>
<td>Bagasse 25g</td>
</tr>
<tr>
<td>A2</td>
<td>ARD 250ml</td>
<td>Water 50ml</td>
<td>Bagasse 25g</td>
</tr>
<tr>
<td>A3</td>
<td>ARD 200ml</td>
<td>Water 100ml</td>
<td>Bagasse 25g</td>
</tr>
<tr>
<td>A4</td>
<td>ARD 150ml</td>
<td>Water 150ml</td>
<td>Bagasse 25g</td>
</tr>
<tr>
<td>A5</td>
<td>ARD 250ml</td>
<td>Water 50ml + Cellulase</td>
<td>Bagasse 25g</td>
</tr>
<tr>
<td>A6</td>
<td>ARD 150ml</td>
<td>Water 150ml + Cellulase</td>
<td>Bagasse 25g</td>
</tr>
</tbody>
</table>
soluble COD in the pre-treatment reactor phase, two sealed 2L reactors were filled with 200g field grass cuttings and 200g sugarcane bagasse respectively. Both biomass samples were dried in an oven overnight and rinsed to remove fine particles and dust. A peristaltic pump was used to pass ARD through each reactor in a bottom to top flow pattern and the outlet was sampled and stored. For the duration of this experiment the ARD flowrate was approximately 0.8 L/day through each reactor. Oxygen demand (COD) was measured as a proxy for soluble organic carbon released.

To operate the model system, different pre-treatment reactor compartments were packed with 250g of dried roadside grass cuttings followed by 250g of sugarcane bagasse with flow in series. An overflow inlet and bottom outlet flow design was used to minimise short circuiting flow. The system was fed coal mine ARD at 4L/day, setting the LFCR hydraulic retention time at 2 days.

Results and Discussion

Batch Experiments

The pH in the batch reactors treating ARD showed a rapid initial change in pH upon contact with the sugarcane bagasse (fig. 2). Solutions with a pH starting above 3.5 displayed a decrease in pH, stopping in the range of ≈pH 3.8. It is suspected this is due to a limited release of organic acids. Vessels with a higher dry mass of sugarcane bagasse showed a higher initial change and end pH after ≈100 hours of contact time. The rise in pH after 50 hours of run-time is theorised to be due to biological activity. This hypothesis was supported by the smell of hydrogen sulfide and visible biofilm on the liquid surface in samples S3, S4 and S5. This could indicate that some microorganisms, including sulfate reducers, are present on bagasse and are viable in relatively low pH environments.

Coal mine ARD had a similar change in pH on contact with the bagasse, though smaller in magnitude than the synthetic vessels due to higher initial acidity (fig.3). The addition of cellulase enzyme mix had a marked effect on pH comparing samples A3 to A5 and A4 to A6. The pH continuing to rise, and the lowering redox potential could indicate biological activity in samples A4, A5 and A6 even with the higher acidity and dissolved metals of real ARD.

The batch experiments with acid and mine drainage indicated that an observable effect on liquid pH can be seen and biological activity present with the relatively low solid to liquid loading of 25g of sugarcane bagasse. Increasing the solid loading in a continuous system or staging multiple in series to attain the desired pre-treatment pH, and the addition of commercial enzymes to assist with breakdown of the organic matter, are two factors to consider in scaled up experiments.
Continuous Experiments
In the continuous pre-treatment experiment, both the outlet pH and oxygen demand were observed to decrease with time (fig 4). The grass cuttings appear to supply more soluble organic material and acid neutralisation than dry bagasse for the duration of the experiment. Investigation into the composition of the outlet organic material is recommended.

Figure 5 shows the change in pH and sulfate concentration with time at the various sampling points in the model continuous system. The pre-treatment reactor (M2 and M3) was filled with ARD before the run was initialised, while the LFCR (M4) had an SRB stock solution and feed comprised of sodium acetate and sodium sulfate. The Constructed Wetland (M5) had a mixture of the runoff from the LFCR and tap water.

The outlets of the two-step pre-treatment reactor (M2 and M3) showed a pH change in excess of 1 pH compared to the ARD feed (M1). The incoming acidity after the pre-treatment step decreased the pH of the LFCR out of the ideal range in which it has been found to operate.

The liquid leaving the LFCR had a lower sulfate concentration than that entering and higher sulfide levels. The sulfate removal and sulfide production were lower than previous experiments using synthetic feedstock where sulfur production was observed (van Hille...
Figure 5 pH and Sulfate concentration for the model continuous flow system as shown in Figure 1 with a 48hr hydraulic retention time

and Mooruth 2011)

Figure 6 illustrates the observed decrease the three highest concentration species of dissolved metals for this ARD throughout the reactor series. The pH in the biomass reactor where most of the metals are removed is too low to directly precipitate manganese. This may be indicative of complexation or adsorption and is an avenue of further study.

Conclusion
This research has shown that it is possible to increase the pH of ARD (albeit minimally) using sugarcane bagasse only and some sulfate reduction can take place at the conditions reached by contacting bagasse with ARD.

Potentially toxic metals may be substantially removed by contacting the ARD with biomass, but the mine water acidity

Figure 6 Snapshot of some metal concentrations at 96 hours for the model continuous flow series as laid out in Figure 1 with a 48hr hydraulic retention time relative to the LFCR
remains too high under the configuration conditions tested, decreasing the pH of the bioreactor over time.

Current research following from this work is focussing on increasing the solid loading rate and the quantification and characterisation of organic carbon flowing through the model treatment system, with the goal of achieving a higher level of sulfate reduction and partial oxidation of sulfide in the linear flow channel reactor.

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Abstract
This study investigates the use of artificial neural networks (ANNs) for mine water quality prediction. The water chemistry of the Witkranz discharge site was used to develop the prediction system. Parameters such as rainfall, air temperature, depth to water table and discharge pH were used as training inputs, while sulfate was used as the training output. A graphical user interface (GUI) was developed by combining long-short-term memory nets (LSTM) for each of the four input parameters and an ANN combining the LSTM outputs to predict future sulfate values. The system was tested using historical data with over 99% training accuracy.

Keywords: artificial neural network, long-short-term memory, prediction system, training accuracy

Introduction
Mining water-related pollution is one of the major environmental challenges in South Africa. Historical coal mining has substantially changed the landscape in a number of provinces at the same time altering the hydrology and hydrogeology. The pollution of the groundwater is associated with acid mine drainage (AMD). Many interventions have been proposed and implemented, adapted to the volumes and quality of the AMD. However, in order to design sustainable future solutions to AMD, knowledge about future mine drainage conditions is indispensable.

The application of artificial neural networks (ANNs) to the fields of water engineering, ecological and environmental sciences have gained momentum in the last two decades (Najah et al. 2011). Chen and Mynett (2003) and Lee et al. (2003) have successfully used data-driven modelling techniques for the prediction of freshwater and seawater quality alike. Najah et al. (2011) have demonstrated that ANNs can be used to predict river water quality, based on historical data. Therefore, ANNs may be an alternative to current methods of mine-water quality prediction. ANN captures the embedded spatial and unsteady behaviour inherent in the AMD-affected area. The architecture and non-linear nature of ANNs make them more suitable than other modelling techniques. Owing to the correlations and interactions between water quality parameters, it is interesting to investigate whether a domain-specific mechanism governing observed patterns exists to prove the predictability of these variables (Najah et al. 2011).

The current study intends investigating the application of ANNs to predict the water quality with a focus on sulfate concentrations from one of the abandoned underground coal mines in Mpumalanga Province, South Africa, based on readily available monitoring and historical water quality data. The study area is the Witkranz discharge site, situated in the town of Carolina. Geologically, the area forms part of the Ermelo coalfield (south of Carolina). 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, where both underground and open-cast methods have been used. Researchers from the Council for Geoscience (CGS) have been working to implement a passive treatment plant at this discharge point and have collected geochemical data over four years. The current project, promoting the application of historical data to predict future
mine water quality, may serve as a prototype for future projects.

**Methods**
The methodology used in this study involves a cascading approach where one-step feeds into the next sequentially, until the last step has been reached. The sequence of the methodology is as follows: Hydrogeochemistry data > Identifying controlling factors > Gather all controlling factors > Pre-process all datasets > Design LSTM model > Carry out prediction tests using model > ANN model evaluation.

**Hydrogeochemistry data**
Hydrogeochemistry data used in this research were collected from the Witkranz discharge point (fig. 1) from 1 November 2014 to 13 June 2018 using conventional best-practice groundwater sampling guidelines, as described by Weaver et al. (2007). A total of forty-six (46) mine water samples were collected and analysed at the CGS laboratory according to the required parameters.

**Input-control factors for sulfate concentrations in mine water**
The first step in the development of a predictive mine water quality system involves understanding the possible factors controlling water quality, in this case, sulfate concentrations of the mine water. Based on the literature survey and our understanding of AMD generation, the following important controlling factors were considered as inputs to the system: precipitation, soil temperature, water table levels and water pH. These datasets for the site were either obtained from various governmental organisations or derived from variables, or measured on site.

**Output — sulfate**
Sulfate concentrations will be used to determine output labels (values) for the given input features as these are a good indicator of AMD pollution (Sakala et al. 2018).

**System development**
The GUI and other system developments were carried out using the Python open-source programming language. The programs are built using several Python built-in libraries: Tkinter, Numpy, Matplotlib, OSGeo, Tensorflow, Sklearn and Pandas.

Fig. 1 illustrates the development of the ANN system for the prediction of mine water quality. The system development may be broken down into data pre-processing and the prediction system architecture (input prediction — LSTM and ANN systems).

![Figure 1 System overview.](image-url)
Pre-processing

Pre-processing data involves reconfiguring the data to a format which can be used by the artificial intelligence (AI) system. The format in which data are gathered requires “cleaning” and formatting before the information can be used. The inputs (rainfall, temperature, pH, depth to water table) and output (sulfate) datasets are pre-processed in Microsoft Excel to attain a format which can be used by the prediction program.

Prediction system architecture

The design of the system architecture involves the generation of a system that uses historical data (features and output labels) to train/optimise its parameters and can be used as predicted labels for unseen/future data. This process involves the following steps:

- Designing the prediction system architecture using a sequential machine learning algorithm (long short-term memory — LSTM),
- Training and validation of the developed system.

Results and discussion

The GUI comprises a launch window and a processing window. The launch window is the main window from where the program is launched and from where the help files and information about the program can be accessed. The processing window prompts the user to load the four input parameters (rainfall, atmospheric temperature, pH values and depth to water table) and the output sulfate values using the “Browse” button. Fig. 2 shows the GUI for the processing module of the prediction program.

LSTM training

One of the most difficult problems associated with programming LSTM systems entails determining whether the LSTM model is performing well on the sequence prediction problem. That is, the model may be obtaining a good prediction score and / or a good model fit but in fact the model underfitted (where the model fits the data too well causing low bias but high variance) or overfitted (where the model does not fit the data well enough causing high bias but low variance) the training data. This can be overcome by using diagnosis plots to monitor the training process both for the training and validation datasets and stopping the training process. Early stopping involves stopping the training process once the performance of the validation dataset stops increasing (i.e. the cost begins to increase steadily instead of decreasing).

After the early stopping points for each of the four parameters have been determined, the LSTMs for each input is run to predict future values for each dataset. Fig. 3 shows a graphic representation of parameters

![Figure 2 Prediction processing window of the GUI.](image-url)
Figure 3 Testing the input predictions for a) rainfall, b) water table, c) water pH, d) air temperature and input parameters for the Witkranz discharge site.
against days with results for the training and prediction. The observation values are shown as green dots, the LSTM fitting model as a black line and the output prediction data as a red line for the four input parameters. Training was done using 1400 days of historical information and 350 days of future prediction.

**ANN network system**

Using the historical input parameters (rainfall, water table, temperature and pH), the ANN is trained, and the trained ANN model is used to predict the future sulfate concentrations by feeding the LSTM predicted future values of each input into the model.

Fig. 4 shows the schematic layout of the ANN system used in the development of the prediction system. The four inputs (which are outputs of the LSTMs for each input) are fed into the ANN input layer which, in turn, is linked to the output layer via the hidden layer. The hidden layer is used to adjust the node connections to establish the relationship between the inputs and the output.

The parameters used for the training are: Tensorflow (Gradient Descent Optimiser) with a value of 0.01 and a batch size value of 100. When the ANN system code is executed, the loss and accuracy graphs are plotted, as shown in Fig. 5. The graph shows the decaying mean square errors (MSE) as the number of training epochs increases which flattens as the number of training epochs increases. This corresponds to the time when the ANN is termed “trained network” with an MSE value of 0.054. The training accuracy increases sharply in the first 200 epochs and flattens around 99% accuracy, showing that the ANN system has been well trained.

The trained ANN model was used to predict sulfate values into the future from the last date of the historical data. Predictions were done from June 2018 to May 2019. The orange line in fig.6 shows the predicted sulfate values from the model. It is encouraging to note that the sulfate values are progressively decreasing over time. One possible reason is that the sulfide-bearing minerals may be depleted as the acid-producing reactions have been continuing for several years. As a part of future work, the system will be validated by collecting samples from the discharge site and will be refined by training the network with more data. Furthermore, the control processes affecting the sulfate concentrations in mine water will also be revisited and the system will be updated accordingly. The idea is to develop a preliminary AI prototype prediction system that can be reviewed and refined as when new data and information become available, a goal which was indeed achieved, as presented in this article.

**Conclusions**

Development of a future mine water quality prediction system should take the factors affecting the generation of AMD into consideration. The factors considered for the current study are rainfall, air temperature, water discharge pH and depth to water table. Sulfate concentrations were used as a proxy for the water quality index. The ANN system was designed and tested using data from

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**Figure 4** Machine learning ANN system for the prediction of mine water quality.
the Witkranz discharge site and over 99% training accuracy was obtained for a sample size of 46.

The effect of the water quality prediction system development are as follows:

- The system can be scaled up and used for the prediction of the future water quality of mine water, groundwater and surface water at regional and national scales. This would help in the management of these natural resources and raising awareness among the public and industry.
- The developing such a system will create more innovative possibilities and support the development of predictive mindsets with many benefits for the scientists involved and humanity at large.

Acknowledgements

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Figure 5 Designed ANN system performance checks during training a) MSE b) training accuracy.

Figure 6 Prediction values for sulfate using the developed prototype.
Mineralogical Attenuation Processes Associated With The Evolution Of Acid Mine Drainage In Sulfide-Rich Mine Wastes

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Abstract

The geochemical evolution of acid mine drainage results in secondary minerals that play a key role in the environmental behavior of the mine wastes. The present work is focused on these newly formed minerals at the Penedono waste dump, characterized by fine grained tails with pyrite and arsenopyrite. Mineralogical study led to an inventory of secondary phases, comprising soluble sulfates, scorodite, and oxyhydroxysulfates. In addition, there is amorphous Fe, As rich-nanoprecipitates. Jarosite and scorodite are abundant minerals, acting as cement for encrusting tails in Fe and As-rich hardpans. These hard structures are relatively insoluble, retaining toxic elements, thereby contributing to natural attenuation of mining contamination associated with the sulphide wastes.

Keywords: Mineralogical control, scorodite, jarosite, salt efflorescences, hardpans

Introduction

Abandoned mines are important focus of environmental impact in regions with substantial mining tradition, like the North of Portugal. In sulfide-rich waste dumps acid mine drainage (AMD) may contribute to the mobility of potentially toxic elements (PTE), being responsible for water, soil and sediment contamination, sometimes over a great distance from the mines. The present study was focused in a sulfide-rich waste dump in the North of Portugal (Penedono mine) (Figure 1). This mine has been exploited for gold and arsenic until the 1990s. Presently, it is abandoned, even though the waste dumps do remain without environmental rehabilitation.

There are several works reporting the occurrence of high levels of PTE in the surrounding soils (Abreu et al. 2007). Nevertheless, some authors show the progressive colonization of the waste dumps by autochthonous species (Gomes et al. 2014), which reveals that natural attenuation processes are underway. Geochemical and mineralogical evolution lead to new mineral phases as documented in other former mining sites (e.g. Hammarstrom et al. 2005; Dold 2014; Olías and Nieto 2015; Valente et al. 2013). Therefore, the main objective of the present work relies in the identification of the secondary minerals and aggregates associated with AMD in the Penedono waste dumps. Moreover, it intends to characterize these materials, including Fe and As-rich hardpans, in order to evaluate their role in the retention of PTE and, thus, their contribution for natural attenuation processes.

Study site

Penedono was a gold and arsenic mine, located in the Northeast of Portugal. Exploitation occurred in hydrothermal deposit with quartz veins with sulfides (Figure 1). The mine wastes have abundant fine particles of quartz and arsenopyrite. Nowadays, the waste dumps present signs of strong instability enhanced by steepness and high gradient slopes. A big ravine with NE-SW orientation contributes to spatial dispersion of the mine wastes (Figure 2).

The study area is characterized by dry summers and cold winters, with average annual precipitation and temperature of
about 1700 mm/year and 21°C, respectively (IPMA, unpublished data). However, between June and September it is possible to register air temperatures higher than 30°C. A wide range of microenvironments was recorded at the waste dumps, with the temperature and humidity varied between 25-40°C and 30-70%, respectively.

**Methods**

Sampling included collection of surface water, salt efflorescences and hardpans in the dry season (June) of two consecutive years. The last were randomly collected to cover diverse terrain settings. Also, sampling tried to represent the macroscopic variety observed in the field, based on colors and occurrence modes. Efflorescent salts were stored in closed vessels. Humidity and temperature were measured at sampling sites with a portable hygrometer.

The mineralogical study was performed by x-ray diffraction (XRD) with CuKα radiation at 40 kV and 30 mA. Identification and paragenetic study were completed by field emission scanning electron microscopy (FESEM) after coating samples with chromium film. Hardpans were gently milled and wet sieved to < 20 µm. Diluted suspensions of this fraction were studied by transmission electron microscopy (TEM).

Water was collected at the sampling sites represented in figure 1. The background hydrochemistry was characterized by the

![Figure 1 Penedono mine with simplified geology, sketch of the waste dumps and water sampling sites](image)
site P0, upstream the influence of the mine. The pH, electric conductivity (EC), and redox potential (Eh) were measured in the field with multiparameter model Orion 5. The samples were stored in pre-washed polyethylene bottles and refrigerated (<4°C). They were analysed for total acidity and sulfate. Metals and arsenic were analysed by inductively coupled plasma mass spectrometry (ICP-MS) in filtered and acidified aliquot until pH < 2.

Blanks, replicates and stock solutions were used to assess quality control of the results. The accuracy of the methods was verified using certified patterns. The measurement precision was within relative standard deviation (RSD) of 5% for all methods.

Results and discussion

AMD properties

Table 1 shows the properties of the surface water. The low pH (3-4) indicates typical conditions of AMD. The sulfate nature is demonstrated by comparison with the background (P0). Also, such a comparison indicates the influence of the waste dumps, generating high contents of metals and arsenic.

Secondary minerals and aggregates

The new minerals are over and mixed with fine grains of quartz and muscovite. Consequently separation for obtaining pure samples is a rather difficult task. Table 2 presents a list of the identified phases, with respective distribution. An estimation of abundance is also provided. Field images in figure 3a-c illustrate habits and occurrence modes of some sulfates, including the relatively uncommon metavoltine, but highly expressive in these waste dumps. It is rare to observe single phases or pure aggregates; generally the sulfates form assemblages more or less complex as shown in the SEM images (Figure 3 d-g).

Hydrous sulfates are distributed throughout the area of the waste dumps. However, the highest abundance and diversity were observed on the exposed slopes, in condition of high evaporation, which leads to salt efflorescences. Also, downstream of the waste dumps, there are abundant gypsum and pickeringite, filling fractures in the margins of the small receiving creek (Figure 1). The group of minerals with the general form $M^{2+}Al_2(SO_4)_2 \cdot 22H_2O$ occurs abundantly, though sometimes it is difficult to assure their refinement. The extremes pickeringite (Mg) and halotrichite (Fe) are the most commonly discriminated. In terms of iron hydrous sulfates, Fe precipitates in different oxidation states, including abundant melanterite, copiapite, and rhomboclase. They are profuse at the base and at middle height of the exposed slopes, mixed and over the fine grained tails.

Table 1 Water properties of AMD and surface background.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>Eh (mV)</th>
<th>SO$_4$</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3-P1 (n=6)</td>
<td>3.5</td>
<td>1196</td>
<td>486</td>
<td>486</td>
<td>36.57</td>
<td>23.36</td>
<td>16.85</td>
<td>2.24</td>
<td>2.54</td>
</tr>
<tr>
<td>P0 (n=2)</td>
<td>6.3</td>
<td>69</td>
<td>240</td>
<td>5.1</td>
<td>2.3</td>
<td>0.290</td>
<td>0.650</td>
<td>0.012</td>
<td>0.00053</td>
</tr>
</tbody>
</table>
### Table 2 Secondary phases associated with sulphide-rich wastes in Penedono; + rare; +++++ very abundant

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>Abundance</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melanterite</td>
<td>FeSO₄·7H₂O</td>
<td>+++++</td>
<td></td>
</tr>
<tr>
<td>Rozenite</td>
<td>FeSO₄·4H₂O</td>
<td>+++</td>
<td></td>
</tr>
<tr>
<td>Szomolnokite</td>
<td>FeSO₄·H₂O</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Copiapite</td>
<td>Fe₂⁺Fe₄³⁺(SO₄)₂·20H₂O</td>
<td>+++</td>
<td>Exposed slopes</td>
</tr>
<tr>
<td>Rhomboclase</td>
<td>HFe₃⁺(SO₄)₂·4H₂O</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Epsomite</td>
<td>MgSO₄·7H₂O</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Starkeyte</td>
<td>MgSO₄·4H₂O</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Halotrichite</td>
<td>FeAl₂(SO₄)⁴·22H₂O</td>
<td>+++++</td>
<td></td>
</tr>
<tr>
<td>Pickeringite</td>
<td>MgAl₂(SO₄)⁴·22H₂O</td>
<td>+++++</td>
<td>Exposed slopes and creek margins</td>
</tr>
<tr>
<td>Wupatkiite</td>
<td>(Co, Mg, Ni) Al₂(SO₄)⁴·22H₂O</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Apjohnite</td>
<td>MnAl₂(SO₄)⁴·22H₂O</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Alunogen</td>
<td>Al₂(SO₄)₃·17H₂O</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Tamarugite</td>
<td>NaAl(SO₄)₂·6H₂O</td>
<td>+++</td>
<td>Exposed slopes</td>
</tr>
<tr>
<td>Kalinite</td>
<td>KAl(SO₄)₂·11H₂O</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Chalcanthite</td>
<td>CuSO₄·7H₂O</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Metavolinite</td>
<td>K₂Na₆Fe₂⁺Fe₃⁺·6O₂(5SO₄)₁₂·18H₂O</td>
<td>+++++</td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>+++++</td>
<td></td>
</tr>
<tr>
<td>Scordite</td>
<td>FeAsO₄·2H₂O</td>
<td>+++++</td>
<td>ubiquitous</td>
</tr>
<tr>
<td>Jarosite</td>
<td>KFe₃⁺(SO₄)₂(OH)⁶</td>
<td>+++++</td>
<td></td>
</tr>
<tr>
<td>Goethite</td>
<td>FeOOH</td>
<td>+</td>
<td>Widespread in hardpans</td>
</tr>
<tr>
<td>Schwertmannite</td>
<td>Fe₈ O₈(SO₄)OH⁶</td>
<td>+</td>
<td>Water emergence</td>
</tr>
<tr>
<td>Amorphous</td>
<td>Fe arsenate and Fe oxyhydroxide</td>
<td>+++++</td>
<td>Widespread</td>
</tr>
</tbody>
</table>

Most of the soluble minerals have been documented in AMD-systems worldwide, like melanterite and copiapite (e.g. Valente et al., 2015; Sánchez-España 2008; Durães et al. 2008). Nevertheless, some less common phases were identified, such as metavolinite. Schwertmannite, usually abundant, was only detected at the base of the waste dump, around P1 (Figure 1). On the contrary, jarosite is ubiquitous. The first was observed at the base, where pH rounds 3.0, which is in accordance with equilibrium conditions for this mineral (Bigham et al., 1994). Lower values are expected in the pore water of the waste dumps, favoring the precipitation of jarosite as noted by the model of evolution of secondary Fe minerals proposed by several authors (e.g. Bigham et al., 1994; Montero et al. 2005). Together with jarosite, scorodite is widespread. As observed by Murciego et al. (2011), these are the two main products of arsenopyrite oxidation. Jarosite occurs as powder masses in dry channels or in crustified aggregates. The same occurs with scorodite, which appears as bluish or greenish powder, plates, and crustified structures, which configure hardpans. Hardpans are aggregates of primary and secondary minerals, in which a cementing material progressively assures the agglutination. Formation of hardpans in sulphide-rich environments has been documented by several authors (e.g. Lottermoser and Ashley 2006; Courtin-nomade et al., 2003). The entire base of the Penedono waste dumps is surrounded by hard and sometimes large crusts (hardpans) of different nature. They enclose grains of inherited phases like quartz, muscovite, feldspars, and sulphides, cemented mainly by an AMD-precipitate that assures cohesion.

Figure 4 illustrates the main types of hardpans, which are mostly Fe-rich and As-rich crusts. In addition to jarosite and scorodite, encrusting cements were found to include clay minerals and amorphous material. Valente et al. (2015) documented the nature of the non-crystalline nanoprecipitates, comprising iron oxyhydroxides and iron arsenates.

Hardpans show varied colors, hardness, and cohesion. The Fe-rich hardpans are cemented by major jarosite often in coexistence with goethite (Figure 4a-b). They form the most cohesive and can appear massive or, more usually, as banded structures with yellow-orange-reddish thin
Figure 3 Salt efflorescences and typical assemblages. a) yellow-greenish botryoidal copiapite in association with a mixture of Al- sulfates; b) Radiated aggregates of acicular minerals of the group pickeringite- Wupatkiite- Apjohnite; c) Yellowish brown crystals of metavoltine; d) SEM images and EDS spectra of platy tamarugite enclosing aggregates of jarosite and tubular copiapite; e) Acicular halotrichite and melanterite (probably adsorption of As); f) Platy alunogen enclosing aggregates of chalcantite; g) Jarosite over a plate of scorodite

Neutralization, precipitation and adsorption are important attenuation processes in the presence of mining wastes (Hammarstrom et al., 2005; Wilkin, 2007). Precipitation of evaporative minerals avoid, although temporarily, release of metals and acidity. On the other hand, jarosite and scorodite are more stable in acid conditions, thus they should be more effective in retention of contaminants. For example, DeSisto et al. (2011) emphasize this role of scorodite due to its relatively low solubility (<1 mg/L at pH

layers. Sometimes, the layers indicate the flow direction at the moment of the tailings deposition as illustrated in figure 4-c. Also, there are whitish fragile hardpans, in which kaolinite is the major cementing material (Figure 4-d). The As-rich hardpans, encrusted by the iron arsenate, assume blue or blue-greenish colors (Figure 4 e-f). Though there are these two extremes (Fe and As), hardpans incorporate intermediate proportions of jarosite, goethite, scorodite and amorphous materials.
3–4) and high contents of As (43–52% As₂O₅). Therefore, by stability of the cement and also the hardness, Fe and As-rich hardpans should be the more efficient supergenic structures limiting the oxidative dissolution of sulphides and, consequently, the mobility of PTE.

**Conclusion**

The inventory of secondary minerals indicated a considerable number of phases, mostly of Fe and Al, which are typical of AMD systems. In their composition and on their surfaces the sulfates contain PTE. Most of them are soluble and therefore with a limited efficiency controlling mobility of metals and As. However, there is a profusion of minerals relatively more stable, like jarosite and scorodite. Furthermore, both may act as cementing material, forming hardpans. Field observations, confirmed by the mineralogical study, indicate the high abundance and the environmental relevance of hardpans. They act as barriers to oxidation and dissolution of reactive phases, thereby inhibiting the mobility of PTE.

**Acknowledgements**

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MINE WATER TREATMENT
Recovery of Metals from Acid Mine Drainage Using Organic Polymer

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Abstract
Metal recovery efficiency of chitosan was investigated in order to prepare “mixed” gelatin hydrogels including some organic solids with a high metal adsorption capacity. At pH 5, 0.1 g of chitosan recovered approximately 90 % of Cu from 50 mL of the simulated solution. Cu recovery using chitosan was affected by pH. At relatively higher pH (>3.0), over 90 % of Cu recovery was maintained. In contrast, lower Zn was recovered in comparison with Cu. Mn recovery was hardly detected within the pH range of 2-5. From these results, it was considered that “mixed” gelatin hydrogel blended with chitosan had a potential for the high-performance adsorbent for Cu recovery.

Keywords: acid mine drainage, adsorption, natural organic polymer

Introduction
Acid mine drainage (AMD) is a serious environmental pollution issue in the mining industry. Some materials including accumulated mining waste, flotation tailings and unmined minerals, etc. often cause the AMD. The generated AMD can have an extremely acidic pH and contain various metal ions (Fe, Cu, Pb, Zn, etc.). Besides, the AMD generation continues even if mining operation is closed. Thus, such AMD pollution issue is also very serious for Japan where almost all mines have already been closed. In order to prevent such ecological threat due to AMD flowing out of the mine area, the AMD should be treated by removal of the contained hazardous metals. A neutralization process is generally applied to the AMD treatment. It is a very effective treatment process because the hazardous metals can be removed from the AMD as hydroxides while a strong acidic pH is adjusted by alkaline chemicals. This neutralization method contributes to reduction of the environmental impact due to the AMD. But, generated metal sludge is sent to repository sites without any reutilization of the metals in many AMD treatment sites. Because the AMD often contains some valuable metals, to use the AMD as a source of metals is desirable for some countries which is poor in metal resources.

Adsorption is one of the effective techniques for recovery of metal ions from water. Recovery and separation of metals by adsorption can achieve both purification of the AMD and metal recovery. Some research topics related to metal removal by adsorption have been reported (Patila et al. 2016). Especially, we are focusing attention on metal recovery using natural organic polymers such as proteins or sugars. And we have investigated a novel adsorbent prepared from using gelatin, a fibrous protein, for recovery of cationic metal ions from AMD (Bessho et al. 2017). In previous study, it was confirmed that alkaline-extracted gelatin hydrogel could had a potential for recovery of some metals from aqueous solutions. But, the Cu recovery efficiency was not sufficient. Generally, increase in the number of adsorption sites will lead to the improvement of adsorption capacity of the gelatin hydrogels. There are some approaches to development of the gelatin hydrogel having an excellent
adsorption capacity of Cu. These approaches includes 1) addition of polar groups to gelatin by chemical modification, 2) preparation of “hybrid” gels with gelatin and other organic compounds and 3) preparation of “mixed” gelatin hydrogels including some organic solids. Considering the simplicity of the hydrogel adsorbent, preparation of the “mixed” gelatin hydrogel is much suitable. Besides, such a “mixed” hydrogel can prevent solid dispersion in liquids.

Thus, chitosan were selected as a natural organic compound to include in gelatin hydrogels. Chitosan is a nitrogenous polysaccharide composed mainly of poly (β-1-4)-2-amino-2-deoxy-d-glucopyranose, and a suitable natural organic polymer as an adsorbent for metal ions due to the presences of the amino and hydroxyl groups (Chatterjee et al. 2005). Chitosan is usually produced through the deacetylation of chitin, a long-chain polymer of N-acetylglucosamine, which composes the carapace or shell of a shrimp or a crab. Possibly, chitosan adsorbents can be produced from food waste. In this study, Cu, Zn and Mn aqueous solutions were prepared as a model solution for AMD. And then, we investigated the basic adsorption behavior of these metal ions to chitosan.

Methods

Materials

As an adsorbent material for metal recovery, chitosan with medium molecular weight was purchased from Sigma-Aldrich Japan Co., Japan. This chitosan sample had a shape of powder and/or chips, and then was used without any purification.

In this study, three kinds of simulated metal solutions were used. Two millimolar of copper, zinc and manganese were prepared from copper sulfate pentahydrate (CuSO₄.5H₂O), zinc sulfate heptahydrate (ZnSO₄.7H₂O) and manganese sulfate pentahydrate (MnSO₄.5H₂O), respectively. These sulfates were purchased from Wako Pure Chemical Industries, Ltd., Japan. Solution pH was, as needed, adjusted to given pH by H₂SO₄ solutions (Wako Pure Chemical Industries). For metal recovery test, 2 mM of simulated Cu solutions at various pHs were mainly used. The simulated Zn and Mn solutions were used to estimate the effect of metal species on recovery of metals using chitosan.

Metal recovery test using chitosan samples

Adsorption tests for a metal recovery using chitosan were mainly performed at room temperature, using the following procedure. After prescribed volumes (10-200 mL) of each simulated solution containing 2 mM of the metal at different pHs was poured into a glass beaker, 0.1 g of chitosan was introduced into the simulated metal solution. The simulated solutions with the chitosan samples were stirred with a magnetic bar for the predetermined time.

Quantitative analysis of metals in solutions

For a quantitative analysis, simulated metal solutions were filtrated through a 0.45 µm mesh membrane filter after the recovery tests. Copper, zinc and manganese concentrations in the filtered solutions were measured by inductively-coupled plasma optical emission spectrometry (ICP-OES, SPS 5510, Seiko Instruments Inc., Japan). Based on results of the ICP analysis, the amount or rate of metal recovery were calculated.

Results

Recovery capacity of Cu using chitosan samples

Figure 1 shows change in the Cu concentration after adding 0.1 g of chitosan to 10 mL of simulated solution at pH 5. This result revealed the Cu concentration drastically decreased just after addition of chitosan. It took about one hour to recover almost all copper from the solution. To estimate the efficiency of Cu recovery by chitosan, the Cu recovery tests were conducted by changing the volume of the simulated solutions. Figure 2 shows the effect of solution volume on recovery of Cu at pH 5. Closed circles and rectangles represent Cu concentration in the simulated solutions and Cu recovery rate, respectively. Initial Cu concentration corresponds to approx. 130 mg/L. In case of 50 mL of the solution volume, over 90 % of Cu could be recovered from the solution. The Cu concentration finally decreased to approx.
10 mg/L. But, the Cu recovery rate generally decreased with increase in the solution volume. In accordance with that, the final Cu concentration increased. Figure 3 shows relationship between solution volume and Cu adsorption capacity at pH 5. This figure implied total mass of Cu recovery from the solution increased while the Cu recovery rate decreased. Finally, Cu adsorption capacity reached approx. 1.2 mmol/g-chitosan.

**Effect of pH on Cu recovery using chitosan samples**

The effect of pH on Cu recovery using chitosan was investigated. At a pH of 2.0-5.0, 0.1 g of chitosan was added to 50 mL of the simulated Cu solutions, and then they were stirred for 24 h. Figure 4 shows chitosan samples after 24 h incubation in the simulated Cu solutions. In case of pH 2.0, the change in state of chitosan sample was not detected. In contrast, the color of the chitosan sample was changed into blue at over pH 3.0. It was considered that the change to blue reflected Cu recovery by adsorption into the chitosan.

Table 1 shows the result of Cu recovery test at various pH values. When the initial pH was 2.0, Cu recovery from the simulated solutions was not detected. This may imply that chitosan dissolved in the solution with lower pH. To the contrary, approx. 90 % of Cu could be recovered from the solutions at...
pH 3.0-5.0. At the same time, the solution pH also increased to around 5. Chitosan has lots of amino (-NH\(_2\)) and hydroxyl (-OH) groups. It is considered that metal can be adsorbed into chitosan due to formation of chelate compounds with cationic metal ions generally. It was implied that Cu recovery using chitosan was mainly induced by formation of chelate compounds.

Comparison of Cu recovery using chitosan with Zn and Mn

To estimate the effect of metal species on recovery using chitosan, Zn and Mn recovery tests were carried out. At a pH of 2.0-5.0, 0.1 g of chitosan was added to 50 mL of the simulated Zn or Mn solutions, and then they were stirred for 24 h. Figure 5 shows recovery of Zn and Mn by chitosan at pH 5. For comparison, the result of Cu recovery was also presented in Figure 5. As mentioned above, around 90 % of Cu could be recovered from the solutions at over pH 3. At pH 2.0, Zn and Mn were not recovered same as Cu. Dissolution of a part of chitosan into the

### Table 1 Result of Cu recovery test using chitosan.

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu recovery (before)</th>
<th>Cu recovery (after)</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2.4</td>
<td>0.0</td>
<td>0%</td>
</tr>
<tr>
<td>3.0</td>
<td>5.0</td>
<td>5.0</td>
<td>90.8%</td>
</tr>
<tr>
<td>4.0</td>
<td>5.2</td>
<td>5.0</td>
<td>91.1%</td>
</tr>
<tr>
<td>5.0</td>
<td>5.4</td>
<td>4.8</td>
<td>87.9%</td>
</tr>
</tbody>
</table>
solutions caused no Zn and Mn recovery. At over pH 3.0, it was also confirmed that all the pHs of Zn and Mn solutions increased to around 6. In case of Zn, some amount of Zn was recovered at over pH 3.0. But, the recovery rate of Zn was between 50 and 60 %, less than that of Cu. The recovery test using the simulated Mn solutions revealed that Mn recovery was hardly detected in the pH range of 2.0-5.0. These results suggest that metal recovery using chitosan may be affected by some properties of metal ions such as ionic radius, ionization tendency and so on.

Consequently, chitosan powder had a possibility for a high performance of Cu recovery from wastewater. From these results, it was also possible that chitosan could selectively recover Cu from solutions containing Cu and Mn ions within the pH range of 3-5. Thus, “mixed” gelatin hydrogel blended with chitosan can be expected to be used as the high-performance adsorbent for Cu recovery.

**Conclusions**

In order to develop gelatin hydrogels having a high-performance adsorption capacity for metal recovery from AMD, preparation of “mixed” gelatin hydrogels blended with other natural organic compound was suggested. Thus, metal recovery efficiency of chitosan was investigated using 2 mM of simulated metal solutions.

When 0.1 g of chitosan was added to 10 mL of simulated Cu solution at pH 5, the Cu concentration drastically decreased just after addition of chitosan. Finally, almost all copper could be recovered from the solution after one hour. Additionally, the Cu recovery tests were conducted by changing the volume of the simulated solutions. In case of up to 50 mL of the solutions, a small amount (0.1 g) of chitosan could recover 90 % of Cu. And then, the Cu recovery rate generally decreased with increase in the solution volume. The Cu adsorption capacity reached approx. 1.2 mmol/g-chitosan.

When the effect of pH on Cu recovery using chitosan was investigated, approx. 90 % of Cu could be recovered from the solutions at pH 3.0-5.0. However, Cu recovery was not detected at pH 2.0. Thus, it was considered that adjustment of solution pH allowed to recover Cu from acidic wastewater. Chitosan mainly has lots of amino and hydroxyl groups. It was implied that Cu recovery using chitosan was mainly induced by formation of chelate compounds.

---

**Figure 5** Effect of pH on recovery of various metals using the chitosan samples.
To estimate the effect of metal species on recovery using chitosan, the behavior of Zn and Mn recovery was investigated. This experiment revealed that much higher Cu recovery rate was provided in comparison with Zn and Mn. Because chitosan especially had a high-performance of Cu recovery, it was considered that “mixed” gelatin hydrogel blended with chitosan had a potential for the high-performance adsorbent for Cu recovery.

Acknowledgements
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References


Abstract

RO membranes are an attractive treatment technology for mine impacted water due to the range of pollutants which they can remove with modest energy requirement. There is lack of data on Ammonia-N removal, which is typically present in appreciable quantities and is toxic toward aquatic life. This paper reports on Ammonia-N rejection data obtained for membranes on a mine water feed. The sea water membrane obtained 27% lower Ammonia-N passage compared to brackish water membranes, but with higher energy requirement. Regressed design parameters were fed into a solution-diffusion model to describe performance of an 8-inch membrane plant. An opex study considered different plant designs treating various Ammonia-N loads, with 0.8 mg/L discharge limit. Brackish water membranes could treat a maximum feed of 7.5 mg/L. From 7.5 – 15 mg/L brackish water membranes with permeate recycle would be most cost effective. From 15 mg/L sea water membranes with permeate recycle is required and could treat up to 22.5 mg/L feed. Permeate recycle is sensitive to power costs and less effective when rejection deteriorates. Future work should consider manipulation of feed pH for better rejection and non-membrane technologies for better risk management.

Keywords: Mine impacted water, RO membranes, Ammonia-N, permeate recycle, capital cost, operational cost, polishing, risk management

Introduction

Extraction of minerals in mining operations requires an explosive typically containing ammonium nitrate. Incomplete reaction allows residual ammonium nitrate to be mobilized in drainages from the site (Hallin et al. 2015; Häyrynen et al. 2009). Unionized ammonia is toxic to fish, with a mean acute toxicity level of 2.79 mg/L Ammonia-N and 1.86 mg/L Ammonia-N for freshwater and saltwater species being reported, respectively (USEPA 1985; USEPA 1989). Mining companies typically deploy membrane systems to treat affected waters due to the broad range of contaminants that can be separated (Aguiar et al. 2016). This enables the water balance over the tailings storage facility (TSF) and waste rock dumps to be managed and to satisfy permitting requirements of environmental authorities. Rejection ratios are used to quantify the extent of separation of solutes from water for different types of membranes with the parameter formally being defined as \(1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}\)×100%. Rejection data, together with water permeability, are the two most important parameters which dictate membrane selection during the process design phase. Ammonia-N RO membrane rejection data for feed streams emanating from mine dewatering operations are scarce. Van Voorthuizen et al. (2005) reported Ammonia-N rejections of 80-90% when treating domestic waste water with low energy brackish water RO membranes. Such technology would not be appropriate when treating mine impacted water of Ammonia-N levels > 10 mg/L and a discharge of 1 mg/L or less has been imposed.

This paper reports on ammonia-N rejection data generated for 4-inch high rejection brackish and low energy seawater RO membranes on a synthetic neutral pit lake feed matrix. Membranes considered in this study included the Toray TML10D (brackish), Hydranautics CPA7-LD-4040 (brackish) and Suez AE90 (low energy sea water). Testing enabled computation of membrane-specific ammonia-N permeability coefficients (B-values), pure water permeability coefficients (A-values) as well as calibration of a feed channel pressure...
drop correlation as a function of feed spacer thickness, membrane leaf length and Reynolds number. These parameters enabled scale up to 8-inch equivalents of the tested membranes as well as prediction of rejection performance for a full-scale RO membrane system fed different levels of ammonia-N (5, 10 and 15 mg/L) and total dissolved solids (TDS) of 1400 mg/L. The operational (opex) costs associated with different RO design configurations are then evaluated to determine the most cost-effective route of producing 40 L/s of treated water meeting a discharge specification of 0.8 mg/L Ammonia-N.

Progressive separation of water causes total dissolved solids to cycle up across an element string in a pilot or full-scale membrane plant. Two consequences arise from a strengthening in feed chemistry along the string: (1) driving force for salt flux across the membrane increases and (2) the feed osmotic pressure is elevated, which combined with dynamic pressure losses across the feed channel lowers the net driving pressure for permeate flux. These two factors ultimately cause a worsening of permeate quality and hence rejection as recovery is increased. The intent of this study was to model the inherent rejection capabilities of the selected membranes under a series of operating conditions corresponding with discrete points across a full-scale element string. A-values and pressure drop characteristics supplied by membrane manufacturers enabled permeate flux and volumetric recovery profiles to be obtained across a two-stage RO operating at 80% overall recovery, which was then used to fix hydraulic conditions for the lead and tail element rejection tests as shown in Table 2. Feed flow rates differed for each membrane for the same test type due to differences in membrane surface area. Permeate flux was assumed to be the dominant factor affecting rejection performance in this regard (Artuğ 2007). Feed chemistry for tail element rejection tests was approximated by purging 78% of lead element rejection test feed solution to permeate at fixed pump speed.

The test rig was designed and built according to the ASTM specification D4194-03 Standard Test Methods for Operating Characteristics of Reverse Osmosis and Nanofiltration Devices – refer to Figure 1 for further details. Major equipment included: 4”x40” single element vessel; feed and charge pumps; concentrate flow control valve; 5/20 µm cartridge filters for feed pretreatment; feed tank temperature controller; chilled water circuit as well as pressure and flow instrumentation on feed, permeate and concentrate lines. Sampling facilities were also provided on feed, permeate and concentrate lines for water quality analyses. The ASTM specification D4194-03 was designed for characterizing nominal single salt rejections of membranes. Hence the specification could not be followed in its entirety in this study. Nevertheless, certain aspects of the specification were adopted to

| Table 1: Targeted feed composition for synthetic mine water used in rejection tests |
|-----------------------------------|----------|---|---|
| pH | General | Cations | Anions | mg/L |
| 7.7 | Ca | SO₄²⁻ | 176 | 1029 |
| Temp | Ca | Mg | Na | Cl | mg/L |
| 30 °C | 180 | 34 | 39 |
| TDS | 1670 mg/L | Na | NH₄⁻ | 9.4 |
| Alkalinity as CaCO₃ | 38 mg/L | NH₄⁺ | |

| Table 2: Rejection test matrix |
|--------------------------------|---------|---|---|---|---|---|---|---|
| Test # | Test class | Membrane model | Area m² | Temp °C | Flux lmh | Recovery % | Feed m³/hr | Permeate m³/hr |
| 1-01 | Lead | TML10D | 6.78 | 30 | 24 | 10 | 1.64 | 0.16 |
| 1-02 | Tail | TML10D | 6.78 | 30 | 12 | 11 | 0.74 | 0.08 |
| 1-03 | Lead | CPA7-LD-4040 | 7.43 | 30 | 24 | 10 | 1.80 | 0.18 |
| 1-04 | Tail | CPA7-LD-4040 | 7.43 | 30 | 12 | 11 | 0.81 | 0.09 |
| 1-05 | Lead | AE90 | 8.36 | 30 | 24 | 10 | 2.02 | 0.20 |
| 1-06 | Tail | AE90 | 8.36 | 30 | 12 | 11 | 0.91 | 0.10 |
enhance the rigour of the test work such as:
(1) a maximum variation of 1°C either side of the chosen operating temperature of 30 °C,
(2) enforcing a maximum of 10% variation for three successive permeate flux, recovery, overall salt and ammonia-N rejections and
(3) at least 60 minutes of stable operation between sample sets. A Hach ammonium ISE probe model ISENH4181AP (USA) was used to measure ammonia-N. Calibration curves were constructed daily using 0.08 mg/L, 0.78 mg/L, 10 mg/L, and 100 mg/L ammonia-N standard solutions to account for probe drift. As per manufacturer recommendation, 5 mL of ionic strength adjuster (ISA) solution was added to 20 mL of sample for calibration and rejection test samples. ISA solution elevates the ionic strength of the sample sufficiently such that any changes in species concentration in the range of interest will not effect the ammonia-N activity coefficient, thereby allowing for the direct conversion of mV output to concentration.

The permeability coefficient for each membrane was determined using Equation 1, while the ammonia-N and overall salt permeability coefficients were determined using Equations 2 and 3 respectively below.

\[
A = \frac{I_v}{(P_{feeder} - 0.5\Delta P - P_{perm} - n_{c} + n_{p})T C P}
\]

\[
B_{ammonia-N} = \frac{C_{p,ammonia-N}I_v}{(C_{T,ammonia-N} - C_{p,ammonia-N})T C P}
\]

\[
B_{salt} = \frac{C_{p,ammonia-N}I_v}{(C_{T,salt} - C_{p,salt})T C P}
\]

**Figure 1:** Diagram of test rig according to ASTM specification D4193-03 where P, T, L, H, and HT are abbreviations for pressure, temperature, low pressure, high pressure, and high temperature respectively.
Results

Experimental Results

Table 3 below presents rejection data as well as the computed membrane-specific performance parameters from each rejection test. Lead and tail ammonia-N permeability coefficients for each membrane differed by <2% and 17% for the brackish water membranes and low energy seawater membrane, respectively. Ammonia-N rejection data was found to be similar for both brackish water membranes. The ammonia-N permeability coefficient was found to be 27% lower for the low energy seawater membrane, but at the expense of a 59% lower pure water permeability coefficient when compared to the brackish water membranes. Computed membrane coefficients and feed channel pressure drop correlations for the 4-inch membranes were assumed to be the same for their 8-inch equivalents. The parameters were used in a simplified solution-diffusion model developed by Miwatek in Python to simulate full-scale system performance.

The calibrated solution diffusion model was utilized to run projections of hydraulic profiles and permeate ammonia-N loading curves across the full-scale 8 inch membrane string. Figures 2 – 5 show experimental test points super-imposed on the hydraulic profiles and ammonia-N loading curves obtained from the Python model.

Table 3: Rejection data and modelled membrane parameters

<table>
<thead>
<tr>
<th>Test class</th>
<th>Membrane model</th>
<th>Feed pressure</th>
<th>Feed Cond</th>
<th>Feed amm-N</th>
<th>Perm Cond</th>
<th>Perm amm-N</th>
<th>A-value</th>
<th>B-salt</th>
<th>B-amm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>TML10D</td>
<td>5.00</td>
<td>1902</td>
<td>10.8</td>
<td>18.6</td>
<td>0.46</td>
<td>4.74</td>
<td>3.6E-08</td>
<td>2.2E-07</td>
</tr>
<tr>
<td>Tail</td>
<td>TML10D</td>
<td>4.10</td>
<td>5450</td>
<td>33.1</td>
<td>102</td>
<td>2.66</td>
<td>5.09</td>
<td>2.5E-08</td>
<td>2.2E-07</td>
</tr>
<tr>
<td>Lead</td>
<td>CPA7-LD-4040</td>
<td>5.40</td>
<td>1873</td>
<td>11.0</td>
<td>14.5</td>
<td>0.46</td>
<td>4.46</td>
<td>2.8E-08</td>
<td>2.2E-07</td>
</tr>
<tr>
<td>Tail</td>
<td>CPA7-LD-4040</td>
<td>4.00</td>
<td>5460</td>
<td>31.4</td>
<td>87.1</td>
<td>2.65</td>
<td>5.17</td>
<td>2.0E-08</td>
<td>2.2E-07</td>
</tr>
<tr>
<td>Lead</td>
<td>AE90</td>
<td>11.7</td>
<td>1902</td>
<td>12.2</td>
<td>9.60</td>
<td>0.37</td>
<td>1.94</td>
<td>1.9E-08</td>
<td>1.6E-07</td>
</tr>
<tr>
<td>Tail</td>
<td>AE90</td>
<td>7.30</td>
<td>5633</td>
<td>37.9</td>
<td>1.93</td>
<td>1.94</td>
<td>1.9E-08</td>
<td>1.3E-07</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2: Modeled feed pressure profile across element string with experimental conditions superimposed

Figure 3: Modeled flux profile across element string with experimental conditions superimposed

Figure 4: Modeled element recovery profile across element string with experimental conditions superimposed

Figure 5: Modeled element permeate concentration across element string with experimental conditions superimposed
importance of the curves is for verification that experiments were executed under representative conditions.

Overall, the experimental conditions of the low energy seawater element are the most representative based on replicating projections from a calibrated solution-diffusion model. There is a substantial difference in experimentally determined and modelled tail element permeate Ammonia-N concentrations for all three membranes tested. This behaviour would be expected if insufficient permeate was purged during cycling up resulting in a less concentrated tail feed.

The ammonia-B value was found to differ by a maximum of 17% between lead and tail experiments for the three elements. As a result of a consistent ammonia-N B-value being obtained the lack of cycling up is thought to have no substantial effect on the validity of the experimental data obtained. By interpolation, it is observed that the permeate concentrations obtained experimentally lie within the element string. The experimental point can be placed approximately element 10 and 11 for the high rejection brackish and low energy seawater elements respectively.

**Opex Study**
The operational cost study utilizes the membrane parameters computed based on experimental data to predict permeate concentrations, feed pressure and feed flow-rate for feed concentrations of 5, 10 and 15 mg/L ammonia-N at a fixed feed TDS of 1400 mg/L using the calibrated solution diffusion model. The study considered four variants of a two-stage RO system: (1) Brackish water membranes, (2) brackish water membranes with tail bank permeate recycle, (3) sea water membranes and (4) sea water membranes with tail bank permeate recycle. For each configuration, 80% overall recovery was targeted with fresh feed of 90 m3/hr to the plant. The B-values obtained for the CPA7-4040-LD and TML10D coincided close enough for the membranes to be equivalent. The data obtained from the modelling exercise is presented in Table 4. The opex study was limited to the pumping costs, i.e. electricity usage, of running the various RO configurations. The pumping costs were thought to be the difference between each of the alternatives as the remaining operating costs will remain approximately constant. In order to estimate the pumping costs, pump and motor efficiencies of 65% and 83% respectively were assumed. Utilities were costed at 0.19 $/kWh which was obtained for a plant situated in Ghana. A discharge limit of 1.00 mg/L ammonia-N for receiving surface waters is recommended by Ghanaian EPA. The RO system is designed to maintain an operational limit of 0.80 mg/L ammonia-N to manage risks of discharging non-compliant water. Table 4 summarizes which of the configurations meet discharge guidelines for a specified ammonia-N feed concentration. Table 4 also shows the pumping costs associated which each configuration.

The high rejection brackish water elements have a lower estimated pumping cost when compared to the low energy seawater elements.

### Table 4: Modelled data from Python for different RO configurations and feed ammonia concentrations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Feed amm-N mg/L</th>
<th>Perm amm-N mg/L</th>
<th>Feed Pressure kPag</th>
<th>Feed Flow m3/h</th>
<th>Ops Limit</th>
<th>Pumping Cost $/m3 Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brackish Only</td>
<td>5</td>
<td>0.54</td>
<td>549</td>
<td>90</td>
<td>✓</td>
<td>0.05</td>
</tr>
<tr>
<td>Brackish Only</td>
<td>10</td>
<td>1.09</td>
<td>549</td>
<td>90</td>
<td>×</td>
<td>0.05</td>
</tr>
<tr>
<td>Brackish Only</td>
<td>15</td>
<td>1.63</td>
<td>549</td>
<td>90</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Brackish with permeate</td>
<td>5</td>
<td>0.26</td>
<td>649</td>
<td>109</td>
<td>✓</td>
<td>0.06</td>
</tr>
<tr>
<td>Brackish with permeate</td>
<td>10</td>
<td>0.52</td>
<td>649</td>
<td>109</td>
<td>✓</td>
<td>0.06</td>
</tr>
<tr>
<td>Brackish with permeate</td>
<td>15</td>
<td>0.79</td>
<td>649</td>
<td>109</td>
<td>✓</td>
<td>0.06</td>
</tr>
<tr>
<td>Sea water only</td>
<td>5</td>
<td>0.39</td>
<td>1182</td>
<td>90</td>
<td>✓</td>
<td>0.12</td>
</tr>
<tr>
<td>Sea water only</td>
<td>10</td>
<td>0.77</td>
<td>1182</td>
<td>90</td>
<td>✓</td>
<td>0.12</td>
</tr>
<tr>
<td>Sea water only</td>
<td>15</td>
<td>1.16</td>
<td>1182</td>
<td>90</td>
<td>×</td>
<td>0.12</td>
</tr>
<tr>
<td>Sea water with permeate</td>
<td>5</td>
<td>0.18</td>
<td>1500</td>
<td>112</td>
<td>✓</td>
<td>0.15</td>
</tr>
<tr>
<td>Sea water with permeate</td>
<td>10</td>
<td>0.35</td>
<td>1500</td>
<td>112</td>
<td>✓</td>
<td>0.15</td>
</tr>
<tr>
<td>Sea water with permeate</td>
<td>15</td>
<td>0.53</td>
<td>1500</td>
<td>112</td>
<td>✓</td>
<td>0.15</td>
</tr>
</tbody>
</table>
This behaviour is due to the lower permeability of the low energy seawater elements. Table 3 shows an experimental A-value of 1.95 lmh/bar for the low energy seawater element which is 60% lower compared to the average A-value of 4.87 lmh/bar for the high rejection brackish water elements. Overall the permeate recycle systems meet the operational limits for all three feed concentrations presented. On a relatively low ammonia-N concentration of 5 mg/L ammonia-N a high rejection brackish water element would provide sufficient separation to discharge water within Ammonia-N specification. A high rejection brackish element with permeate recycle is able to maintain operational limits with feed concentrations up to 15 mg/L ammonia-N. The fact that a permeate concentration of 0.79 mg/L \( \text{NH}_3 \text{N} \) is achieved at 15 mg/L ammonia-N shows a feed of 15 mg/L ammonia-N is the threshold for utilization of high rejection brackish water elements with tail bank permeate recycle. If the feed increases past a feed of 15 ammonia-N a low energy seawater element with tail bank permeate recycle would be required at a resultant increase in the cost of approximately 150%. The maximum Ammonia-N feed level which a low energy sea water element with tail bank permeate recycle configuration could handle would be 22.5 mg/L.

Conclusions
The study presented herein revealed similar Ammonia-N rejection characteristics for both brackish water membranes. The low energy sea water membrane provided better Ammonia-N rejection, but at the expense of substantially higher energy requirement. For each of the membranes, the Ammonia-N B-values were an order of magnitude larger than the overall salt B-values confirming the fact that Ammonia-N has substantially lower rejection compared to the bulk average of ionic species in the feed. An opex study was performed considering multiple RO configurations which could be used to treat varying levels of feed Ammonia-N to a discharge specification of 0.8 mg/L. At 5 mg/L, the brackish water membrane only option would be most cost effective. Brackish water membranes would require tail bank permeate recycle to meet discharge specification above 7.5 mg/L to a maximum of 15 mg/L and would be more cost effective than running seawater membranes only. Permeate recycle is attractive due to low initial capital expenditure and ease of operation. Nevertheless, permeate recycle has multiple drawbacks including: sensitivity to power costs; vulnerability to diminishing returns when membrane degradation becomes relevant as well as the fact that spare capacity of the system is being used to reprocess treated water whereas priority should be assigned to processing additional fresh RO feed. Future work should entail investigation of other process levers, such as manipulation of feed pH to ensure all of the dissolved ammonia species are in the ionized (\( \text{NH}_4^+ \)) form. Other types of polishing technologies should also be explored such as the use of zeolite or breakpoint chlorination. Implementation of non-membrane based technologies as a backstop would make sense from a risk management perspective.

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The use of passive treatment systems to remediate AMD from abandoned coal mines, eMalahleni, South Africa – column experiments

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Abstract
In contributing towards mine water treatment solutions in South Africa, an experiment on Dispersed alkaline substrate (DAS) and reducing and alkalinity producing system (RAPS) systems was performed in the laboratory. The main aim of the study was to investigate the effectiveness of DAS and RAPS in treating AMD. Both treatment systems were able to raise the pH from an average of 3 to 8. Contaminants such as Fe, Al, and Zn were removed below detection limit. The column experiments remediated acid water successfully for 21 weeks after which the DAS system clogged while RAPS was continuing to treat AMD successfully.

Keywords: Passive treatment technologies, DAS, RAPS

Introduction
Owing to the nature of previous legislation in South Africa (SA), mines were abandoned without rehabilitation as the main focus at the time was on production and profit with little or no regard to the environment (Manders 2009). Many of abandoned coal mines generate contaminated mine water and, over the years, disposal, discharge, and seepage of such polluted water have resulted in the degradation of the water quality of streams and underground water (McCarthy 2011).

Passive treatment technologies are progressively gaining favor as a choice for long-term remediation of polluted mine water in many parts of the world owing to their association with low costs of implementing, operation, monitoring and maintenance (Hedin et al. 1994; Watzlaf et al. 2004), since they rely on natural ameliorative processes to remove contaminants in water (Hedin et al. 1994). Passive treatment systems utilise naturally available energy sources such as topographical slope, microbial energy, photosynthesis and chemical energy to operate successfully over its design life (PIRAMID Consortium 2003).

DAS and RAPS were investigated in treating mine water from an abandoned coal mine in eMalahleni, RAPS, a combination of anoxic limestone drain and a compost wetland, is one of the traditional passive treatment options for net-acidic mine water treatment (Riefler et al. 2008; Kepler &McCleary 1994) and DAS is a passive system introduced in Spain by Rötting et al. (2008) with the intention of solving the clogging problems associated with most of the passive treatments. Rötting et al. (2008) described DAS as a system composed of coarse matrix (e.g. wood shavings) for high permeability mixed with a fine-grained alkaline material (e.g. calcite) to provides a bulk reactive surface area, for reaction with mine water before it is coated (Rötting et al. 2008; Macias et al. 2012). DAS basically include neutralisation of mine water where metals precipitate out as oxyhydroxides while RAPS presents anaerobic/reducing conditions where metals precipitate out as metal sulfide before neutralisation process. Some of the differences between DAS and
RAPS treatment systems are listed in Tab. 1, which might be advantages and disadvantages associated with the two systems.

**Materials and methods**

**Feedstock**

AMD treated for this study was collected from a discharge collecting point of an abandoned mine situated about 25km South East of eMalahleni. A 25L polyethylene container was used to carry the acid water from the site to the laboratory. The container was rinsed many times (about 5 times) before filling it with the AMD. Tests for pH, redox (pE), EC, TDS and dissolved oxygen (DO) were performed in the field, as they are, likely to change with time, using pH and EC meter, also called multi-meter. The multi-meter was calibrated every time before use. For the conductivity probe, EC solution was used for calibration and pH calibration solutions, 4.0, 7.0 and 10.0, were used for the pH probe. AMD samples were collected weekly following WRC 2000 procedure. Water samples were collected using 100 mL polyethylene bottles that were rinsed at least three times using the water to be sampled. The samples were filtered using a 0.45 μm filter membrane for elemental (major-, minor- and trace-element) and anion analyses. Elemental analysis samples were also acidified using 3M nitric acid (HNO₃) for preservation purposes. Immediately upon collection, samples were placed in a cooler (at 4 °C) for transportation and storage. Chemical analyses were carried out using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC). X-Ray diffraction (XRD) and X-Ray fluorescence (XRF) analysis were used for the reactive material (limestone) for mineral and elements (traces and major) identification and concentrations before and after use respectively.

**Experimental setup**

Experimental design consisted of two passive treatment systems, DAS and RAPS. DAS system (Fig. 1) was comprised of three columns with the first column containing a mixture of 25 % (v/v) limestone and 75 % (v/v) wood shavings for neutralization processes. The second column was comprised of manure to create anaerobic conditions and the third column was made to collect the treated water before exposure to oxygen. A constant upward flow movement of 0.15 L/min mine water was maintained in the system while also maintaining residence time of 24 hours. RAPS system (Fig. 2) consisted of three columns, first and second columns were containing a layer of 30% (v/v) manure underlain by 50% (v/v) limestone. The downward flow movement of 1.2 L/min mine water was maintained in the system with a contact time of 24 hours.

**Results**

**Feedstock characterization**

**Mine water**

Tab. 2 provides an initial chemical composition of the mine water in question. It can be noted that the mine water is characterized by low pH (2.7), and high concentration of SO₄²⁻ (1006.4 mg/L), metals

<table>
<thead>
<tr>
<th>Table 1 Some of the differences between DAS and RAPS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DAS</strong></td>
</tr>
<tr>
<td>Comprises of fine particle sizes of alkaline material that provide a large reactive surface area and dissolves before being coated by precipitates</td>
</tr>
<tr>
<td>No reducing organic matter, the system only uses alkaline material that is meant to add alkalinity and raise pH in the system, precipitating metals as metal hydroxides</td>
</tr>
<tr>
<td>Lack of sulfate reduction</td>
</tr>
<tr>
<td>Efficient treatment of mine water expected as the system is expected to efficiently use the alkaline material</td>
</tr>
<tr>
<td>High Fe(III) and Al concentrations can be treated</td>
</tr>
</tbody>
</table>

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
and metalloids such as Fe (132.1 mg/L), Al (109.9 mg/L), and Mn (7.3 mg/L), exceeding industrial water standards limits as set by the South African Department of Water Affairs (DWAF, 1996). Minor to trace concentrations of Co, Ni, and Zn were also noticed in the mine water.

Reactive material
X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analysis were used for the limestone characterization for mineral and elements (traces and major) identification and concentrations before and after use respectively.

Passive treatment results
Tab. 3 summarize water quality of acidic mine water and treated water from DAS and RAPS systems.

Fig. 3 shows the change in pH of the AMD and the treated water from DAS and RAPS systems over time (weeks). An increase in the pH of the water throughout the treatment systems was observed to an average of 8 in both systems. Substantial alkalinity, as CaCO$_3$, was generated in the systems from 0 mg/L in the acid mine water to an average of 320.2 mg/L DAS system and 230.6 mg/L in RAPS system. Fig. 4 shows an increase in the Ca$^{2+}$ concentration that was witnessed in the DAS (493 mg/L) and RAPS (376 mg/L) passive systems compared with mine water Ca$^{2+}$ concentration of 49 mg/L. Average of 478.2 mg/L Ca$^{2+}$ concentration was detected in DAS A, 507.8 mg/L was analyzed in DAS B and 495.2 mg/L was detected in the RAPS C after exposure to oxygen. An increase in pH, alkalinity and Ca$^{2+}$ concentrations were expected as the limestone reacts with the acid water.
Figure 3 pH of inflow and outflow water in the passive treatment system

Figure 4 Ca\textsuperscript{2+} concentration of inflow and outflow water in the passive treatment system

Table 4 Average values of forms of iron and dissolved oxygen after 21 weeks

<table>
<thead>
<tr>
<th></th>
<th>Total Fe (mg/L)</th>
<th>Fe ferrous (mg/L)</th>
<th>Fe ferric (mg/L)</th>
<th>DO (mg/L) @19.80c</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMD</td>
<td>132.1</td>
<td>0</td>
<td>132.1</td>
<td>7.94</td>
</tr>
<tr>
<td>DAS A</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>7.66</td>
</tr>
<tr>
<td>DAS B</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>7.86</td>
</tr>
<tr>
<td>DAS C</td>
<td>15</td>
<td>2</td>
<td>13</td>
<td>7.85</td>
</tr>
<tr>
<td>RAPS A</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>7.19</td>
</tr>
<tr>
<td>RAPS B</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>7.40</td>
</tr>
<tr>
<td>RAPS C</td>
<td>19</td>
<td>3</td>
<td>16</td>
<td>7.48</td>
</tr>
</tbody>
</table>
Referring to Fig. 5 below, treated water is classified in having high concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{HCO}_3^-$ ions. According to the diagram, mine water had 0% concentration of $\text{CO}_3^{2-} + \text{HCO}_3^-$, 100% concentration of $\text{SO}_4^{2-} + \text{Cl}^-$ ions. This contaminated water contained about 0.7% of $\text{Ca}^{2+} + \text{Mg}^{2+}$ ions and 93% concentration of $\text{Na}^{+} + \text{K}^+$ ions. The treated water for DAS and RAPS systems showed an addition in the concentration of $\text{CO}_3^{2-} + \text{HCO}_3^-$ and $\text{Ca}^{2+} + \text{Mg}^{2+}$ ions. There was a reduction of $\text{SO}_4^{2-}$ ions in the treated effluents of both DAS and RAPS.

**Metal and metalloids removal**

There was substantial contaminants removal in both treatment systems (>95 %) except for Mn and $\text{SO}_4^{2-}$. This was primarily due to limestone dissolution which increased the pH near neutral. ICP-MS and IC results revealed that the average concentration of total Fe in acid water was measured at 132.1 mg/L. This concentration was 1321-fold higher than the required limit, as per the domestic water use standard and according to the spectrophotometer, this was all in $\text{Fe}^{2+}$ ion form. Referring to Tab.4, DAS A reduced 97.7% of the total Fe concentration, and the remaining 2.3% was comprised of 67% of $\text{Fe}^{3+}$ and 33% of $\text{Fe}^{2+}$ ions. DAS B further reduced 99% of the total Fe concentration which was in the $\text{Fe}^{2+}$ ion form. DAS C showed an increase of 11.4% in the total Fe concentration which was made up of 87% $\text{Fe}^{2+}$ ions and 13% was $\text{Fe}^{3+}$ ions. RAPS A managed to reduce 98.5% of total Fe concentration from the initial 132.1 mg/L in the AMD and the remaining 1.5% was all in $\text{Fe}^{2+}$ form. RAPS B increased the concentration of the Fe from RAPS A by 0.8% which was all $\text{Fe}^{2+}$. A further 14.4% increment of Fe concentration after exposure to oxygen in RAPS C was analyzed and detected to be 84% $\text{Fe}^{3+}$ and 16% $\text{Fe}^{2+}$.

Average Al concentration of the inlet was 110 mg/L. As presented in Fig. 6 and 7, while the neutral pH level was reached, both systems managed to reduce the Al concentration. White precipitates were observed at the inlet.
point of the both DAS and RAPS columns and this could be associated with precipitation of Al as Al(OH) such as gibbsite mineral. DAS A had an average of 0.05 mg/L, DAS B showed an average of 0.02 mg/L and DAS C showed an average concentration of 0.02 mg/L in 21 weeks of operation. Similar to DAS, RAPS system also managed to reduce the Al concentration of AMD as seen in Figure 35. RAPS A had an average of 0.04 mg/L, RAPS B gave an average of 0.02 mg/L and RAPS C gave an average concentration of 0.03 mg/L.

There was minimal Mn reduction by the two passive treatment systems even though the concentrations were still high above the water quality range of the domestic water standard. Average concentrations of Mn for RAPS A, B and C were found to be 3.3 mg/L, 3.3 mg/L and 4.8 mg/L for 21 days of running the experiment. According to the study by Thomas & Romanek 2002, Mn needs a very high pH, greater than 8, and high oxidising conditions to precipitate out. Average $\text{SO}_4^{2-}$ concentration for AMD was
analysed to be 1006 mg/L after 21 weeks. No \( \text{SO}_4^{2-} \) concentrations were achieved by both systems. The same trend of not being able to decrease the sulfate concentration was also experienced in the study done by Nairn & Mercer (2000), instate, the concentration was increased by the treatment system.

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**Conclusions**

It can be concluded that from the experiments, the DAS system with the setup explained in this study blocked after 21 weeks of operation while the traditional treatment system, RAPS, was still able to treat acid water efficiently without any signs of clogging. Generation of alkalinity led to pH increase from an average of 3 in contaminated mine water to 8, which is neutral conditions in the two systems solely from limestone dissolution. High concentrations of contaminants such as Fe, Al, and Zn were completely removed to below ICP-MS detection limit except Mn. There was no SO42- reduction in both systems which may be due to various reasons such as that the organic substrate in both the treatment systems does not contain any sulfate reducing bacteria (SRB) which are important microorganisms in reducing sulfate to sulfide.

**Acknowledgements**

The authors would like to thank the Council for Geoscience for funding the project and all colleagues who participated in the project.

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Abstract
In this study, SH-MWCNTs/MoS2 nanohybrid was synthesized via hydrothermal method. The nanohybrid composite was then characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and Energy-dispersive X-ray spectrometry (EDS) to confirm the successful incorporation of relevant binding groups. The synthesized adsorbent was then used for the removal of Hg\(^{2+}\) ion from aqueous solution and its adsorption behavior and capacity determined using the kinetic models. It was that Hg\(^{2+}\) ion uptake onto SH-MWCNTs/MoS2 nanohybrid composite occurred through chemisorption mechanism, achieving an adsorption capacity of 0.9661 mg/g. The SH-MWCNTs/MoS2 nanohybrid nanocomposite therefore showed potential for the removal of Hg\(^{2+}\) ion from contaminated water.

Keywords: Mercury, water pollution, ASM, SH-MWCNTs/MoS2 nanohybrid, adsorption

Introduction
Artisanal and small-scale mining is a livelihood activity of considerable economic importance in developing countries, supporting the lives of millions of people across Africa, South America and Asia. One of the most recorded ASM activities is gold mining, which takes place through soil excavation and gold extraction from the soil. Mercury is used for the extraction of gold from the soil in a process called amalgamation which is considered as a cheap and reliable way of gold recovery from low-grade ore (Spiegel 2009). It is however reported that the rudimentary practice of mineral extraction during artisanal and small-scale gold mining contributes to the emission of 1000 tonnes of mercury into the environment every year (Swain et al. 2007). Mercury is known as a very toxic element that can pose a serious threat to the life of humans, animals and other ecological entities (Zabihi et al. 2009). River pollution by mercury from ASM activities generally occurred in remote, poor and rural areas where access to clean water is a challenge, compelling the community to rely on untreated water sources for their various needs. Such communities require a facile and affordable technology such as adsorption to treat their water; few adsorbents have been tested for the removal of mercury from water, ranging from grafted polymer cellulosic materials to surfactant impregnated clayish materials which all suffer a number of disadvantages including lower adsorption capacities, instability and lower affinity for mercury.

Carbon nanotubes have shown remarkable performance as adsorbent because of their intraparticle porosity, large surface area and sufficient stability during regeneration; while on the other hand, sulphur has been demonstrated to have high affinity for mercury. In the context of this study, mercapto propyl trimethoxysilane (3-MPTES) was grafted to multi-wall carbon nanotubes to form the composite SH-MWCNTs which was then used to synthesize SH-MWCNTs/MoS2 nanohybrid composite with the aim to develop an effective adsorbent with high affinity for mercury and can be used to treat...
water contaminated with mercury; to the best of our knowledge, this the first time such composite has been tested for the removal of mercury from water.

Methods

Preparation of SH-MWCNTs/MoS2 nanohybrid composite

The first step consisted of the grafting of mercapto propyl trimethoxysilane (3-MPTES) on multi-walled carbon nanotubes (MWCNTs) resulting in the formation of SH-MWCNTs that was reacted with sodium molybdate to form SH-MWCNTs/MoS2 through hydrothermal method (Fosso-Kankeu et al., 2018).

Characterization of the adsorbent

The synthesized adsorbent was pulverized using the pestle and mortar to form a powder samples suitable for analysis by the SEM and FTIR. The IRAffinity-1S Fourier transform infrared spectrophotometer from the University of Johannesburg was used with a spectral range of 4000 to 500 cm\(^{-1}\). The JEM-2100 multipurpose electron microscope was used for the SEM-EDS characterization. The magnification for the SEM image was set at 10 µm.

Adsorption experiments

Batch equilibrium sorption experiments were carried out at different time intervals (10, 15, 30, 50, 60 and 70 mins) with fixed Hg concentration (2 mg/L) in 100 mL glass bottle with blue screw cap, adsorbent dose (SH-MWCNTs/MoS2 nanohybrid) 0.05g, shaking speed of 200 RPM and total volume of Hg\(^{2+}\) solution was kept 10 mL in a rotary shaker. These experiments were performed at pH6.

After the sorption equilibrium was reached (60 min), the solution was separated from the adsorbent by Millipore membrane filtration. The initial and equilibrium Hg\(^{2+}\) ion concentrations in each bottle were determined by ICP-OES.

Results and discussion

Physico-chemical properties of the adsorbent

FTIR

The FTIR spectrum showed predominant peaks at 2917, 1617, 1521, 1441, 1109, 739 and 675 cm\(^{-1}\) which corresponded to the presence of the following functional groups: H-C-H assemetric, C-C=C symmetric stretch, C-C=C asymmetric stretch, C-O stretch, C-H rock and C-H bend respectively; these are suitable groups to interact with and bind to Hg2+ ion in solution.

SEM analysis

The EDS spectrum (Fig. 2a) shows the presence of elements such as C, Si, S, Na and Mo which are primary components of mercapto propyl trimethoxysilane (3-MPTES), multi-walled carbon nanotubes (MWCNTs) and sodium molybdate, therefore indicating that all the compounds were effectively incorporated in the composite and the synthesis was successful. The SEM image (Fig. 2b) recorded at 10 µm shows an homogeneous distribution of small bead of large surface area suitable for the adsorption of metal.

Adsorption kinetic studies

The kinetic studies were performed by collecting and analyzing the samples at the predetermined time interval (10 min) until the consecutive residual Hg\(^{2+}\) ion concentrations became closer. The kinetic data for the adsorption of Hg\(^{2+}\) ion onto nanohybrid at 5 mg/L Hg\(^{2+}\) ion concentration were tested with the well-known kinetic models namely pseudo first order model and pseudo second-order model. The parameters of these kinetic models are provided in Table 1 and the graphs are plotted in Figure 3.
achieved. Such rapid adsorption can be possibility because of a great number of various functional groups observed in Fig. 1 on to the surface of SH-MWCNTs/MoS2 and because of the high porosity and high surface area existing in MWCNTs, while the presence of sulphur in Nanohybrid also support the process of Hg\(^{2+}\) adsorption, because sulphur is well known to have high affinity for mercury. At the same time, the adsorption of Hg\(^{2+}\) ion well fitted the pseudo-second-order kinetic equation (Figure 3); the correlation coefficient ($R^2$=0.999) is close to 1, the rate constant (K' (g.mg\(^{-1}\).min\(^{-1}\)) was calculated to be 2.53. This therefore implies that the adsorption of Hg\(^{2+}\) ion onto SH-MWCNTs/MoS2 is dominated by a chemisorption mechanism (Fosso-Kankeu et al. 2016a, b; Fosso-Kankeu et al. 2017; Leudjo Taka et al. 2018) attributed to the interaction of binding groups including Sulphur at the surface of the adsorbent with Hg\(^{2+}\) ion.

**Conclusion**

The present work revealed the feasibility of using new adsorbent (SH-MWCNTs/MoS\(_2\) nanohybrid) for the removal of Hg\(^{2+}\) ion from aqueous solutions. The efficiency of Hg\(^{2+}\) ion

Table 1 Different parameters of Adsorption kinetics of Hg\(^{2+}\) onto SH-MWCNTs/MoS\(_2\) nanohybrid

<table>
<thead>
<tr>
<th>Kinetics models</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (mg.g(^{-1}))</td>
<td>0.9661</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>$K'$ (g.mg(^{-1}).min(^{-1}))</td>
<td>2.5311</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (mg.g(^{-1}))</td>
<td>0.1539</td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>$K_1$ (min(^{-1}))</td>
<td>8.75 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9115</td>
</tr>
</tbody>
</table>
removals was found to be greater than 95% at 5mg/L by using nanohybrid. The adsorption behavior is well described by pseudo-second-order kinetic and Sips isotherm models. The best behavior of adsorbent for retaining elemental mercury because of their (i) high sulphur content, (ii) large surface area, and (iii) large total pore volume, especially a large micropore volume, where the potential for interaction between the solid sorbent and mercury molecules is substantially greater than that in the wider pores.

Acknowledgements
The authors are grateful to the financial support from the North-West University.

References


Figure 3 Adsorption kinetics of Hg2+ onto SH-MWCNTs/MoS2 nanohybrid according to (a) Pseudo-first-order model, and (b) pseudo-second-order model
PAHs In Coal Tar As Water Contaminants and Their Removal by Photocatalytic Degradation

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Abstract
This study focuses on the identification of PAHs in coal tar produced from simulated pyrolysis and the synthesis of 2D g-C₃N₄ photocatalyst for the degradation of the predominant PAH in the coal tar, namely naphthalene. Herein, a 2D g-C₃N₄ was prepared through calcination and employed in the photo-catalytic degradation of naphthalene, in water. The as synthesized nanomaterial was characterized with scanning electron microscopy (SEM), FTIR and X-ray diffraction (XRD), and the successful synthesis confirmed. The effect of time on the photocatalytic degradation of naphthalene was investigated; it was found that visible light was required for irradiation of the catalyst, while rapid degradation was achieved in the first 25 min followed by slow degradation rate resulting in 60% removal of naphthalene in solution.

Keywords: PAHs, g-C₃N₄, Photocatalytic degradation, pyrolysis, Coal tar

Introduction
Water has dependably been regarded as a basic crude material for social advancement and organization (Alam., 2002). The accessibility of quality water for drinking and other important purposes is an extraordinary issue worldwide due to population increase and the rapid development of enterprises (Benyon et al., 2007), especially in developing countries. Water quality can be influenced by effluents from anthropogenic sources that incorporate household sewage, wastewater treatment plants, farming area use, industrial and mining activities; sources which may release organic pollutants into the aquatic environment through different pathways (Javier et al., 2002).

PAHs enter water bodies through atmospheric deposition and direct releases of substances through petroleum spills into municipal wastewater treatment plants, industrial discharges, stormwater runoff, landfill leachate, and surface runoff (Abdulazeez, 2017). Many studies have been conducted recently regarding runoff sources of PAHs (Brown and Peak, 2006; Nekhavhambe et al., 2014; Hussein and Mona, 2016), but so far the potential of coal tars from pyrolysis or underground coal gasification to contribute to PAHs in the environment has been neglected. Rainfall runs off the parking lot and road surfaces, transporting PAHs that originate from tire particles, leaking motor oil, vehicle exhaust, crumbling asphalt, atmospheric deposition and parking lot sealants (Nilsson et al., 2018) are some of the main focus lately. PAHs attach readily to sediment particles leading to high concentrations in bottom sediments of water bodies (Mahmood and Ali, 2004). PAHs are chemical pollutants with two or more benzene rings. One of the main disease caused by PAHs such as naphthalene is hemolytic anaemia in children (Haritash and Kaushik, 2009; Kim et al., 2013; Atif et al., 2015). These organic pollutants are toxic, carcinogenic and mutagenic; thus, their release into natural water bodies is dangerous to both the environment and human health (Shafy and Mansour, 2016; ATSDR...
2005). Therefore, it is required to degrade or minimize some pollutants that are resistant to biological degradation. Numerous strategies, such as chemical approaches (redox, complexation, and ion exchange methods), biological methods (aerobic and anaerobic), and physical techniques (adsorption, precipitation, reverse osmosis, and membrane filtration) have been employed to segregate organic pollutants from water (Kumar et al. 2017a; Kumar et al. 2017b).

Among them, advanced oxidation processes (AOP) are gaining substantial attention for the degradation of organic effluents from water. AOPs are also favorable due to their easy operation, very fast process, and lack of by-products (Mukwevho et al., 2019). In this method, semiconductor nanomaterials are employed to catalyze the degradation of pollutants. Recent studies have shown that the application of metal-free semiconductor photo catalyst, i.e. carbon nitride (C₃N₄), affects positively the photo degradation of some organic pollutants, the as-prepared g-C₃N₄ metal including compounds could adequately degrade organic pollutants. Wang et al. also revealed that g-C₃N₄ with a band gap of 2.7 eV accomplished usefulness functionality as a stable photo catalyst for H₂ evolution from water under visible light irradiation. Carbon nitrides have pulled in much consideration since the theoretical prediction of their remarkable mechanical and electronic properties of some stages.

Thus, this study is aiming to develop a nanomaterial-based technique for the removal of PAH’s identified in coal tar. As-prepared catalyst was characterized by FTIR, XRD and SEM, then used for the degradation of naphthalene under simulated sunlight.

**Methods**

*Chemical and reagents*

Melamine (C₃H₆N₆ 99%), Naphthalene (C₁₀H₈ 99%) and dichloromethane were obtained from Sigma-Aldrich, South Africa.

*Simulation of coal tar production*

The coal was pyrolysed under N₂ atmosphere using an automated Fischer Assay setup. The condensable materials were condensed in a flask immersed in an ice bath and the non-condensable volatiles were allowed to escape to the atmosphere. The condensed material mainly tar was measure and send for analysis in a GC-MS. Samples for GC-MS analysis were prepared by dissolving tar into dichloromethane in vials. Approximately 1 microliter of prepared sample was injected into the GC column.

*Synthesis of photo catalyst*

The g-C₃N₄ was prepared by heating melamine, respectively. The reaction was performed in an alumina crucible with a cover which can form a semi closed atmosphere to prevent sublimation of precursors. 3 g of the initial reactant was put into a crucible, heated to reach temperatures of 500°C in a muffle. The obtained yellow material was ground into powder.

*Characterization*

The obtained g-C₃N₄ was characterized by X-ray diffraction for phase identification Philips model PANalytical X’Pert pro pw 3040/60 (Netherlands), at a power of 1.6 kW used at 40 kV with a Cu Kα (λ = 0.154 nm) radiation source. The FT-IR spectrum was collected in an Avatar 360 infrared spectrophotometer (Nicolet, USA) with the prepared powders diluted in KBr pellets. The morphology was assessed using Auriga FEG-SEM (Carl Zeiss, Germany).

*Photocatalytic degradation*

The performance of the as-synthesized photocatalysts was analysed for the degradation of naphthalene under visible light. In the visible light irradiation experiments, 100 mg dosage of the as-synthesized catalyst was added into 100 mL aqueous naphthalene solution (25 ppm). Prior to exposure to light, the suspension was mixed for 30 min in the dark to achieve the adsorption-desorption balance of naphthalene on the catalyst. The reactor was then irradiated under visible light, emitted by a 300 W xenon lamp with a UV cut-off glass filter (λ >420 nm). Toward the completion of each experiment the agitated solution mixture was filtered through a 0.45 µm membrane and the residual concentration of naphthalene was determined spectrophotometrically at a wavelength of 275 nm (λmax). The photocatalytic efficiency of naphthalene
using as-prepared photocatalyst was then calculated using Equation (1) (Kumar et al. 2017). Photodegradation efficiency (%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)

Where \( C_0 \) is the initial naphthalene concentration and \( C_t \) is the remaining naphthalene concentration in solution at time, \( t \).

**Results**

*PAHs in coal tar*

The analysis of coal tar produced from the Fischer Assay experiment, allowed to identify a host of PAH dominated by naphthalene (Table 1). The PAHs identified using the GC-MS could be classified as lighter PAHs with relatively low toxicity. Due to the predominance of naphthalene in the coal tar and its toxicity, it was further considered in the study for photocatalytic degradation.

**Characterization**

In Fig 1b the XRD patterns of the as-prepared pure g-C\(_3\)N\(_4\) NSs are shown. The results revealed that the sample is crystalline in nature. The observed peaks in the XRD patterns of g-C3N4 NSs are in good agreement with JCPDS card No. 87-1526, respectively (Kumar et al. 2015; Sun et al. 2012). The diffraction peaks at 27.3° and 13.1° result from the crystal planes of (002) and (100) respectively. The overall morphology of the as-prepared g-C3N4 NSs is represented in Fig. 1a. The diffraction peaks at 27.3° and 13.1° result from the crystal planes of (002) and (100). A 2D sheet-like morphology with varied thickness was noticed (Fig. 1a). These sheets are fluffy and contain clearly visible porous layers. This can be attributed to step-wise formation of g-C\(_3\)N\(_4\) via melamine (Intermediate stage) and thermal condensation with evolution of NH\(_3\) (Yu et al. 2017).

**Photocatalytic degradation activities**

The photocatalytic effect of g-C3N4 were investigated on the naphthalene molecules in simulated contaminated water. 100 mg of photocatalyst dosage was added to 100 mL of the 25 mg/L naphthalene aqueous solution which was first stirred for 30 min in the dark to reach the adsorption desorption equilibrium and then exposed to the simulated natural sunlight for 4 hours for photo-degradation of naphthalene molecules. It was observed that partial photo-degradation of naphthalene occurred in the presence of visible light in the absence of any photocatalyst, decreasing the concentration of naphthalene by 7 mg/L from 25 mg/L initial concentration in solution (shown as photolysis in Fig. 2). Degradation experiments were additionally investigated in the dark in the presence of the catalyst. There were no noteworthy changes in the degradation efficiency of naphthalene in the absence of light radiation, demonstrating that the use of light is essential to increase

---

**Table 1 Coal tar PAH composition**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Area</th>
<th>Number of rings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtalene</td>
<td>15.22</td>
<td>2</td>
</tr>
<tr>
<td>1,4-Methanonaphthalene</td>
<td>1.78</td>
<td>2</td>
</tr>
<tr>
<td>1-Naphthalenecarbonitrile</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>0.6</td>
<td>3</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.77</td>
<td>3</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.01</td>
<td>3</td>
</tr>
</tbody>
</table>

---

**Figure 2** Remaining naphthalene concentration in solution using 0.1mg.mL\(^{-1}\) of g-C\(_3\)N\(_4\) as photocatalyst for 100 mL, 25mg.L\(^{-1}\) naphthalene contaminated aqueous solution with time.
photodegradation of the naphthalene. The use of the synthesized photocatalyst (g-C\textsubscript{3}N\textsubscript{4} NSs) allowed to degrade 15 mg/L of Naphthalene after 4 hours of visible light irradiation, respectively.

The outcomes revealed that the photocatalytic activity enhances with an increase of the irradiation time. This might be related with the progressive occupation of binding sites at the surface of the catalyst by naphthalene over time; once naphthalene binds to the surface of the catalyst, the sequence of charge separation and transfer of electron-hole pairs for the photodegradation of naphthalene, continuously takes place and leads to reduction of naphthalene concentration in solution.

**Conclusion**

It was observed that coal tars generated from pyrolysis processes contain a host of PAHs which are likely to contaminate our water sources. The development of the g-C\textsubscript{3}N\textsubscript{4} photocatalyst was confirmed by different characterization techniques. The various degradation experiments such as photolysis, degradation in dark and with catalyst under visible light conditions were achieved to establish best reaction conditions for the degradation of naphthalene under visible light. Furthermore, the modification of g-C\textsubscript{3}N\textsubscript{4} need to be considered in order to enhance the photocatalytic activity towards other PAH pollutants.

**Acknowledgements**

The authors are grateful to the sponsor from the North-West University and the Water Research Commission (WRC) (Project No 2974) in South Africa. The Authors wish to express gratitude toward Prof. Ray and the DST/CSIR National Centre for Nano-Structured Materials, South Africa for permission to utilize some of their instruments.

**References**


Abstract
In this study spent coffee beans were transformed into biochar using a hydrothermal method where after it was pre-treated through surfactant impregnation to enhance its adsorption capacity. The non-treated and pre-treated biochars were characterized using FTIR spectroscopy analysis, which revealed a successful preparation of biochar with the potential for adsorption. The adsorption potential and mechanism was predicted using thermodynamic study.

The adsorption of cadmium on the pre-treated (PT) biochar was found to occur spontaneously while it was the case for the non-treated (NT) biochar the adsorption reaction was not thermodynamically favourable. For both adsorbents, the adsorption of the cadmium was endothermic in nature due to the large positive enthalpy values, confirming that the adsorption of cadmium on NT biochar and PT biochar occurred through a chemisorption mechanism. Although the high concentrations of metals in the coal leachate resulted in competition for binding sites at the surface of adsorbent, relatively high adsorption capacity was achieved for the removal of cadmium from the coal leachate.

It could be therefore concluded that the temperature change substantially influences the adsorption behaviour and capacity of the prepared absorbents.

Keywords: Spent coffee beans, biochar, surfactant impregnation, cadmium, coal tailings leachate, thermodynamic, adsorption

Introduction
The substantial decrease of coal grade over time has contributed to the increased production of large amount of fine coal with lower value from the separation processes which is over discharged in the environment in the form of tailing dumps (Oruc et al. 2010). These tailings dumps contain considerable amount of inorganic impurities such as metals which are often mobilised and released from the tailings following the formation of acid mine drainage itself due to the weathering or oxidation of sulphide minerals such as pyrite (Fosso-Kankeu et al. 2017a). The dispersion of metal such cadmium in surface and ground waters constitutes an environmental risk, due to the potential of cadmium adversely affect the equilibrium of the aquatic system and cause harm to human or animal relying on contaminated water. Concerns related to such risks have been growing over the years as the as recurrence of AMD formation has been reported in several geographical areas in the past decades. Furthermore, the conventional methods so far considered to remediate pollution are very expensive and not affordable in developing countries. The quest for affordable and sustainable technologies has resulted into the development of adsorption technologies that make use biodegradable, widely available adsorbents that can be obtained at negligible cost.
Biochar can be produced by using organic materials as a feedstock. One of these materials is spent coffee grounds. Over 120 million bags of coffee are produced worldwide each year, which correspond to 7 million tons of coffee waste (Zuorro & Lavecchia 2012). These spent coffee grounds have no commercial value and are usually sent to compost facilities for disposal (Zuorro & Lavecchia 2012). This makes spent coffee beans an abundant feedstock available for the production of biochar. The adsorption capacity of biochar can be improved through physical or chemical methods. Temperature plays an important role during adsorption, in principle higher temperatures provide enough energy to reactants for them to react or come into contact; it is therefore expected that higher temperature will enhance the adsorption of metal onto the adsorbents. However, the multitude of studies have shown different trends, an increase of the adsorption of palladium onto immobilized bayberry tannin with increase of temperature (from 30 to 50°C) was reported by Wang et al. (2005), while Fujiwara et al. (2007) recorded a decrease of adsorption of different metals onto L-lysine modified crosslinked chitosan resin at higher temperature. According to these findings, it should be important to determine the optimum temperature for a specific adsorption process. Hence the focus of this study, which consists to investigate the effect of temperature on the performance of spent coffee-based biochar during the adsorption of cadmium.

**Methods**

**Biochar production**

A slurry of spent coffee beans was prepared for a 3 vol% biomass loading. The hydrothermal liquefaction (HTL) reactor tanks were filled with 60 L slurry, sealed and pressurized with Nitrogen gas (Baseline 5.0 bar) to 90 bar, where after the reactor temperature was increased to 305 °C. The HTL plant produced a product which is a mixture of an aqueous oil phase and biochar solid phase. The biocrude was separated from the aqueous phase via pressure filtration. The filtered biocrude was then dissolved in acetone to separate it from the biochar. The produced biochar was finally separated from the acetone solution in a Büchner filter. Before drying it for 12 hours at 105 °C. The dried biochar was crushed to a particle size less than 250 μm using a ceramic mill.

**Biochar pre-treatment**

The biochar was impregnated with sodium dodecyl sulphate (SDS) by adding 10 g of biochar to 1 L SDS solution (10 g/L); the mixture was incubated and stirred at 120 rpm for 24 hours at 60 °C.

The solution was then filtered by Büchner filtration. The biochar was then dried at 65°C for 12 hours, then the dried biochar was crushed to finer particles using a ceramic bowl.

**Characterization of the biochar**

The pre-treated (PT) and non-treated (NT) biochars were characterized by Fourier Transform Infrared Spectroscopy (FTIR) having an IRAffinity-1S from Shimadzu. The spectrometer had a spectral range from 4000 to 400 cm⁻¹. This process was used to identify the functional groups of the biochars.

**Adsorption experiments**

All the adsorption experiments were carried out in a batch system using NT and PT biochars separately. The biochar dosage was fixed at 0.2 g per 50 mL solution. The adsorption capabilities of treated and untreated biochar were tested, thus 2 sets of adsorbents were tested for each experiment. The effect of temperature on the adsorption behaviour was done by performing kinetics experiment for initial cadmium concentration of 50 mg/L and the temperature of the solution was increased from 35°C, 45°C and 55°C respectively.

**Results and discussion**

**Characterization of adsorbents**

The spectra of the treated and not treated biochars (Figure 1) show almost the same pattern of peaks. Substantial peaks were observed in the range 2100-2200 cm⁻¹ which can be ascribed to the presence of adsorbent group C≡C deriving from the alkynes functional group. The peak at 2650 cm⁻¹ suggests the formation of formic acid dominated by the carboxylic group which plays an important role in the binding of metals. Important binding groups such as C-H stretch and C=O can relate and play
substantial roles during the adsorption process (Kantcheva 2003).

**Thermodynamic study**

To evaluate the thermodynamic properties of the biochar, batch adsorption experiments were conducted at three different temperatures (35°C, 45°C and 55°C). To calculate the enthalpy change (ΔH°, KJ/mol), entropy change (ΔS°, J/mol/K) and gibbs free energy (ΔG°, KJ/mol) the van’t Hoff equation below was used:

\[
\ln K_a = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]

where \( K_a \) is the distribution coefficient, which is equal to \( q/c_p \); T is the absolute temperature in Kelvin (K); and R is the universal gas constant (0.008314 KJ/mol/K). The values of ΔH and ΔS can be calculated from the respective slope and intercept of the trendline equation of van’t hoff plot (Figure 2) (Lalvani et al. 1997; Leudjo et al. 1997; Fosso-Kankeu et al. 2017b). The values obtained were tabulated as shown in Table 1.

![Figure 1](image1.png)  
**Figure 1** FTIR spectra of Non-treated and Pre-treated biochars

![Figure 2](image2.png)  
**Figure 2** Thermodynamic analysis on the adsorption of Cd with (a) NT biochar, and (b) PT biochar with SDS

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( K_a )</th>
<th>Temperature</th>
<th>ΔG (kJ/mol)</th>
<th>ΔS (J/mol/K)</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT biochar</td>
<td>0.1071</td>
<td>308</td>
<td>4075.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1406</td>
<td>318</td>
<td>3822.43</td>
<td>25.3</td>
<td>11879</td>
</tr>
<tr>
<td></td>
<td>0.1532</td>
<td>328</td>
<td>3569.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0941</td>
<td>308</td>
<td>-210.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PT biochar</td>
<td>1.142</td>
<td>318</td>
<td>-392.6</td>
<td>18.2</td>
<td>5382</td>
</tr>
<tr>
<td></td>
<td>1.2442</td>
<td>328</td>
<td>-574.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where there are few structural changes in the adsorbent and adsorbate for the adsorption of Cd.

The Arrhenius activation energy $E_a$ allows a better understanding of the mechanism of adsorption, it was therefore determined by plotting $\ln K_2$ vs $1/T$ which is a relationship between the temperature and kinetic studies as illustrated in Figure 3.

The Arrhenius equation (Equation 2) allows to determine the activation energy as well as the adsorption rate.

$$K_2 = Ae^{-E_a/(RT)}$$ (2)

Where $K_2$ is the equilibrium constant of the pseudo-order model, $A$ is the pre-exponential factor and $E_a$ is the activation energy.

The $E_a$ can therefore be calculated from the slope of Equation (2). $E_a$ > 40 KJ/mol is an indication of a chemical adsorption process, $E_a$ < 40 KJ/mol indicates a physical adsorption or attraction process (Leudjo et al. 2018). The activation energy values calculated 6.6 KJ/mol and 7.8 KJ/mol for the NT biochar and PT biochar respectively were < 40 KJ/mol, implying that of the attraction of cadmium onto the adsorbents was predominantly of a physical nature. It could therefore be concluded physisorption and chemisorption concurrently take place during the uptake of cadmium by the adsorbents, which is due to the porosity of biochar as well as the presence of active groups at the surface which chemically react with cadmium.

Application of biochar for the treatment of coal tailings leachate

Samples of 100, 200 and 250 mg/L dissolved metals in coal leachate were spiked with 30 mg/L cadmium then exposed to the different biochars for adsorption. The results are shown in Figure 4.

As seen from Figure 4 at a 100 mg/L metal concentration, the adsorbent showed the highest affinity for cadmium adsorption from the solution. With the increase of the total metallic concentration the adsorbents ability to adsorb the cadmium decreases substantially due to competition for binding sites on the adsorbents by other metals present in solution. This trend was shown by both the NT and PT biochar. It is however clear that the PT biochar outperformed the NT biochar for each metallic feed concentration, validating the use of SDS impregnation in the removal of cadmium from aqueous mine tailings solutions.

Conclusions

The aim of this was to valorise organic waste for the treatment of water polluted with cadmium. It was found that biochar generated from spent coffee beans has the potential to adsorb cadmium from aqueous solution; the performance of biochar was enhanced through chemical treatment using the surfactant sodium dodecyl sulphate. The adsorption capacity of the both adsorbents increased with an increase of temperature; however, only the reaction between cadmium and the pretreated biochar was thermodynamically favourable. The adsorption was found to occur through a combination of physical and chemical mechanisms. The pretreated biochar achieved high adsorption capacity for the removal of cadmium from the coal leachate and could therefore be considered industrially for the treatment of such solution. The use of spent coffee beans as adsorbent could an
economically viable alternative as it could be obtained at no cost.

Acknowledgements
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References


Justification the Possibility of Sludge Storage Use for Liquid Wastes from the Potash Industry as Settling Ponds

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Abstract

In process of the enrichment of potash ores during the potassium chloride production by flotation, liquid wastes are formed - a mixture of clay-salt slurries and industrial wastewater; the utilization of such mixtures is a complex environmental and technological problem.

In Russia, the main method of disposal of liquid waste from potash producing industrial units is wastes release into sludge storage basins with further return of the clarified water into the production cycle or injection of clarified liquid waste into underground horizons.

Performed analysis of the facilities operation at Uralkali’s mine departments, calculated water and material balances of the sludge storage facilities, data of the suspended solids sedimentation efficiency and the water mineralization reduction made it possible to consider such facilities not only as environment protection units, but also as waste treatment facilities. Calculations of the speed and time of fine clay particles sedimentation, changes in water mineralization in the sedimentation pond depth due to the density and thermal stratification, allowed to develop the technology of the facility liquid waste treatment and to determine its main structural features with the possibility to release the part of slightly mineralized water into the water body during the pre-flood period.

Key words: potash production industry, liquid waste, brine, sludge storage unit, sediment pond

Introduction

The Verkhnekamskoye mine field of potassium-magnesium salts is one of the world’s largest deposits of potassium salts. Commercial development of the field began in the 30s of the XX century. The mining and processing of ores are accompanied by the formation of substantial waste volumes – solid halite waste and liquid clay-salt slimes, whereas the utilization and processing of such wastes is one of the complex environmental and technological problems. Taking into account the composition of the feedstock containing 23 – 27% KCl, the process of one ton of potassium chloride production generates formation of 0.1 - 0.5 tons of clay-salt sludge. The solution of ecological problems regarding potash mine fields development is of current concern, both in Russia and abroad.

Data on methods of potash production facilities liquid wastes disposal and handling were analyzed. The results demonstrated that following main methods were used worldwide (Baturin, 2012, Goldberg, 1994):

• release of sludge containing brine into ocean and sea bodies (Canada, Brasil, Great Britain);
• regulated release of brine into rivers (Germany, France, Russia);
• pumping into underground absorbing strata (Germany, Belorussia, Canada)
• storage in special sludge accumulation units (Russia).

The determination of options for the liquid waste disposal (diffused discharge into rivers, underground discharge by injection wells and by brine and sludge storage units) depends on the natural hydrological and geological - hydrogeological conditions, so for each mine field the method and/or a set of methods will be different. It is most advisable to use an integrated approach to the problem while using several options or an options’ combination.

In Russia, despite the existing experience of liquid wastes processing, the main method of such waste disposal is still the storage in sludge storage units with the return of clarified water into the production cycle or injection of clarified liquid waste into underground absorbing horizons. Sludge storage unit is usually considered as a hydraulic engineering structure for waste accumulation.

Basing on the analysis of the operation of sludge collectors at PJSC Uralkali (four production complexes in Berezniki and three production complexes in Solikamsk) and the processes occurring in these collectors, the purpose of this work was to substantiate the possibility of using sludge collectors as waste treatment facilities (sedimentation ponds).

**Characteristics of the research objects**

**Liquid waste**

During flotation processing of Verkhnekamsky mine field potash ores the specific yield of clay-salt sludge per one ton of finished product is 0,5- 0,6 m$^3$/t, including 0,32 -0,35 t/t of the solid particles phase.

**Solid particles phase characteristics**

Mineral content density: 2,2 ÷2,4 t/m$^3$.

Particle-size distribution:

<table>
<thead>
<tr>
<th>Size, mm</th>
<th>&gt;0,1</th>
<th>0,1-0,063</th>
<th>0,063-0,045</th>
<th>&lt; 0,045</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size frequencies, %</td>
<td>2 – 6</td>
<td>2 - 4</td>
<td>1,0 -2,5</td>
<td>70-89</td>
</tr>
</tbody>
</table>

Clay sludges are of the fine nature (mass content of <0,045 mm particles is 70-80%); by the capillary forces action they have the moisture-binding capacity and create difficulties in their processing and disposal.

**Solid particles phase chemical composition:**

- mass content of KCl (expressed in terms of solid part), % - 10,0 -12;
- mass content of NaCl (expressed in terms of solid part), % - 18,0 -20;
- mass content of insoluble residue, % - 68 - 72,0.

**Liquid phase characteristics**

Liquid phase density: 1,22 t/m$^3$.

**Liquid phase chemical composition:**

- mass content of KCl, % - 5,7 -6,0
- mass content of NaCl, % - 15,3 -20;
- dry residue, % - 21,0 -26;
- water, % - 79,0 – 74,0

After mixing of clay-salt slurries with industrial effluents the Liquid/Solid ratio can change from 10 to 14 and doesn't exceed the value of 35. The average chemical composition of liquid waste entering the sludge storage unit is shown in the table 1.

The presented data demonstrate that liquid effluents are characterized by a high content of suspended solid particles and mineral impurities.

**Sludge storage unit**

The structure of the facilities for mining industry wastes storage usually includes systems of waste hydraulic transportation, their hydraulic packing, sludge storage unit and clarified brine circulation system. Sludge storage unit is usually a structure of bulk plain-type or bulk ravine-type. The construction consists of a bed-base,
enclosing dams of primary and secondary embankment, hydraulic dumps and other structural elements

**Research results and their investigation**

To substantiate the possibility of using the sludge storage facilities of potash production industry liquid wastes as a treatment plant for effluents clarification and sewage sanitation, the analysis of such facilities operating experience at the mining departments of PJSC Uralkali was carried out. By way of example, the operation of sludge storage unit BKPRU-3 is considered. Characteristics of the chemical composition of wastewater entering the sludge storage unit and of clarified (circulating) wastewater are shown in table. 1. As can be seen from the presented data, the content of suspended solids in the clarified waste water substantially reduces (purification efficiency is more than 99.9 %). In clarified circulating brines there is a decrease in the content of mineral impurities: the chloride ions content is reduced by 46 %, the dry residue content - by 45.6 %. The increase in ammonium ions share can be explained by the decomposition of organic amines used as flocculants.

Sedimentation rates for suspended solids with known granulometric composition in mineralized solutions at

<table>
<thead>
<tr>
<th>Component</th>
<th>Measure unit</th>
<th>Waste water</th>
<th>Clarified waste water (recycled brine)</th>
<th>Concentration change, (± %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended matter</td>
<td>mg/L</td>
<td>60125</td>
<td>9,1</td>
<td>-99,98</td>
</tr>
<tr>
<td>Dry residue at t=105°C</td>
<td>mg/L</td>
<td>351900</td>
<td>191492,0</td>
<td>-45,6</td>
</tr>
<tr>
<td>Chlorides</td>
<td>mg/L</td>
<td>192800</td>
<td>104667,0</td>
<td>-46,0</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>mg/L</td>
<td>215,28</td>
<td>484,38</td>
<td>+55,0</td>
</tr>
<tr>
<td>K-cation</td>
<td>mg/L</td>
<td>59800</td>
<td>27908,0</td>
<td>-53,2</td>
</tr>
<tr>
<td>Ca- cation</td>
<td>mg/L</td>
<td>2060</td>
<td>2287,0</td>
<td>+11,0</td>
</tr>
<tr>
<td>Mg- cation</td>
<td>mg/L</td>
<td>684</td>
<td>511,0</td>
<td>-25,3</td>
</tr>
<tr>
<td>Na – cation</td>
<td>mg/L</td>
<td>79300</td>
<td>48500</td>
<td>-50,5</td>
</tr>
<tr>
<td>Sulphate- ion</td>
<td>mg/L</td>
<td>2690</td>
<td>2403,0</td>
<td>-10,7</td>
</tr>
</tbody>
</table>

*Table 1 – average chemical composition of liquid waste entering the sludge storage unit*

*Figure 1. Sludge storage unit BKPRU-3*
different temperatures were calculated (I. Studenov, 2014). The sedimentation time for finely suspended impurities in mineralized waters depending on the temperature and the structure height is from 1.2 to 17.8 days. For effective deposition of fine impurities, the sludge storage unit capacity should provide at least 10 days’ period for wastewater contact in the construction.

Complex chemical-physical and microbiological processes have place in sludge storage units; such processes provide effluents clarification, water mineralization degree changes by the depth, toxic organic substances degradation and water decontamination.

Main processes occurring in the sludge storage units:

1. Waste water dilution by atmospheric precipitation.

Analysis of the sludge storage units’ operation at the PJSC Uralkali, water balance estimation for BK11PY - 1,2,3,4 sludge storage units demonstrated that the average dilution coefficient is in frames of 1,16 - 1,2.

2. Water clarification due to the long-term ponding

Durability of suspended matter ponding in the sedimentation pond (sludge storage unit) is > 10 days. It allows to achieve 99,9% removal of suspended solid particles (with particle size of <0,045 мм) from waste water.

Suspected fine clay particles sedimentation can be accelerated by their enriching coagulation in highly concentrated electrolytes solutions. Besides, particles coagulation in result of water freezing-defrosting is possible in winter and spring seasons.

3. Processes of dissolution and crystallization for solid phase of clay-salt slurries

The solid phase of clay-salt slurries includes sylvite KCl (mass content of KCl (expressed in solid content), % - 10,0 - 12) and halite NaCl (mass content of NaCl (expressed in solid content), % - 18,0 - 20). The sludge is a coherent stable colloidal system, but in result of prolonged storage in the sludge storage unit the slow salts dissolution occurs. When the temperature regime changes under the influence of seasonal temperature fluctuations, salts solubility in water changes and their crystallization in the bottom part of the sludge storage pond is possible.

4. Density stratification of mineralized water by the sludge storage pond depth

In summer seasons the density stratification of mineralized water by the sludge storage pond depth is possible. In upper more heated water layers the solubility of salts, especially potassium chloride, increases, and, respectively, the density of the water layer, which then slowly sinks into the bottom horizons, increases too, i.e., density concentration convection of sodium-potassium chloride brines is observed. In the bottom layers the formation of saturated salt solutions is possible. At low temperatures, the density and viscosity of concentrated sodium and potassium chloride solutions (16-20 mass.% ) increases, and the near-surface layers being heavier fall down, displacing the less dense layers. This phenomenon can also lead to temperature and concentration stratification through the depth of the sedimentary pond (sludge storage unit) and in winter seasons.

Estimation of freezing points for sodium and potassium chloride solutions demonstrated that at concentrations of sodium chloride of 15,0 – 18 % and potassium chloride of 9 - 12%, these values are (-11) - (- 15 °С) and (- 3,8) - (-5,9 °С) respectively. At low temperatures the solution viscosity increases, and formation of a layer representing suspension of ice and viscous solution has place. Depending on the capacity, the sludge storage ponds area can be 60-250 hectares, thus the unit structure parts at large distances from waste water input points can be covered with ice and snow. In periods of spring ice melting the layer of desalinated weakly-mineralized water will form. A.Sosnovsky in his paper (2011) demonstrates, that when melting about 50% of the artificial ice obtained by the salt water freezing, the concentration of sodium ions and chloride ions is 900 and 700 times lower, respectively, than that of the initial source
water. According to R. Cherkasov (1989) and others, the boundary of the mineralization jump from 0 to 70,000 mg/L in chloride ion content is fixed at a depth of 5 m. During this period, it is possible to adjust the discharge of part of the clarified and desalinated waters into the water body, taking into account the hydrological and hydrochemical regimes of this water body. To determine the layer of desalinated water in the storage pond (sludge storage unit), it is proposed to carry out an interval sampling of clarified water with a depth step of 0.5 m, for example, at the distance of 100 m. The samples mineralization should be controlled by the content of chloride ion, potassium and sodium ions. Basing on the water samples analysis results, the depth of the mineralization jump is determined.

At this depth range (0-5 m) the average concentration of desalinated water ($C_{op}$) is determined based on water samples chemical analysis results – Discharged water volumes should be calculated in such a way that the content of mineral impurities will not exceed the required normative indicators in the water body.

5. **Degradation of organic impurities under influence of halo-tolerant and halo-philic bacteria**

Waste water discharged into the sludge storage units includes organic impurities – ethoxylated amine, polyacrylimide, aliphatic amines, as well as mono- and polyaromatic compounds, which are persistent toxic substances (Bachurin & Odintsova, 2009). Reagents content is 3-5%. In recent years, studies have been conducted to identify halotolerant and halophilic bacteria and microorganisms in clay-salt slime and determine their ability to destroy toxic organic compounds. In the research performed by E. Korsakova (2013) it was found that there are actinobacteria of the *Actinomycetales* type (destructors of toxic organic compounds) in potash production wastes. *Rhodococcus wratislaviensis* KT112-7 strain, isolated from clay-salt slurries, can destruct toxic organic compounds – ortho-phthalic and benzoic acids among them – in presence of sodium chloride with elevated concentrations. The toxic substance destruction effectiveness exceeds 80%.

When necessary, for improvement of the efficiency of organic impurities removal from effluents it is advisable to add to effluents the *Rhodococcus wratislaviensis* KT112-7 microorganism strains produced from potash industry wastes.

6. **Waste water decontamination processes.**

In the sludge storage unit, water disinfection processes have place as a result of the influence of osmotic pressure caused by different salt concentrations in highly mineralized wastewater and in the cytoplasm of bacterial cells. High osmotic pressure leads to dehydration of microbial cells and their destruction. The effectiveness of pathogens destruction is 98-99%.

Therefore, sludge storage unit can be considered as a wastewater treatment complex – sedimentation pond which provides industrial effluents purification to the level corresponding to requirements for the circulating brine quality, and their return to the technological needs; and to carry out the regulated discharge of treated wastewater part into the water body.

For effective and environmentally safe operation of facilities the environment protection measures aimed at prevention of negative ecological effect of facilities should be provided at the design stage:

- construction of contour embankment around the perimeter of the pond area, preventing the spreading of brines beyond this area,
- to prevent brines filtration and their penetration into underground waters, along the bed of the sedimentation pond (sludge storage unit), as well as along the upper slope of contour embankment, it is necessary to install an anti-filtration screen made of geomembranes based on polymeric materials, for example, high-
regulated discharge of treated water into the water body. Advanced arrangement of facilities, effective anti-filtration protection, use of modern instrumentation, continuous production and environmental monitoring of facilities will substantially reduce their environmental impact and ensure trouble-free operation of the system.

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Abstract
A biological passive mine water treatment system, which is environment-friendly and energy saving, has been developed by JOGMEC. In this “JOGMEC process”, contaminated mine water is treated in a vertical-flow anaerobic bioreactor that utilizes SRB. It is necessary to introduce compact passive treatment system with a higher flow rate (shorter HRT).

Keywords: AMD, Passive Treatment, Sulfate Reducing Bacteria

Introduction
Japan Oil, Gas and Metals National Corporation (JOGMEC) has been researching on passive treatment system since 2007 and has focused on treatment methods to remove metal ions contained in acid mine drainage, AMD, as sulfide by utilizing sulfate reducing bacteria (SRB). Field tests have been conducted with anaerobic reactors filled with “rice bran” and “rice husk” for AMD since 2014. Continuous removal of metal ions for more than 300 days has been confirmed with hydraulic retention time (HRT) of 50 hours even under the conditions close to natural environment that the ambient temperature dropped to around -15°C in the winter. Besides, continuous removal for more than one year has been confirmed with the HRT of 25 hours. As described above, it has been confirmed that AMD can be treated for a long period under HRT of 12.5 to 50 hours by “JOGMEC process” which removes metal ions as sulfide using an anaerobic reactor filled with agricultural wastes such as rice husk and rice bran. Then, since November 2016, the pilot-scale demonstration tests for AMD containing iron, zinc, copper, and cadmium ions was started.

Table 1 Mine Water Quality (average)

<table>
<thead>
<tr>
<th>pH [-]</th>
<th>T-Fe [mg/L]</th>
<th>Zn [mg/L]</th>
<th>Cu [mg/L]</th>
<th>Cd [mg/L]</th>
<th>SO₄²⁻ [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>38</td>
<td>15.4</td>
<td>4.9</td>
<td>0.06</td>
<td>310</td>
</tr>
</tbody>
</table>

Methods
The pilot-scale demonstration tests had been carried out at an abandoned mine site in Japan. In these tests, the AMD (Table 1 shows the concentration of each metal ion) was treated with two-step passive treatment systems. The first step was Iron oxidation reactor, in which ferrous ions in AMD were oxidized to ferric ions and precipitated as oxides utilizing the function of iron oxidizing bacteria. The second step is Anaerobic reactor. In this reactor various metal ions were precipitated as sulfides resulting from the reaction with hydrosulfide ion generated by SRB. The appearance and treatment flow of facility for these tests are shown in Fig.1.

The iron oxidation reactor is a PVC tank (W 1.6 m × D 1.3 m × H 1.0 m). For the activation of aerobic iron-oxidizing bacteria utilized in the iron oxidation reactor, raw AMD water was introduced into the reactor like a shower to raise the dissolved oxygen concentration. The iron oxidation reactor was filled with rice husk as carrier of iron-oxidizing bacteria and capturing material of precipitated iron oxides. Rice husk was filled with the thickness of about 0.5 m in
the reactor. The volume was about 1 m$^3$ and was half of reactor. AMD was introduced into the iron oxidation reactor at a flow rate of approximately 5.2 L/min, and under this condition the HRT was 2.5 hours.

In the anaerobic reactor, sulfate ions were reduced by SRB and then hydrosulfide ions were generated. They reacted with metal ions contained in AMD and resultantly the products were precipitated mainly as sulfides. The reactor was made of concrete and its dimensions were W 3 m × D 2 m × H 2.5 m, and was buried in the semi-underground, 1.8 m out of 2.5 m in height is installed in the ground. AMD was treated at a flow rate of about 2.6 L/min and the HRT in the anaerobic reactor was 30 hours.

As the contents, at the bottom of the reactor, limestone (particle size 20 to 40 mm) was filled to a thickness of about 0.15 m to prevent clogging of the perforated drain pipes. At the middle area of reactor rice husk layer existed for SRB reaction site and capturing precipitates. Three materials were mixed in this layer, 750 kg of rice husk for substrate, 3,000 kg of limestone (particle size 20 to 40 mm) for pH buffering, 75 kg of soil for resource of bacteria. Furthermore, rice bran as organic matter was filled in the upper layer. In order to keep a good permeability inside the reactor, rice bran was divided into mesh bags and filled in consideration of maintainability such as additional filling and removing. Four ports were set at 4 ports in the depth direction (1st port: 0.50 m from the top of the rice husk layer, 0.75 m at the 2nd port, 1.00 m at the 3rd, 4th port: 1.25 m) of the anaerobic reactor and then samples can be obtained using those ports.

The AMD before and after treatment were periodically sampled and analyzed. Items for monitoring were temperature, pH, Oxidation-Reduction Potential (ORP), metal concentrations (such as iron, copper, zinc, and cadmium), sulfate ion concentration, total sulfide ion concentration that hydrogen sulfide, hydrogen sulfide ion, and other sulfide ion were fixed as sulfide ion under strong alkaline condition, and analyzed with a spectrophotometric method using methylene blue, and chemical oxygen demand (COD).

**Results**

(1) Iron oxidation reactor

Fig.2 shows ferrous ion (Fe$^{2+}$) and total iron concentrations of treated water. Most of
Ferrous ion was oxidized to ferric ion (Fe$^{3+}$) with iron oxidation reactor, and total iron was decreased from 30 - 40 mg/L to less than 10 mg/L (Domestic effluent standards of total iron concentration is 10 mg/L). The performance of iron ion removal has been stably maintained throughout the year. Especially in summer season, in the area of 300 - 400 days in Fig.2, the performance was better and the concentration of total iron was 2 - 5 mg/L.

(2) Anaerobic reactor

Since May 2017, the test was carried out under the conditions of 25 hours of HRT and 1.0 m of thickness of the rice husk layer (middle of the anaerobic reactor). Although dissolved zinc ion concentration after filtration was low, zinc content in particulate compounds in the effluent gradually increased. These phenomena were probably caused by inadequate trapping of particulate zinc sulfides in the reactor. And then, the thickness of rice husk layer was thickened to 1.25 m to capture particulate zinc in April 2018.

Fig.3 shows the ORP transition of each depth of the anaerobic reactor and outflow, and Fig.4 shows the performance of zinc removal. According to Fig.3, Outflow was stably under the reductive atmosphere and the ORP were -200 – -300 mV. The ORP of each depth of anaerobic reactor was less than 0 mV, under the 2nd port (at 75 cm from the top of the rice husk layer) was less than -200 mV. According to Fig.4, zinc concentration decreased from 16 mg/L to less than 2 mg/L, and zinc ion concentration in filtered water with the 0.45 µm syringe filter was nearly 0 mg/L. Total zinc concentration in outflow decreased to less than 2 mg/L (Fig.4) with 125 cm as the thickness of the rice husk layer, whereas it was found to be 10 mg/L with the thickness of 120 cm. This implies that the particle products were efficiently captured owing to the thicker rice husk layer.

Since July 2018, the flow rate of anaerobic reactor was increased from 2.6 L/min to 3.2 L/min, it means that HRT was same as before April 2018.

Fig.5 shows the transition of ORP in the anaerobic reactor. ORP of each depth were all negative values, and were also -200 – -300 mV for outflow after the HRT was shortened.

Fig.6 shows the performance of zinc removal. Zinc was not detected from filtered samples, and most of zinc ion was removed. However, zinc was detected from unfiltered samples, and the particulate zinc was found to be approximately 6 mg/L.

**Discussion**

After the rice husk layer of anaerobic reactor was thickened for promotion to capture the particulate containing zinc, zinc concentration was resultantly almost 0 mg/L.
in nonfiltered samples. It was presumed that the area of negative ORP and sulfate reduction reaction of SRB were also thickened and the efficiency to capture particulate products was promoted. However, in the case that the flow rate of anaerobic reactor increased and HRT was shortened in the same condition as before thickening the rice husk layer, the particulate containing zinc was detected again from the anaerobic reactor outflow.

Then, the zinc concentration of each depth of the anaerobic layer was less than outflow. From this result, particulate containing zinc was detected in outflow, not because the sulfate reduction reaction of SRB or the ability to capture sulfide metal were insufficient, but because the flow in the rice husk layer was not homogeneous. In other words, it is considered that precipitation reaction of zinc occurred when treated water and untreated water mixed at the bottom of the anaerobic reactor after passing the rice husk layer. It was suggested that it is important to maintain the homogeneity of the flow in the anaerobic reactor to a certain extent in order to make the processing more stable. On the other hand, although the particulate containing zinc was detected in the outflow under the condition of a shortened HRT (25 hours), the throughput in the same area was increased compared to before thickening the rice husk layer (1.0 m), that is, it is thought that the processing could become efficient and the equipment could be made compact by making the reactor deep.

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![Figure 5 ORP (HRT: 25 hr)](image)

![Figure 6 Zn concentration (HRT: 25 hr)](image)
Responding to Minnesota’s Regulatory Sulfate Standard for Wild Rice Waters

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Abstract

A common challenge for industries and communities in Minnesota (USA) is a restrictive standard of 10 mg/L sulfate for waters associated with wild rice. This poses a substantial challenge for wastewater treatment facilities and businesses. Reverse osmosis and nanofiltration are expensive options and generate substantial waste. The work reported here is a suite of alternative materials and technologies for removing sulfate cost-effectively with reduced waste handling. This program encompasses development of new materials, barite precipitation, and biological reduction of sulfate to sulfide with iron dissolution by electrolysis. Minnesota’s stringent regulatory standard will require application of multiple technologies.

Key words: sulfate, remediation, Minnesota (USA), water quality regulation, wild rice

Introduction

High levels of sulfate can alter sulfur cycling in natural systems, particularly freshwater. In northeast Minnesota, sulfate loading is largely associated with mining operations and increased interest has emerged for developing technologies to treat the high levels of sulfate in the circumneutral water (Bavin and Berndt 2008). A set of empirical observations of aquatic vegetation communities and water quality in Minnesota (USA) lakes in the 1940s found that few populations of wild rice (Zizania palustris) grew in areas with aqueous sulfate concentrations greater than 50 mg/L, and healthy populations were associated with water column concentrations of 10 mg/L or less (Moyle 1944). These observations led the state legislature to promulgate a Class 4A water quality standard, Minnesota Rule 7050.0224, which sets upper limits of water column SO⁴ concentrations to 10 mg/L in waters with “wild rice present”. Wild rice is a widely distributed annual emergent grass that provides habitat and food for waterfowl and wildlife. Wild rice (also known as manoomin), is economically and culturally important to the Ojibwe peoples, whose creation story is linked to this species (Schuldt et al. 2018). Declines in wild rice productivity and extent have implicated elevated sulfate levels, and the potential causal mechanism is associated with elevated concentrations of sulfide in the sediment pore waters (Myrbo et al. 2017; Pastor et al. 2017). Pore water sulfide is controlled by microbially mediated sulfate reduction, with sediment total organic carbon (TOC) and sediment iron concentrations serving as the dominant controlling variables (Pollman et al. 2017). The Minnesota Pollution Control Agency (MPCA) has proposed a revision to the sulfate rule, which would have taken into consideration site-specific TOC and Fe concentrations (MPCA 2019); however, an administrative law judge rejected this revision in 2018, therefore, as of March 2019, the restrictive 10 mg/L limit is still the current standard.

Chemical, biological and physical processes can reduce sulfate concentrations to below the US EPA drinking water standard of 250 mg/L. However, sulfate reduction below 200 mg/L primarily relies on membrane-based technologies such as reverse osmosis (RO) or nanofiltration (NF), which generate large volumes of liquid waste that is technically challenging and costly to manage (Aubé et al. 2018, mining waste); Bolton & Menk, Inc (2018, municipal wastewater).
The B&M report stated that the removal of sulfate from water in Minnesota using RO is especially difficult because the climate does not lend itself to evaporation of the RO reject, and the State has a prohibition against injection of the concentrate. This appears to make Zero Liquid Discharge (ZLD) the required option if RO is used. In a technology review for MN, Barr Engineering and BMI (2018) concluded that RO and NF were the most desirable technologies in the suite of technologies considered.

In comparison to the material- and energy-intensive RO and NF, biological sulfate reduction is a promising and more economical alternative for sulfate removal, and this process has been applied beneficially in both active (off-line sulfidogenic bioreactors) and passive treatment systems (constructed wetlands, permeable reactive barriers; Miao et al. 2012; Neale et al. 2018). However, the performance of these biological sulfate treatment systems is highly variable, which is particularly true in passive biological treatment. In a large part, this is due to technical challenges of supplying defined substrates (e.g. ethanol, lactate, hydrogen gas as electron donors) for promoting and sustaining biological sulfate reduction (Garcia-Saucedo et al. 2008; Eljamel et al. 2009).

A solution to achieving Minnesota’s wild rice standard will likely be based on a portfolio of technologies, including physical, chemical, and biological processes. The Natural Resources Research Institute (NRRI) is working on such a portfolio, starting with testing of a bioreactor system (Hudak et al. 2017; not discussed further herein), and more recently focused on four different pathways (fig. 1). Below we briefly discuss 1) development of a new natural modified peat material that utilizes anion exchange properties for capturing sulfate at low pH; 2) preliminary testing of a barite precipitation process; and 3) development of a bioelectrochemical reactors.

**New Material Development: Anion-Exchange**

We have developed peat granular products designed to remove potentially toxic metals from mine and storm waters (Kolomitsyn 2017a, b, Kolomitsyn 2019). We are also developing a new peat-based material with introduced anion exchange properties that can be used as a weak anion exchanger for treatment of sulfate in acidic solutions. Peat does not naturally have any anion exchange capacity and by itself exhibits a nitrogen content of only 2.57%. Chemically, peats are largely organic material, which contain hemicellulose, cellulose, lignin, humic and fulvic acids. Lignin, humic and fulvic acids are naturally occurring phenol-containing polymers. Natural peat is susceptible to a hydrolysis reaction under pH 8.0 and higher. The hydrolysis releases humic acids into the solution and, therefore, colors the water. It also leads to destruction of the peat structure. In order to create a stable material, peat was granularized and treated with heat,

![Figure 1 Sulfate remediation program to meet Minnesota (USA) water quality standard for wild rice waters.](image-url)
leading to the development of APTsorb150 peat granules (fig. 2). These granules are stable without losing structural integrity at \( \text{pH}=10.2 \). When \( \text{Na}_2\text{CO}_3 \) pre-treated APTsorb150 granules were treated with a solution of HCl, and then subjected to the Duff reaction (Duff 1934, Grimblat 2016) with hexamethylenetetramine, the nitrogen concentration increased from 2.93% to 7.1% and the introduced anion exchange capacity rose from 0 mEq/100 g to 80 mEq/100g.

The total anion exchange capacity of APTsorbNH2 and the weak anion exchange nature of the introduced amine groups on the surface of peat granules were demonstrated through bench-scale column test using 4500 mg/L solution of \( \text{H}_2\text{SO}_4 \) in water (fig. 3). As can be seen from the Run 1 results depicted in fig. 3 the APTsorbNH2 granules for the column bed volumes 1-6 removed virtually all of the \( \text{H}_2\text{SO}_4 \) acid that was introduced into the column. The breakthrough was reached starting with bed volume 7, indicating that the anion exchange sites on the peat APTsorbNH2 granules began to saturate with the \( \text{SO}_4^{2-} \) anions. We detected that a portion of the acid introduced into the column remained in the aqueous solution and exited the column. At about bed volume 19, the concentration of the effluent plateaued at around 4000 mg/L, showing that all of the anion exchange sites on the peat granules had become saturated with the \( \text{SO}_4^{2-} \) anions.

Granules were regenerated by washing with a 0.1N solution of NaOH, followed by washing with deionized water until...
the effluent reached a neutral pH. A 4500 mg/L solution of $\text{H}_2\text{SO}_4$ in water was then introduced to the column (Run 2) and the loading cycle was repeated. The curves for the Run 1 and Run 2 are very similar, demonstrating that the performance by the APTsorbNH$_2$ granule media was repeatable after the media was regenerated using 0.1N NaOH solution. These data suggest that nitrogen introduced to peat granules under modified Duff reaction conditions exhibited amine like properties. The resulted new peat granular material, APTsorbNH2, behaves like a weak anion exchanger and the properties are retained even after media regeneration.

**Chemical Precipitation, Barite Process**
Since sulfate readily precipitate with barium ion, barite ($\text{BaSO}_4$) precipitation has been applied to treat high strength sulfate waste streams and has been extensively studied in the mining industry (Bosman, et al., 1990, Hlabela, et al., 2007, Swanepoel, et al., 2012). Barium salts such as barium sulfide, barium carbonate, barium hydroxide are known to remove sulfate from the solution from high levels (>1000 mg/L) to 100 mg/L. However, to date, no detailed studies have characterized the effect of the barite precipitation on sulfate removal from municipal wastewater. We have examined the potential of barite precipitation processes for achieving $\text{SO}_4$ concentrations below 10 mg/L in municipal wastewater containing $\text{SO}_4$ concentration below 200 mg/L.

A general schematic of the barite precipitation process is provided in Fig. 4. This process consists of the following unit operations: source water is chemically treated
by the addition of barium salts in a rapid mixer with standard turbine paddles. Flocculants such as ferrix and polymers are added to assist in forming larger and denser barite particles. We tested the effect of flocculant dose and mixing intensity to generate flocs of the suspended barite precipitates. The settling characteristics of the treated water were determined in settling column. The overlying water was filtered through a dual media filter to remove colloidal solids and floc fines. For each of the process approaches described above, performance data were collected and monitored for trends indicative of sulfate removal from the municipal wastewater. Data included conductivity, pH/temperature, turbidity, barium chemical doses, flocculant doses, mixing speed, sulfate concentration for the feed and the discharge flow streams. Other data collected, and monitored includes run times and sulfate recoveries.

The removal of sulfate ions by precipitation strongly depends on the dosage amount of barium $SO_4$, mixing intensity, reaction time and other lab conditions, which are essential parameters for the design of a full-scale treatment system.

We are currently optimizing the process parameters to obtain information about the viability of the process, and identify design parameters needed for the field pilot-scale test at wastewater treatment plants. Moreover, sludge disposal methods including various pre-treatment options will be evaluated based on different regulatory requirements and the leachability of barite sludge.

Bioelectrochemical Reactors

We have developed a novel bioreactor to stimulate biological sulfate reduction and simultaneously facilitate the subsequent removal of the reduced sulfide by applying iron electrolysis under low electrical potential. Batch and flow-through bioelectrochemical reactors were developed to test the effect of low voltage on the efficacy of sulfate reduction and iron sulfide formation. Experimental bioelectrochemical reactors with stainless steel electrodes were composed of creek sediment affected by mining activities (Second Creek, MN) and were fed with a synthetic mine water medium with a sulfate concentration of 1000 mg/L. The reactors were operated at 0-2V producing cathodic reductions.

![Figure 6](image_url)

Figure 6 Change in pore water sulfate concentration at the cathode throughout the duration of sediment bioelectrochemical batch reactors operated at 2V and 0V (left) and black band precipitate formation in the reactor after 14 days of 2V applied to system (right). Black band precipitation is identified as iron sulfide through acid volatile sulfide analysis and SEM equipped with energy dispersive X-ray spectroscopy.
The sulfur chemistry in the pore water of the reactors was assessed to determine indigenous microbial activity. The application of electrical potential resulted in active sulfate reduction in 14 days in comparison to control reactor (fig. 6). Iron sulfide formed in the reactors were examined with scanning electron microscopy and x-ray diffraction. Based on 16S rRNA amplicon sequencing analysis, the enhanced sulfate reduction appears to be associated with an increased population of sulfate reducing bacteria (Desulfovibrio and SRB2) in the response of a constant supply of hydrogen through electrolysis. In addition, the experimental results were used to validate a mathematical model of the system, which will then be used for process optimization. Sediment batch and packed-bed bioelectrochemical reactors demonstrated biological sulfate reduction enhancement, with subsequent iron sulfide capture. This work presents a proof of concept application of electrical potential to enhance the performance of biological sulfate treatment in a controlled manner.

Conclusions
We have successfully developed and patented a novel peat-based particle that can be used to remove sulfate from acidic mine water. The material can be regenerated to extend their life cycle beyond a single use. In addition, we have successfully demonstrated that barium chloride can be used to reduce sulfate concentrations from ≈100 mg/L to below 10 mg/L. Finally, we have successfully completed bench-scale tests of a bioelectrochemical process to remove sulfate from sediment pore water with the simultaneous production of iron sulfide. Further pilot testing is ongoing to extend the range of sulfate concentrations of the influent waters, to extend the applications from municipal wastewater treatment systems to industrial applications. We envision a set of cost-effective solutions will be available within the next few years to address Minnesota’s unique wild rice standard.

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References


Mine Waters of the Mining Enterprises of the Murmansk Region: Main Pollutants, Perspective Treatment Technologies

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Abstract

One of the most important environmental tasks in the activities of the mining industry is wastewater cleaning. The main difficulty lies in large volumes of water. This leads to high economic and material costs in the implementation of various cleaning schemes. The priority contaminants of mine waters of two mining enterprises of the Murmansk region were analyzed: JSC Kola MMC and LLC Lovozersky GOK. Thus, for the water of Severnyi Mine, JSC Kola MMC, the main pollutants are sulfate (720 mg/L), nitrogen compounds (70 mg/L), nickel (0.35 mg/L), copper ions (0.007 mg/L), and suspended solids (25 mg/L). The priority pollutant in the mine water at Karnasurt Mine, LLC Lovozersky GOK is fluoride (15 mg/L). For each enterprise, strategies and perspective technologies for mine waters treatment were considered.

Keywords: mine waters pollution, priority contaminants of mine waters, technologies for mine waters treatment

Introduction

Murmansk Region is home to of the largest mining and minerals projects in the Russian Arctic and in the Russian Federation as a whole. The region supports a major share of the national economy demand for phosphate ore, zirconium, vermiculite, niobium, tantalum, rare earth metals. Nickel, copper, cobalt, iron ore, and nepheline minerals are extracted in Murmansk Region (Masloboev et al., 2016).

One of the greatest environmental challenges in the mining industry is mine water treatment. The main challenge is the large mine water volume resulting in the high costs involved in the implementation of treatment processes. Besides, mine water is a complex multicomponent system containing – in addition to solutes – colloids, suspended inorganic and organic solids.

For instance, JSC Apatit, a major apatite-nepheline ore mining and concentration project, operates two open-pit and two underground mines and two processing plants. Wastewater (mine and pit water, storm runoff, and industrial wastewater) is discharged from seven outlets into five fishery water bodies. Common pollutants include suspended solids, petroleum products, nitrogen compounds, aluminum, molybdenum, fluorine.

JSC Kovdorsky GOK extracts and concentrates complex ores into three salable concentrates – iron, apatite, and baddeleyite. Key pollutants in the site’s wastewater are manganese, molybdenum, strontium, sulfate, phosphates.

The wastewater produced by JSC Olkon, the operator of six open-pit and one underground ferruginous quartzite mines and a concentrator plant, exceeds the maximum permissible concentrations of nitrogen compounds – nitrates, nitrites, and ammonium ions.

In this paper, we use two major mining operations in Murmansk Region – JSC Kola MMC and LLC Lovozersky GOK – as case studies to study mine water removal and treatment solutions and key pollutants. For each operation, we examine their respective wastewater strategies and prospective treatment processes.
Description of mining operations and wastewater

Severnyi Mine, JSC Kola MMC

Severnyi Mine extracts sulfide copper-nickel ore, which is supplied to Kola MMC’s smelter and concentrator. Its central industrial processes are drilling and blasting, ore extraction and overburden removal, ore handling and transportation.

Mine water is handled at Severnyi Mine by two pumping stations at the horizons -33 m and -440 m. The pumping station at the horizon -33 m is fed from the pumps evacuating mine water from the ventilation rockshaft’s and cage shaft’s different horizons. The pumping station at -440 m is fed from the pumps evacuating mine water from the central ventilation shaft’s and western ventilation shaft’s horizons. The daily mine water flow is nearly 28,000 m$^3$. Water discharge flows vary considerably over the years. Fluctuations are up to 12% of the average and are related to the inflows for process needs.

Mine water treatment plant with a capacity of 500 m$^3$/h is composed of a mine water receiver tank, a mixer, primary treatment facilities – two interconnected settling ponds, high-rate filters, a chemicals feed plant, a pumping station for feeding wash water to the tower, a chlorinator plant, and a wash water tank. Wash water from the filters and sediment from the clarifiers is discharged into the concentrator’s tailings sump.

Environmental monitoring data collected by Kola MMC since 2010 indicate that the mine water from Severnyi Mine discharged into the rivers Bystraya and Hauki-Lampijoki falls short in terms of its chemistry of the applicable environmental and health standards for suspended solids, sulfate, nickel, nitrogen compounds, and petroleum products.

Chemical analysis of the mine water and water samples collected from the mine’s different horizons revealed some patterns of the distribution of pollutants and identified local pollution maxima. By its composition and the total content of pollutants, the most polluted water samples come from the pump sump at the horizon -80 m (share approx. 20%).

Karnasurt Mine, LLC Lovozersky GOK

LLC Lovozersky GOK’s Karnasurt Mine extracts and concentrates ore into a loparite concentrate. Loparite is a source mineral in the production of rare earth metals, tantalum, and niobium. LLC Lovozersky GOK is a major Russian supplier of these mineral commodities. The company operates Karnasurt Mine, including a concentrator and auxiliary plants and facilities.

The mine’s tunnels accumulate seepage water from the penetrated aquifers and due to precipitation and surface runoff seepage through cracks in the rock. To avoid flooding of the underground workings, the accumulated water is pumped to the surface. The deposit’s rocks contain a highly water-soluble mineral – villiomite (NaF). Therefore, the mine water pumped to the surface has an elevated content of fluoride ions, which is substantially above the applicable MPCs. In addition, the mine discharge has elevated concentrations of manganese, iron, and petroleum products. The suspended minerals in the discharge originate from the ground ore surfaces, petroleum products (kerosene, gasoline, fuel oil) leak from the mining machinery and mechanisms used to extract the ore and are in a dissolved and emulsified form.

Mine water is collected by catchwater drains, sent to the receiver and pumped from there to the surface. Untreated mine water is then discharged into the Sergevan river. The mine water flow rate varies considerably throughout the year. As a result, there are substantial fluctuations in the concentrations of pollutants, with an sharp increase during the spring flood. The daily mine water flow is nearly 27,000 m$^3$.

Selection of a mine water treatment strategy and process

Severnyi Mine, JSC Kola MMC

The main pollutants of the initial mine water composition have been identified on the basis of physical and chemical analysis
Taking into account pollution type, operating and capital expenditures, as well as large volumes of waste mine waters for their purification, the following methods were tested: chemical coagulation, electric coagulation, mechanical filtration, sorption filtration and their combining, which were chosen from the most widely used methods (reverse osmosis, ion-exchange, chemical coagulation, electric coagulation, filtration, cementation, sorption and others).

Due to chemical coagulation inefficiency, caused by low water temperature (below 4 °C) and high supply rate of reagents, the process including the following main stages (fig.) has been suggested for industrial implementation of waste mine waters purification.

- mechanical treatment of the input mine water to remove coarse particles by settling in ponds,
- electrochemical treatment (electro-coagulation using soluble electrodes of grade St.3 steel) of the clarified water,
- flocculation (formation of Fe$^{2+}$ compounds) and additional oxidation of electrochemical coagulant (Fe$^{2+}$ to Fe$^{3+}$) by air oxygen,
- coagulant settling in thin-layer sedimentation tanks (batch thickeners) with a selective feed of a flocculant in a wide range of pH values (5-10),
- mechanical filtration of the clarified water,
- sorption post-treatment in carbon filters,
- sediment collection and dewatering.

The main advantages offered by the proposed electrochemical mine water treatment process are:

1. rapid formation of floccules and sorption of the dissolved metals (iron, nickel, copper) and other impurities,
2. treated water quality unrelated to the input concentration of suspended substances and dissolved impurities,
3. high water clarification performance offered by the large specific surface area and sorption capacity of the electrochemical coagulant; possibility to remove nitrogenous and organic compounds from the water, both by sorption and through their decomposition (on the anodes) into gaseous CO$_2$, gaseous NO$_2$, and water. the high rate and efficiency of the coagulation and sediment compaction processes, since the resulting iron hydroxide floccules are denser than aluminum hydroxide floccules and act more effectively over a wide pH range,
4. lower water corrosivity (through the formation of hydrogen and Fe$^{2+}$ compounds – both potent reducing agents – in the process of electrocoagulation) and lower corrosion rate of the piping when the treated water is recycled to the process,
5. complete exclusion of a chemical coagulant (aluminum polyoxychloride), acids, and alkalis from the process. Potential reduction in the flocculant feed rate by up to 50-100%;
6. elimination of nitrite and ammonium nitrogen oxidation (to nitrates or elemental nitrogen) with sodium hypochlorite,
7. reduced dependence of the water treatment performance on its temperature and changes in pH values,
8. reduced frequency of washing the filters and reduced pure water feed rate to the washing process,
9. reduced reagent delivery and storage costs,
10. reduced environmental impact,
11. improved safety of the water treatment process.

The proposed process is straightforward to implement and easy to operate, which allows to maintain the required water treatment performance at low specific capital and operating costs (Oncel et al., 2013).

The high rate of the coagulation processes (when using electrocoagulation) allows the use of smaller reactors.

When using electrocoagulation, the settling tanks (batch thickeners) will provide high removal performance (higher than 90-95%) of the bulk of the dispersed suspended substances, including hydrolysis products of the dissolved metals.

The proposed combined mechanical and physicochemical water treatment process allows to:

- achieve compliance of the treated water with the quality standards required for recycling the water to the process,
- in terms of some of the criteria, achieve compliance with the MPCs for fishery water bodies.

Karnasurt Mine, LLC Lovozersky GOK

The priority pollutant in the mine water at Karnasurt Mine is fluoride (15 mg/L). Currently, several processes for the removal of fluorine have been developed and are being used, including chemical precipitation and coagulation, ion exchange, sorption, electrocoagulation, and membrane processes (e.g. Jadhav et al., 2015). The effectiveness of the process used is controlled primarily by the initial concentration of fluorine and the volume of treated water.

Analysis of the mine water flow by quantity and pollution level has shown that up to 70% of the water entering the mine is relatively clean water (0.001-0.7 mg/L). It has primary pollution comparable to the MPCs in mine water released into fishery water bodies. Thus, if the secondary pollution of the water entering the mine is prevented by intercepting the seepage before it gets contaminated in the mine, the volume of treated water can be substantially reduced. It will then be possible to conduct treatment inside the mine’s workings.

The strategic goal of mine water treatment at Karnasurt Mine is to bring wastewater
released into the Sergevan River to the requirements of the MPCs for fishery water bodies. In order to achieve this, the following is deemed necessary:

- penetrated clean water sources should not be allowed to mix with contaminated mine water by channeling via dedicated pipelines to the surface,
- in all newly developed horizons with a sufficient water inflow, local pumping stations should be deployed to be able to recycle the mine water to the process.

Retrofitting the clean water removal system for delivery into water drainage pipelines will prevent secondary pollution by suspended material in the drainage ditches of the haulage workings. To accumulate water volume and head in the haulage workings and voids, waterproof protective dams will be constructed.

One, two, and more cascade structures are planned for mine water settlement (clarification) in ponds in inclined, horizontal, and vertical mine workings with enclosing dams of various designs. To improve the performance of the process, combined reagent treatment is proposed using iron sulfate as a coagulant and flocculant Praestol 2515.

As a sorbent of fluoride ions, we investigated the use of a magnesium-containing product of acid treatment of the copper-nickel ore concentration tailings, composed of brucite Mg(OH)$_2$ with a calcite CaCO$_3$ admixture (Bajurova et al., 2015).

The use of brucite for wastewater treatment to remove potentially toxic metals and strontium was investigated by Bochkarev and Pushkareva (1998, 2009). A combined sorption process for the removal of metals from natural water and process solutions in a wide range of concentrations was proposed.

Using a mixture of brucite and calcite makes it possible to achieve a recovery of F- of up to 88-95% within an 4-5 hours, and at relatively low concentrations (1-10 mg/L), values below 0.75 mg/L, which is the MPC for fishery water bodies. Sorption by a mixture of brucite and calcite is explained by the isomorphic substitution of hydroxyl/carbonate ions with fluorine with the formation of poorly soluble calcium and magnesium fluorides without any changes in the crystal lattice. Pilot tests are being planned.

**Conclusions**

1. In the treatment of the mine water at Severnyi Mine operated by JSC Kola MMC, mechanical removal from the input runoff of coarse impurities by settling in settling ponds followed by electrocoagulation and filtration in mechanical and sorption filters can offer high performance. The advantages of electrochemical coagulation include wide pH ranges and the potential high degree of water purification from metal cations and organic compounds at low temperatures of the mine water.

This will however involve changes in the storage of the resulting waste – sediment from the settling ponds is a fine-grained ore material stored in the ore stockpile, sediment from electrocoagulation can be used as an insulating layer at the tailings disposal site.

2. To implement mine water treatment at Karnasurt Mine operated by LLC Lovozersky GOK to the MPC standards for fishery water bodies, mixing of the relatively clean seepage water with the contaminated mine water should be prevented by pumping the former via dedicated pipelines to the surface. Treatment of small mine water volumes in the mine's finished voids can be organized by setting up settling ponds in inclined, horizontal, and vertical mine workings with enclosing dams of various designs.

To improve the performance of the process, combined reagent treatment is proposed using iron sulfate as a coagulant and flocculant Praestol 2515. A magnesium-containing product composed of brucite with a calcite admixture is recommended as a fluoride ion sorbent.

**Acknowledgments**

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References


Electrochemical treatment of mining waters

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Abstract
This research is intendent to study the removal of cyanide, sulfate, chloride and nitrate from mining waters using electrochemical treatment. Tests were performed in batch and continuous modes with real and synthetic mining waters. Electrolysis and electrocoagulation with different electrodes materials (iron, aluminum for electrocoagulation, Ti-coated and carbon for electrolysis) resulted in favouring of anions removal. Additionally, performances comparison of electrolysis and electrocoagulation for cyanide removal was completed. Sulfate removal of 95% was achieved using electrocoagulation with iron anode and aluminum cathode. Electrocoagulation favored the almost complete removal of nitrate regardless the electrodes material tested, when electrooxidation was found to be inefficient for treatment of nitrate-rich waters. Cyanide concentration decreased from 100 mg/L to 1 mg/L during the electrocoagulation with iron anode in 5 min treatment time. A review on total suspended solids (TSS) removal from waters by electrochemical techniques is also provided.

Keywords: anions, TSS, electrochemical treatment, mining water

Introduction
Mining waters are often heavily contaminated with anionic and cationic species. Among the most prevalent and harmful compounds are toxic metals and anionic contaminants, such as sulfate, nitrate, chloride and cyanide. Moreover, high concentration of total suspended solids (TSS) may hinder the downstream processes. It is essential to treat discharged water and bring the concentrations of dissolved contaminants and TSS to acceptable discharge levels. Another mining water management concept is to reuse and recycle water within the process sections. Firstly, it makes mining operation more economical and environmental friendly. Secondly, it allows for treating water only to a level suitable for a certain process rather than to an acceptable discharge level.

Generally, high concentration of nitrate results in detrimental effect on the environment and the usage of water in industry. Nitrate is described as non-toxic or only toxic to infants as it causes the blue-baby syndrome. Nitrate has to be removed due to possible contribution to the eutrophication of standing surface water bodies. According to the European Environmental Commission (EEC) recommendations for drinking water the maximum allowable concentration of nitrate is 50 mg/L. Nitrate concentration in mining waters may vary from tens to hundreds milligrams per liter. One of the main sources of nitrate in the water is the utilization of nitrogen-based explosives. Water contamination with nitrates and other N-compounds is a result of incomplete detonation, dissolution of explosives and spillage during blasting activities. However, the real source of nitrate in mining waters is questionable doubtful. Many mines are surrounded by human settlements, thus other sources of nitrate that contribute to an increase in its concentration are human and animals wastes as well as fertilizers. Despite the real source of nitrogen, it is obligatory in most countries to bring the nitrate concentration to a desire level. Recently, electrochemical water treatment methods are developed to treat nitrate-rich waters. Lacasa et al. (2011) reported nitrate elimination from groundwater by electrocoagulation, continuous electrochemical treatment of drinking and mining water was studied.
by Kumar et al. (2009) and Mamelkina et al. (2017), and the performance of electrocoagulation and electoreduction was compared by Koparal et al. (2002).

High sulfate concentration contributes to substantial pollution of water bodies, challenges the reproduction of soils and hinders the process operations. In the world of mining, sulfate is defined as a final oxidation product of sulfuric minerals. Globally, the discharge limit for sulfate varies from 250 mg/L (USA) to 2,000 mg/L (Finland) (Nariyan 2018). Mining waters typically contain from hundreds to several tens of thousands of milligrams per liter of sulfate. The level of sulfate in mining waters is increasing through the use of sulfuric acid during the mining processes. However, the main source remains to be an acid mine drainage. One of the main reasons for treatment of sulfate-rich waters is to meet the discharge requirement or enable the reuse and recycling of water within the process. Among possible promising techniques to eliminate sulfate is electrochemical treatment. The performance of electrocoagulation process using bipolar and monopolar arrangement of electrodes was described by Nariyan et al. (2018), whereas Mamelkina et al. (2017; 2019) studied batch and continuous electrochemical treatment. Fernando et al. (2018) provided a comprehensive review on possible challenges and opportunities of treatment of sulfate-rich mining waters. Pulkka et al. (2014) provided a broad review on sulfate, nitrate as well as other anions removal by electrochemical methods.

Cyanide is defined as a carbon/nitrogen compound reported as highly toxic for the environment and harmful for people health. Cyanide presents in several forms, such as ionic, molecular HCN, salt and metal-complexes. Regulated limit for WAD-cyanide at one of the Finish mines is 0.4 mg/L. One of the main sources of cyanide in mining waters is its utilization during the leaching of gold and silver. Among other industries releasing cyanide with the effluent are automobile, photography and pharmaceuticals manufacturing. Electrochemical oxidation and electrocoagulation were tested in order to prevent the release of cyanide to water bodies (Perez 2017); (Moussavi 2011). Kuyucak et al. (2013) delivered a comprehensive review on cyanide removal from effluents emanating from gold mining and metallurgical processes.

Another water quality indicator is the presence of total suspended solids. Total suspended solids (TSS) are usually defined as particles with the size over 2 microns presented in water. TSS refer to all suspended solids, organic and inorganic, by mass. On the one hand, excessive amount of suspended solids in water may increase flooding risks, deteriorate water quality for aquatic and human life as well as hamper navigation. On the other hand, in mineral processing the presence of suspended solids in water flows favors flotation of minerals. However, the ranges of optimal concentration of TSS in process water is still questionable and more investigation is required to obtain the concentration range that facilitate the flotation process. The concentration of TSS in the discharged waters at Finish and Swedish mines is regulated. The discharge limits vary from 5 to 20 mg/L. The TSS level can be as high as 240 mg/L (Ledo coal mine) and may increase up to several thousands. TSS removal by coagulation mechanism was studied by Irfan et al. (2013); continuous and batch electrocoagulation was tested by Azarian et al. (2018) and Sardari et al. (2018); electroflotation was proposed for removal of TSS from water streams by Mohtashami et al. (2019). This paper is dedicated to the removal of cyanide, sulfate, nitrate and TSS using electrochemical treatment. The effects of electrode material, treatment time, operation modes and applied current were studied. In addition, the performance comparison of electrocoagulation and electrooxidation for cyanide and nitrate is provided.

**Materials and methods**

Electrocoagulation tests to remove sulfate were previously performed in batch (Mamelkina 2019) and continuous (Lacasa 2011, Mamelkina 2017) modes. Electrocoagulation and electrooxidation tests to remove nitrate and cyanide were performed with artificial mining waters using batch EC-reactors. Treated volume of mining waters was 1 L. The following combinations
of electrodes (anode/cathode) were tested Fe/Fe, Al/Al, Fe/Al, Fe/C, Al/C, Fe/Ti, Al/Ti, Ti/Ti, C/C, Ti/C, C/Ti (anode/cathode). The removal of nitrate, ammonia, total nitrogen and cyanide was monitored. The applied current was 0.3 A (0.18 mA/cm\(^2\)), 1 A (6 mA/cm\(^2\)) and 3 A (18 mA/cm\(^2\)). The operating pH values were 3, 7 and 11. The duration of the experiments varied from 30 min to 5 hours.

Synthetic mining waters were prepared using pure water and analytical grade chemicals. Based on the average values provided by several Nordic mines, treated eluent contained sulfate 1000 mg/L, nitrate 10 mg/L, chloride 150 mg/L and cyanide 100 mg/L. Cyanide was analyzed using titration by silver nitrate solution with rhodanine as an indicator. Concentrations of sulfate, nitrate and chloride were measured using ion chromatography with a Metrohm 930 Compact IC Flex coupled to a conductivity detector.

Results and discussions

The performance of electrochemical treatment is mainly affected by the current density, reactor design, process operation mode, pH of treated waters, electrodes’ material and arrangement as well as by presence of other contaminants. Summary of the results on sulfate removal by electrocoagulation is given in the table (tab 1.). Obtained results prove the suitability of electrocoagulation to treat mining waters. It can be seen that elimination of sulfate is the highest at batch mode when Fe anodes and Al cathodes are used. Continuous operation allowed 70% removal of sulfate at acidic pH. High removal of sulfate during batch operation was achieved regardless the initial pH whereas continuous treatment was only efficient at pH 2. The reason for high performance at pH 2 can be the excess amount of positively charged ions presented in treated water. These ions (Fe\(^{3+}\), Fe(OH)\(^{+}\) and FeOH\(^{+}\)) are the most common ones at acidic pH and favors the removal of sulfate by surface charge neutralization.

To study the removal of nitrate the variety of electrode combinations were tested at three different pH 3, 7 and 11. Electrocoagulation was performed using Al and Fe as anodes while the electrochemical oxidation was tested using Ti-coated and carbon (both inert) electrodes. The results of nitrate elimination presented in Fig. 1. showed high performance of electrocoagulation. Almost complete removal of nitrate was obtained after 30 min of treatment using Al/Fe. Additionally, results showed that the electrocoagulation treatment is a pH depended process and acidic pH favours its performance. The increase in nitrate concentration during the electrooxidation with inert Ti-coated and carbon electrodes revealed adsorption as the main removal mechanism of nitrate. The increase in concentration was most probably due to the reduction of ammonia ions presented in treated mining waters.

In addition to nitrate removal, the decrease in chloride content was observed. The initial chloride concentration was 150 mg/L, the applied current was equal to 3 A, at initial pH 3 using C/Ti, Fe/Al and C/C electrodes pairs the removal of chloride was as high as 79%, 74% and 63%, at pH 7 85%, 70% and 85%, at pH 11 0%, 75% and 85% respectively. No chloride removal was observed when other combinations of electrodes were tested.

The influence of current densities and

<table>
<thead>
<tr>
<th>Operation mode</th>
<th>Water source</th>
<th>Operational conditions</th>
<th>Studied compounds</th>
<th>Achieved results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>Synthetic</td>
<td>3A, pH 4 and 10, Fe electrodes</td>
<td>sulfate, Zn, Cu, Ni, nitrate</td>
<td>50% removal of sulfate, 99% removal of Zn, Ni, Cu, nitrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3A, pH 3, 7 and 11, Fe anode, Al cathode</td>
<td>sulfate, nitrate, chlorine</td>
<td>95% removal of sulfate, 99% removal of nitrate, 75% removal of chloride</td>
</tr>
<tr>
<td>Real</td>
<td>Synthetic</td>
<td>2A, pH 7, Fe electrodes</td>
<td>sulfate, Zn, Cu, Ni, nitrate</td>
<td>30% removal of sulfate, 90% removal of nitrate, 99% removal of Zn, Ni, Cu</td>
</tr>
<tr>
<td>Continuous</td>
<td>Synthetic</td>
<td>6.25A, pH 2, Fe electrodes</td>
<td>sulfate, Zn, Cu, Ni, nitrate</td>
<td>70% removal of sulfate, 99% removal of Zn, Ni, Cu, nitrate</td>
</tr>
</tbody>
</table>
Electrodes materials was studied in regards of cyanide removal. The tests were only performed at pH 11 due to the safety reasons and due to possible formation of HCN gas when operating at lower pH values. It should be noticed that the application of carbon electrodes was limited by the pH decreasing up to 6 that did not allow safe handling of cyanide solutions. Thus, the results obtained only using Al, Fe and Ti-coated electrodes were presented with an exception of Fe/C pair when the pH was maintained at around 11. The summary of the result on cyanide removal is given in Fig. 2. The concentration less then 1 mg/L of cyanide was achieved using Fe as anode regardless the applied current. However, the same cyanide removal was observed using Ti/Al pair. Application of inert electrode as anode resulted in very small amount of solids added to the system, solids were mainly formed due to the insignificant dissolution of Al cathodes. The shortest treatment time of 5 minutes was obtained at applied current 3A using Fe/Fe, Fe/C and Fe/Ti pairs. At current of 0.3A and 1A almost complete removal of cyanide was observed after 30 minutes.

Conclusion

Treatment of mining waters by electrochemical methods at the laboratory scale enabled the removal of harmful contaminants. Moreover, this study provides further understanding about the phenomenon occurring during the process. Thus, the highest sulfate
removal using continuous electrocoagulation is possible by the neutralization of the particle charge. Nitrate is removed by electrocoagulation while electrooxoxidation was found to be inefficient. Cyanide was removed due to both adsorption and oxidation. The knowledge about the removal mechanisms of the anionic contaminants from mining waters and operational parameters tested favor the possible development of electrochemical treatment technologies and scale-up of the existing units.

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References
Abstract
Polymers such as polysaccharides are added into froth flotation circuits to render gangue or non-valuable minerals hydrophilic and these as a consequence are prevented from reporting to the concentrate. Recent flotation research on PGM ores suggests that changes in water quality, specifically inorganic electrolytes and their ionic strengths may affect the coagulative-flocculative nature of solid mineral particles in flotation pulps in the presence of polysaccharides such as carboxymethyl cellulose (CMC). This could well have considerable implications on the hydrophilicity of gangue minerals and therefore the concentrate grades owing to interactions between process water electrolytes, the polysaccharides and solid mineral particles. Thus this study considers the effect of ionic strength of process water and specific ions on the coagulation of talc particles using CMC. This investigation has shown that the settling time of talc particles decreased in increasing ionic strength of process water. It was shown that when talc particles were contained in Ca\(^{2+}\) and Mg\(^{2+}\) electrolyte solutions, their settling time was shorter compared to when they were present in Na\(^+\) electrolyte solutions. The reduction in settling time implies that there was an improvement in the hydrophilicity and coagulation of talc particles in concentrated electrolyte solutions.

Keywords: Coagulation, Electrolytes, Flotation, Polysaccharides, Water quality

Introduction
Polysaccharides such as carboxymethyl cellulose are widely used in water treatment clarifiers for the removal of solids from the water being treated such that water is recovered through the clarifier launders with less solid particles. This is achieved through CMC adsorption onto solid particles, forming larger flocs with the solid particles that are easy coagulate. These coagulated CMC-solid particles flocs settle down the bottoms of the clarifier and are removed as sludge through the clarifier underflow. Literature suggests that the efficacy of CMC adsorption onto solid particles is enhanced in waters containing Ca\(^{2+}\) and Mg\(^{2+}\) in high concentrations or ionic strengths. The same polymer finds its wide use in the froth flotation of talcuous Cu-Ni-Pt sulfide bearing ores as a depressant for talc. The prevention of talc from reporting to the concentrate is an important aspect in the concentration of these ores as talc is naturally floatable. Its depression requires reagents such as CMC. Even in froth flotation, as is in the case in water treatment clarifiers, it is reported that to achieve a desired CMC-talc adsorption (and therefore depression), there needs to be polyvalent cations in solution. These polyvalent cations or oxyhydroxyl species act on the talc surface. This action of cationic inorganic electrolytes passivates talc since talc is naturally negatively charged. The highly negatively charged (CMC) then favourably adsorbs onto the passivated talc surface rendering it hydrophilic and in so doing prevent talc from attaching to air bubbles that move up the pulp phase. The scarcity of water in Cu-Ni-Pt concentrators has resulted in the use of recycled water with increased amounts of inorganic electrolytes. This introduces challenges and opportunities to understand how different physico-chemical aspects of flotation will behave when operating with process waters of high

Inorganic Electrolytes on the Efficacy of a Carboxymethyl Cellulose as a Coagulant for Talc: Implications for Talc Depression in Flotation

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salinity. One such aspect is the depression of naturally floatable gangue which is generally accepted to be talc in sulfidic Cu-Ni-Pt ores (Corin et al., 2011). Previous research has shown that the adsorption density of CMC on talc is strongly affected by the ionic strength of the process water (Wiese et al., 2008). Laskowski et al. (2007) found that the depression of talc was enhanced in the presence of Ca2+ compared to K+. Furthermore, the presence of metal hydroxyl species resulted in a further improvement in talc depression because the metal hydroxyl species acted as bridges between CMC and the talc surface (Laskowski et al., 2007). Recent studies showed that the recovery of floatable gangue per g of water recovered decreased with increasing ionic strength of process water; this thus suggested that floatable gangue particles were more coagulated in high concentrations of inorganic electrolytes and hence their retarded floatability (Corin et al., 2011; Corin and Wiese, 2014; Manono et al., 2018, 2012). This thus suggested that there may well be interactions between the ions present in process water and CMC. Such interactions in turn affected the hydrophilicity of talc and the coagulative nature of talc particles and may well have important implications on the talc depression in flotation. However there is little evidence supporting the claims of a coagulative-flocculative phenomenon of talc particles in increased inorganic electrolytes in the presence of CMC although this phenomenon is well established in the removal of solids in water treatment clarifiers Chong et al. (2014). It is the basis of this paper that the application of the principles governing coagulation be explored to elucidate the speculation that there is an improvement in gangue depression upon the addition of CMC in saline waters in flotation. Water treatment clarifiers imitate the process of flotation since physicochemical separation in these clarifiers occurs due to differences in surface properties of the particles except that there is no air injected into clarifiers or thickeners. Thus, some coagulative-flocculative behaviour of mineral particles should be observed in the pulp phase on flotation cells and this could potentially be responsible for the inhibition of bubble-particle attachment.

Thus the purpose of this investigation was to provide experimental evidence to the speculation of a coagulative-flocculative behaviour of talc in the presence of CMC in highly concentrated electrolytes. Thus settling tests were performed on talc in synthetic plant water as well as single salt solutions of Ca2+, Mg2+ and Na+ containing Cl in order to ascertain whether there are specific ion effects on talc coagulation. Zeta potential measurements were performed on talc suspensions in order to investigate the changes on the mineral surface with water quality. Furthermore, the microflotation of talc was investigated to ascertain the question of talc depression in degrading water quality.

**Methods**

The mineral used for settling tests was talc. 1 kg of talc was pulverised using a swing mill in small batches for approximately 15 seconds. Each pulverised batch was dry sieved through -160 μm, -75 μm and -38 μm consecutively. The oversized particles were re-pulverised until the -38 μm was achieved. The final product was split using a rotary splitter and stored in air tight bags. In order to satisfy the objectives of this study, coagulation tests, adsorption studies, zeta potential tests and microflotation tests were performed on talc in the presence of selected inorganic electrolytes shown in Table 1.

**Coagulation Tests**

Settling tests were performed on talc both in the presence and in the absence of CMC. Standard settling tests were performed to determine the settling time. For each settling test, 9 g of sample was added to 90 mL of the water type in a 100 mL beaker to make the mixture 10% solids. Each pulverised batch was dry sieved through -160 μm, -75 μm and -38 μm consecutively. The oversized particles were re-pulverised until the -38 μm was achieved. The final product was split using a rotary splitter and stored in air tight bags. In order to satisfy the objectives of this study, coagulation tests, adsorption studies, zeta potential tests and microflotation tests were performed on talc in the presence of selected inorganic electrolytes shown in Table 1.

Settling tests were performed on talc both in the presence and in the absence of CMC. Standard settling tests were performed to determine the settling time. For each settling test, 9 g of sample was added to 90 mL of the water type in a 100 mL beaker to make the mixture 10% solids. The mixture was adequately mixed for 1 minute using a magnetic stirrer, and then the pH adjusted to 9 using NaOH or HCl. The suspension was mixed at 500 rpm for 4 minutes to adequately disperse the mixture after pH adjustment. If the test was in the presence of CMC, 90 μL of CMC solution was added and conditioned for 3 minutes at 300 rpm. 3 minutes was chosen as the conditioning time as this was approximately the typical time for standard UCT batch flotation procedure. A lower speed of 300 rpm was used for uniform mixing and
to avoid breaking the flocs. After mixing, the slurry was carefully transferred to a 100 mL graduated cylinder and a stopwatch was started immediately thereafter. Measuring cylinders were used to determine the settling time instead of beakers as the longer length of the cylinders gave better visual representation of the extent of clearness of the mixtures and observing the extent of settling was improved thereby resulting in more accurate results. The cylinder was monitored until a clear supernatant liquid was observed against a clear background. A picture was taken, printed and stuck next to the working bench to serve as a basis for the clear supernatant liquid for the remaining tests.

**Zeta Potential Tests**

Firstly, synthetic plant water and single salt solutions under investigation were added into six test beakers, the pH solution was adjusted using dilute stock solutions of HCl and NaOH such that there existed a test beaker with a pH of 2, 4, 6, 8 and 10. Secondly, 0.0625 g of talc sample with a particle size of -25 µm were added onto each of the six test beakers. Thirdly, the suspension contained in a test beaker was placed on a magnetic stirrer for 15 minutes. The pH of the suspension was again measured and corrected as necessary. And finally, 1 mL of suspension was transferred into a Malvern Dip Cell and inserted into a Malvern Zetasizer for zeta potential measurements. All zeta potential measurements were performed in triplicate to ensure reproducibility and reliability of the test results. It is important to note that for each pH condition, the third step was performed just before zeta potential measuring so as to avoid any unnecessary time dependent reactions with the ions that would blind the comparability of the results from one pH to another.

**Table 1** Concentration of ions present in synthetic plant water (SPW) and single salts.

<table>
<thead>
<tr>
<th>Water type</th>
<th>Ca^{2+} (mg/L)</th>
<th>Mg^{2+} (mg/L)</th>
<th>Na^{+} (mg/L)</th>
<th>Cl^{-} (mg/L)</th>
<th>SO_{4}^{2-} (mg/L)</th>
<th>NO_{3}^{-} (mg/L)</th>
<th>NO_{2}^{-} (mg/L)</th>
<th>CO_{3}^{2-} (mg/L)</th>
<th>TDS (mg/L)</th>
<th>Ionic Strength [mol/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1SPW</td>
<td>80</td>
<td>70</td>
<td>153</td>
<td>287</td>
<td>240</td>
<td>176</td>
<td>-</td>
<td>-</td>
<td>17</td>
<td>1023</td>
</tr>
<tr>
<td>CaCl\textsubscript{2}</td>
<td>285</td>
<td>-</td>
<td>-</td>
<td>503</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>788</td>
<td>0.0213</td>
</tr>
<tr>
<td>MgCl\textsubscript{2}</td>
<td>-</td>
<td>173</td>
<td>-</td>
<td>503</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>676</td>
<td>0.0213</td>
</tr>
<tr>
<td>NaCl</td>
<td>-</td>
<td>-</td>
<td>490</td>
<td>755</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1245</td>
<td>0.0213</td>
</tr>
</tbody>
</table>

In order to investigate the extent to which CMC adsorbs onto talc in synthetic plant water, CaCl\textsubscript{2}, MgCl\textsubscript{2} and NaCl, 90 mL of the particular synthetic plant water or single salt solution was measured into a conical flask and 270 µL of the 1% CMC stock solution was added to it. This was followed by the addition of 9 g of talc and thereafter the contents of the conical flask were conditioned in an Ecobath for 3 minutes (Mhlanga et al., 2012). This meant that the initial concentration of CMC in the conical flask was 30 mg.L\textsuperscript{-1} (equivalent to 300 g/t). Immediately after conditioning, the solution (supernatant) from the conical flask was filtered using a 0.22 µm Millipore syringe filter. The determination of CMC concentration in the filtrate was made possible through the use of the du Bois calorimetric method (du Bois et al., 1956). The amount of CMC adsorbed onto the mineral surface was calculated by deducting the concentration in the supernatant from the initial 30 mg/L. The experiments were conducted in triplicate for each synthetic plant water and single salt solution.

**Microflotation Tests**

Microflotation tests were performed using 3 g of talc at a size fraction of +38-106 µm. 50 mL of the either SPW, CaCl\textsubscript{2} or NaCl were added to the mineral sample; the mixture was then ultra-sonicated for 5 minutes to allow for good dispersion of the mineral mixture. The suspension was then transferred to a UCT Microflotation Cell and the pulp was circulated by a peristaltic pump set at 90 rpm. 90 µL (300 g/t) of 1% CMC solution was then added to the cell and conditioned for 1 minute. The cell was then topped up with the particular inorganic electrolyte solution to the 250 mL mark. Through a microsyringe, air was introduced at the base of the cell at
a flow rate of 7 mL/min. Concentrates were then collected at 2, 6, 12 and 20 minutes of flotation and a tailings sample was taken after the collection of the last concentrate. The concentrates and tailings were filtered, dried and weighed. The procedure was repeated for the selected inorganic electrolyte solutions and all tests were done in duplicate to minimise experimental error.

Figure 1 shows the settling time of talc particles in various inorganic electrolytes. Figure 1 demonstrates that the settling time of talc decreased in the order of SPW>NaCl>CaCl$_2$>MgCl$_2$ in both the absence and presence of CMC. There was a further decrease in the settling time of talc particles in the presence of CMC compared to when there was no CMC in the system. The decrease in the settling time of talc particles with the divalent Ca$^{2+}$ and Mg$^{2+}$ compared to Na$^+$ is said to be a result of an increase in the hydration layers around on the talc surface. This could also be a result of the stronger CaOH$^+$ and MgOH$^+$ species which may have formed on the surface of talc and thus leading to a more coagulated pulp (Laskowski et al., 2007). It is known that the presence of divalent cations in talc containing systems, where oxyhydroxyl species may form on the surface of talc, promotes the adsorption of the negatively charged CMC ligand onto the passivated talc surface. The enhanced talc-CMC adsorption in turn results in the formation of larger flocs which are easy to coagulate.

Figure 2 shows how the zeta potential of talc changed with pH under various inorganic electrolyte solutions. It can be seen that the potential of talc particles was more negative in synthetic plant water compared to the rest of the inorganic electrolyte solutions with MgCl$_2$ resulting in the most positive zeta potential compared to all the tested single salt solutions across the given pH range. It can also be seen that the divalent Ca$^{2+}$ and Mg$^{2+}$ containing single salt solutions resulted in a more positive zeta potential compared to the monovalent Na$^+$ containing single salt solution. Between pH 4 and pH 12, the zeta potential increased with increasing pH for CaCl$_2$ and MgCl$_2$ whilst an opposite trend was observed for SPW and NaCl in that the zeta potential decreased with increasing pH. At pH 2, all tested inorganic electrolyte solutions resulted in the same zeta potential. It is also interesting to note that for the divalent cations, a zeta potential of 0 mV was achieved at about pH 4 and pH 8. The less negative zeta potential in Ca$^{2+}$ and Mg$^{2+}$ single salt solutions could be explained by the presence of stronger oxyhydroxyl species such as CaOH$^+$ which are said to passivate the talc surface. The phenomenon of a passivation of talc particles is in agreement with the decrease in settling time in the presence of Ca$^{2+}$ and Mg$^{2+}$. This potentially explains the stronger talc coagulation in divalent cation single salt solutions compared to the monovalent cation single salt solution.
Figure 3 shows that the adsorbed concentration of CMC onto talc particles increased in the order of SPW<NaCl<CaCl₂<MgCl₂ though the difference between the single salts is very minimal. There is however a trend of an increase in CMC absorption with the divalent cations compared to the monovalent cations. The difference in the adsorbed concentration of CMC onto talc particles may be due to the changes seen in the zeta potential of talc, in that the presence of Ca²⁺, Mg²⁺ and oxyhydroxyl species create a conducive environment for CMC adsorption onto talc (Burdukova et al., 2008).

Figure 4 illustrates the effect of selected inorganic electrolytes on the floatability of talc without CMC. It can be seen that the rate of recovery was higher in CaCl₂ compared to NaCl and that synthetic plant water resulted in the least rate of recovery. It is however worth noting that the final recovery of talc was the same for all tested inorganic electrolytes.

Figure 5 illustrates the effect of selected inorganic electrolytes on the floatability of talc in the presence of CMC. NaCl resulted in the highest rate of recovery compared to CaCl₂ and SPW.

Figure 6 shows the total recovery of talc in the presence of selected inorganic electrolytes with and without CMC. It can be seen that in the absence of CMC, CaCl₂ resulted in the highest recovery compared to NaCl whilst SPW resulted in the smallest recovery. Figure 6 also shows that the presence of CMC led to a substantial decrease in talc recovery in each case.
Figure 4 The effect of various inorganic electrolytes on the microflotation of talc in the absence of CMC.

Figure 5 The effect of various inorganic electrolytes on the microflotation of talc in the presence of CMC.

Figure 6 The total recovery of talc in selected inorganic electrolytes.
water type. In the absence of CMC, the Ca\textsuperscript{2+} ion gave the highest recovery of talc, followed by Na\textsuperscript{+} and SPW. This finding is in line with literature as it is expected that monovalent cations would result in lower amounts of solids recovered as floatability is improved with higher valency of electrolytes owing to an improved bubble particle attachment (Craig et al., 1993). In the presence of CMC, the opposite trend was observed as Na\textsuperscript{+} with the least depressive resulted in the highest recovery. This finding is in line with literature in that, divalent cations such as Ca\textsuperscript{2+} reduce the natural flotation of talc more compared to monovalent cations such as Na\textsuperscript{+} (Parolis et al., 2008; Shortridge et al., 2000). This is explained by the fact that hydroxo species, particularly those of calcium, selectively adsorb onto gangue minerals. Such species enhance the depressive action of carboxymethyl cellulose (CMC) onto gangue via an acid-base interaction between the positively charged mineral surface (talc) and the negatively charged CMC molecule (Burdukova et al., 2008; Laskowski and Castro, 2015; Laskowski et al., 2007). The Na\textsuperscript{+} salt is said to be unable to form hydroxide complexes which are known to be the drivers of cation adsorption on mineral surfaces (Ansari and Pawlik, 2007). The floatability findings of this work are in line with the zeta potential results which showed that in Ca\textsuperscript{2+}, the mineral surface is more passivated, creating a conducive environment for CMC adsorption which in turn results in a coagulated pulp as shown by the lower settling time in Ca\textsuperscript{2+} and Mg\textsuperscript{2+}.

Conclusions
The coagulation of talc particles was enhanced in the presence of divalent cations. The zeta potential results showed that the mineral surface was more passivated in the presence of divalent cations compared to monovalent cations. The increase in the zeta potential suggested a conducive environment for CMC to adsorb onto talc as shown by the higher CMC adsorption. This in turn led to coagulated talc particles. This result could explain the decrease in the floatability of talc in Ca\textsuperscript{2+} and CMC containing systems.

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References
To Recycle or Not? A Bench Scale Simulation of Water Recirculation in Sulfidic Cu-Ni Ore Flotation

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Abstract
The mining industry recycles and re-uses its process water as a way of responding to the global scarcity of water. The recycling of water may increase the salinity of process water. Residual reagents may also be present in the recirculated water. It is thus important to mimic water recycling so as to investigate the effect that water recirculation and residual reagents will have on flotation performance. This work showed increases in the electrical conductivity of recirculated water suggesting an accumulation of ions in the recirculated water. This in turn resulted in an increase in the amount of water and solid particles reporting to the concentrate. Cu and Ni recoveries remained unchanged showing that the increase in solids recoveries was due to increases in gangue recovery which in turn led to a minimal decrease in the concentrate grades. Furthermore, there was an increase in residual xanthate and CMC with each recirculation.

Keywords: Coagulation, Electrolytes, Flotation, Polysaccharides, Water quality

Introduction
Flotation as a process through which valuable minerals are separated from non-valuable minerals uses water as a transport medium. With water being an essential part of the flotation process, it stands to reason that its quality or chemistry is of paramount importance in the concentration of Cu-Ni-Pt sulfide ores since interactions between reagents and solid particles in flotation pulps depend on the surface chemistry of the pulp phase. Given the high water usage in flotation circuits, water conservation efforts such as process water recirculation are being proposed. This however presents a challenge in that increased use of recycled water in flotation may effect the process owing to an accumulation of inorganic and organic species which may interfere with important aspects of flotation. These species may inadvertently activate gangue and thereby decreasing the grade of the concentrate (Rao and Finch, 1989). It is for this reason that flotation circuit optimisation efforts must consider the effect of water recirculation on the quality of water as well as the resulting effect on the selectivity of the process. These efforts should be targeted towards ensuring that optimal recoveries of the targeted minerals are achieved without the dilution of the concentrates. It is also reported that water recirculation may be advantageous in several aspects beyond just enhancing water use efficiency, but could potentially reduce operating costs and increase the profitability of the plant through a reduction in reagent dosing since recycled water may contain residual reagents such as collectors, depressants and frothers which are very important to flotation. This benefit may also arise from the fact that reagents such as frothers could be reduced in their dosages for as long as the water contains inorganic electrolytes enough to inhibit bubble coalescence and in turn yield the desired froth stability at lower or no frother dosages (Manono et al., 2018, 2012; Slatter et al., 2009). This action of inorganic electrolytes on the stability of the froth rises from the fact that recirculated water may contain high concentrations of divalent ions such as Ca²⁺, Mg²⁺ and SO₄²⁻ which are said to compress the electrical double layer and increase the efficiency of the particle-bubble attachment process by reducing the electrostatic repulsion between the bubble and particle (Liu et al., 2013). Not only can these divalent compress the electrical double layer, but they can favour the formation of
smaller stable bubbles, thereby increase the
bubble particle collision rate (Liu et al., 2013).
It is however said that despite the advantages
of using recycled water, there may well be
drawbacks in using recycled water in that if
there is no proper control of water quality
and reagents dosing, residual reagents and
excessive amounts of inorganic electrolytes
in recirculated water may cause overly stable
froths which may in turn reduce the selectivity
and result in decreased concentrate grades
(Slatter et al., 2009; Rao and Finch, 1989).
Furthermore recirculated water may contain
high concentrations of oxyhydroxyl species,
carbonate and sulphate precipitates. These
may coat the surface of the sulfide mineral
meant to be floatable and thereby hinder the
interaction of the collector with the mineral
surface (Bruckard et al., 2011; Ikumapayi et
al., 2010; Levay et al., 2001; Ma et al., 2009).
This in turn would decrease the sulfide
mineral recoveries.

Thus this study considered a bench scale
simulation of water recirculation in a sulfidic
Cu-Ni ore flotation. The study aimed at
investigating how long it would take for solids
in the tails to settle such that a supernatant
of recyclable quality can be obtained in
order to mimic and assess the recyclability of
water from the tailings ponds. The amounts
of residual depressant and collector present
in the recyclable liquid supernatant (water)
were also considered. Furthermore, the clear
supernatant was analysed for its inorganic
content present in the recycled water by
measuring the pH and electrical conductivity.
The effect of recirculation was examined on
key flotation measurable outputs, namely, the
recoveries and grades of valuable (Cu and Ni)
sulfide minerals.

**Methods**

For each test, 3 kg of a Merensky ore was
milled in a stainless-steel rod mill with the
water being investigated. Sodium isobutyl
xanthate (SIBX) was used as a collector and
added to the mill at a dosage of 150 g/ton as
is the general practice in most Cu-Ni-PGM
concentrators. Milling was performed such
that a grind of 60% passing 75 microns was
attained. The milled slurry was transferred
to an 8 L flotation cell, after which the relevant amount of water was added to the
cell such that the slurry contained 37.5%
solids. The impeller speed of the 8 L cell was
set to 1200 rpm. A feed sample of the slurry
was taken from the float cell after which
the slurry was conditioned with Depramin
267, a carboxymethyl cellulose (CMC) as a
depressant at a dosage of 300 g/t. This was
conditioned for 2 minutes after which DOW
200 was added as a frother at a dosage of 40
g/ton and allowed to condition for 1 minute.
After all reagents had been conditioned, an air
valve of the cell was opened to allow the froth
to develop and the air flowrate was maintained
at 12.9 L/min for all flotation tests conducted.
Four concentrates were collected at time 2, 6,
12 and 20 minutes by scraping the froth into
collection pans at 15 seconds interval. The
froth height in the cell was controlled and
maintained at 2 cm by topping up with water.
After each flotation test, two tailings samples
were taken. The water recovered in each of the
four concentrates was measured and recorded.
The four concentrates along with the feed
and tailings samples were filtered, dried in
the oven and weighed before they were sent
for further analysis. The water recovered
during the filtration of the concentrates was
discarded. The bulk of the tailings from the
flotation tests was filtered in the filter press
and the water recovered was recirculated in the
flotation system. A sample of the recirculated
water was taken for analysis to determine the
residual collector and depressant content in
the water. All flotation tests were conducted
in duplicates. The analysis of the Cu and Ni
content in the concentrate, feed and tails
samples was conducted using the Bruker
X-Ray Fluorescence (XRF) S4 Explorer
Spectrometer. For each of the concentrates, the
difference between the total mass of valuable
mineral (i.e. chalcopyrite and pentlandite)
and the total mass of the concentrates was
determined to be the mass of the gangue
minerals. To determine the inorganic content
present in the recycled water, a sample of the
clear supernatant obtained after the filtration
of the bulk tailings was analysed using an
electrical conductivity (EC) and pH meter
The EC and pH meter were used as proxies to
determine the ionic strength of the recyclable
plant water. To mimic and assess the
recyclability of water from the bulk tailings, a
settling time test was conducted to determine
the time it takes for the solids to settle such that a supernatant of recyclable quality can be obtained. To determine the settling time, a tailings sample was drawn from the float cell into a 250 mL conical flask. The sample was agitated using a plastic stirring rod; prior to the timing of the settling began. The settling time of the solids was determined once the solids had settled and solids surface became visibly stagnant. The settling time of the solids was determined after each run of the flotation tests for both the original test and the duplicate, to determine if the implication of ion accumulation after each recycle would have an effect on the solids settling time. Supernatant samples were taken after the filtration of the bulk tailings to analyse the residual xanthate collector in the recirculated water. The concentration of residual xanthate in the recirculated water was determined using a UV/Vis spectrometer. To determine the residual CMC depressant present in the recyclable water, a similar procedure to that of the determination of the residual collector was followed in accordance to the du Bois method (du Bois et al., 1956). The concentration of ions present in the fresh synthetic plant water (SPW) is shown in Table 1.

**Table 1** Concentration of ions present in the fresh synthetic plant water (SPW).

<table>
<thead>
<tr>
<th>Water type</th>
<th>Ca(^{2+}) (mg/L)</th>
<th>Mg(^{2+}) (mg/L)</th>
<th>Na(^+) (mg/L)</th>
<th>Cl (mg/L)</th>
<th>SO(_4^{2-}) (mg/L)</th>
<th>NO(_3^-) (mg/L)</th>
<th>NO(_2^-) (mg/L)</th>
<th>CO(_3^{2-}) (mg/L)</th>
<th>TDS mg/L</th>
<th>Ionic Strength [mol/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPW</td>
<td>240</td>
<td>210</td>
<td>459</td>
<td>861</td>
<td>720</td>
<td>528</td>
<td>-</td>
<td>51</td>
<td>3069</td>
<td>0.0727</td>
</tr>
</tbody>
</table>

**Figure 1** Total solids and water recovery using SPW and recirculated water.

Figure 1 illustrates the effect of water recirculation on the total amounts of water and solids recovered during the flotation of the selected Merensky ore. There is a general trend of an increase in solids and water recoveries as the water changes from fresh synthetic plant water to the 3rd recycle. This result could be due to an increase in the stability of the froth as the electrical conductivity and therefore ionic strength (IS) increased in the same order as shown in Figure 2. This trend is in line with previous findings which have shown that increases in IS stabilise the froth more, thereby resulting in increases water and solids recoveries. (Manono et al., 2018a)

Figure 2 shows the alkalinity and electrical conductivity of the fresh synthetic plant water and recirculated waters. It can be seen that as the number of recycles increases, the electrical conductivity of the water had a steady increase. The alkalinity of the water decreased with each recycle. These results suggest that the recirculation of water increased the amount of electrolytes in water. These are said to be in agreement with speculations made by previous authors and hence the premise of this work (Levay et al., 2001; Manono et al., 2018b; Muzenda, 2010; Rao and Finch, 1989; Slatter et al., 2009)

Figure 3 shows the residual SIBX collector present in the supernatant to be recycled after each flotation test. An increase in the residual collector is seen with each recirculation of process water. It is however clear that as the number of cycles increases, the change of
Figure 2 pH and Electrical Conductivity of SPW and recirculated water before flotation.

Figure 3 Residual concentration of SIBX in various waters after flotation.

Figure 4 Residual CMC present in various waters after flotation.

Figure 5 Settling time of solids in the tailings after flotation.
an increase in residual SIBX is lower than the 2 mg/L which remained after floating with fresh SPW in that the step change of an increase in SIBX concentration between SPW and Recycle 1, Recycle 1 and Recycle 2, and Recycle 2 and Recycle 3 is ≈0.6 mg/L on average. This may well imply that the interaction of the collector with the mineral surface in flotation is affected by the quality of the water used during flotation.

Figure 4 shows the concentration of the residual CMC present in each of the waters that were to be recycled from their flotation tails. A steady increase in the concentration of CMC in the recyclable supernatant is observed in that after floating with SPW as the water source, 9 mg/L of CMC remained in the tailings water and 31.4 mg/L CMC remained in the tailings water after flotation with Recycle 3.

Figure 5 illustrates the settling time of solids from the tails for the fresh synthetic plant water as well as the recycled waters after flotation. It can be seen that the settling time of solids decreased as the number of recycles increased. It is believed that the tails become more coagulated as the number of recycles increased owing to the reported increase in electrical conductivity as it has been shown that increases in the ionic strength of plant water results in increases in mineral particle coagulation especially when CMC is part of the system (Manono et al., 2018a).

Figure 6 shows the recovery and grade of Cu after floating with fresh synthetic plant water and recirculated water. It can be seen that Cu recovery in fresh SPW and recirculated waters was well within 80%. Both the 1st and 3rd recycled waters yielded the lowest Cu recovery (≈78%) whereas the fresh SPW and the 2nd recirculation of water yielded the highest Cu recoveries averaging 83%. The concentrate Cu grade showed a slight decrease with each recirculation though it may not be statistically significant as the difference was well below 0.5%.

Figure 7 shows the recovery and grade of Ni after floating with fresh synthetic plant water and recirculated water. Both the fresh SPW and 2nd recycled waters yielded the lowest Ni recovery (41% and 42% respectively) whereas the 1st recirculated water and the 3rd recirculation of water yielded the highest Ni recoveries (of 45% and 44% respectively). It is important to mention that this trend is the opposite of the Cu flotation recoveries. The concentrate Ni grade remained fairly constant regardless of water recirculation.

Figure 8 shows a trend of a slight increase in the amount of gangue reporting to the concentrate with each recirculation. This provides reasons for the slight decrease in mineral grades with recirculated water.

This investigation has shown that as the water is recirculated, the electrical conductivity (EC) increases. This can be ascribed to an accumulation of ions. This suggests that with each recirculation, the ionic strength of the water increased. Although the recirculation of water increased the amount of water recovered owing to an increase in froth stability, the solids recovered showed...
very slight increases. The slight increase in solids recovered is due to a very minimal increase in gangue recovery as seen in Figure 8. The recirculation of water did seem to have a strong effect on the recoveries and grades of Cu and Ni. The increase in gangue recovery between the initial and final run was very minimal to effect the concentrate grades and therefore proves that in the current study, water recirculation had little or no effect on flotation performance.

Conclusions
It was shown that recirculating water increased the electrical conductivity of the process water as well as the amount of residual reagents. However, there was no evidence of a negative influence on the recoveries and grades of Cu and Ni. The slight increase in solids recovery is a result of a little more gangue being entrained and recovered into the froth owing to a more stable froth. On the basis of the findings of this work, plant water recirculation may prove beneficial owing to increases in the inorganic electrolytes and residual reagents in the process water which seemed not to have affected flotation negatively.

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Figure 7 Nickel recovery and grade in fresh SPW and recirculated water.

Figure 8 The amount of gangue recovered in fresh SPW and recirculated water.
from the South African Minerals to Metals Research Institute (SAMMRI) and its members are also acknowledged.

**References**


Abstract
A two-step neutralization process is proposed to recover iron and copper separately. A new experiment equipment for continuous operation of this process was developed and manufactured. Three types of Acid Mine Drainages (AMD), which are most environmentally influential in Bor copper mine area in Serbia, were selected for the experiment. They were supplied for the experiment without any pre-treatment. Approximately 1.8 cubic meters of AMD for each type was treated by 5L/min by the new equipment using industrial hydrated lime. As a result, it was confirmed the proposed process is effective for AMD treatment and metal recovery. Iron and copper were recovered in the sludge separately.

Keywords: AMD, neutralization, metal recovery, copper mine, pH control

Introduction
Acid Mine Drainage (AMD) treatment is a serious matter for mining industry especially the case of abandoned or long-time operating mines. The cost for such treatment is perpetually incurred by the industry or the public sector. It is a heavy burden to them for long time. Metal recovery processes for AMD have been proposed in previous researches (e.g. Mongi et al., 2007, Masud et al. 2008, Macingova & Luptakova 2012), however the process should be simple and practical to apply for real situation. This research purpose is to confirm the possibility to recover iron and copper separately by simple and practical process to mitigate the treatment cost by metal recycling benefit.

In Bor area in Serbia, all of the waste water from the mine area is flowing out to natural environment without any treatment now. Bor mining complex is located 230km south-east of Beograd, Serbia. The mine drainage water in the area is released to the downstream without any treatment through tributaries of Danube River. It is suggested that the mine drainage water in Bor mining area gives environmental impact to the river water of Danube River (UNEP 2002).

There are two major mines and copper smelter/refinery in the area. The Bor underground mine has a history of more than 100 years, and Bor open-pit mining opened in 1923. The total amount of ore mined from the open-pit was approximately 100 million tons with the waste of approximately 170 million tons. There are other mines which are the Veliki Krivelj open-pit mine and the Cerovo open-pit mine. Waste rocks, low grade ores and flotation tailings are left in surrounding areas, and causing environmental problems. The mining influenced water including waste water from the copper smelter and refinery plant flow into Krivelj and Bor Rivers, then down to Danube. Not only the Serbian government and municipal people but also international organizations have strong concern to such environmental situation (JICA 2008, Stojadinovic et al. 2011).

Previous research conducted between 2011 and 2013, financed by Japan International Cooperation Agency (JICA) and Japan Society for the Promotion of Science (JSPS), showed that the environmental impacts to the river water of River Danube caused by the mine drainage and various mine wastes are not clear. However, serious environmental impacts
were recognized in Bor mining area to the downstream basin by 30 km along Bela River (Masuda et al. 2017, Masuda et al. 2016). There exist flotation tailings, waste rocks and AMD with relatively high content of copper in the mine area (Masuda et al. 2012).

Experiment

Experiment equipment

Figure 1 shows the process diagram of the Two-Step Neutralization Experiment Equipment. It was installed in the storage house in Mining and Metallurgical Institute Bor, Serbia in 2016. The equipment is separable to 5 units and transportable by a small track to settle and use at any AMD site.

The pH is controlled by Proportional-Integral-Differential Controller (PID). The pH meters are installed at outlet points of each pH control tank. PID calculates and controls each tank’s pH by adjusting each Lime Slurry Pumps automatically to the set up values on the 1st and 2nd steps. Operator can set up the pH values by PID prior to or during the experiment. The pH data is indicated on the display in front of the controller and recorded on SD memory card.

Waste water is fed to the Waste Water Tank at first and pumped up to the pH control tank A in the 1st step, then mixed with the neutralizer from the Lime Slurry Tank. From this point, the waste water flows down to the end of the process, which is the outlet of the Thickener B of the 2nd step, by gravity. It is continuously running down to this point. After the 1st step consists of the pH Control Tank A, the Flocculation Tank A and the Thickener (A) follows by the 2nd step consists of the pH Control Tank B, the Flocculation Tank B and the Thickener (B). Agitators to mix the tanks are attached to each pH Control Tanks and Flocculation Tanks to mix the reagent with the waste water. Sludge is precipitated in the bottom of the Thickener A and B incrementally during the experiment. Precipitated sludge can be discharged by manually using the pump and fed to the Filter Press for dewatering. The flow rate capacity of the equipment is from two to five litter pre minutes (2-5L/min.)

Figure 2 is a picture of the equipment installed in the storage house. A new experiment equipment was developed and manufactured in Japan. It was shipped from Japan to Serbia and installed in a storage house of 9.5m x 4.5m space area in MMI-Bor.

Figure 1 Two step neutralization process diagram
Experiment method

Based on samplings and chemical analysis of various AMD in Bor area, three AMD sites, which are more influential to the environment, were selected for the experiment to confirm the effectiveness of AMD treatment to improve the river environment and the possibility to recover the metals contained in the AMD. Figure 3-A shows the effluent water from overburden dump site of open-pit operation named “Saraka Stream”. Figure 3-B shows waste water from underground mining operation named “Underground Waste Water. Figure 3-C shows the seepage water from mixture of mine waste materials named “Robule Lake”.

Industrial hydrated lime (Ca(OH)₂) was used for the neutralizer, which is produced a local lime stone mine. ACCOFLOC@ A-95, which is produced in Japan and imported to Serbia, was used for flocculation in both steps. Lime milk density is 2.5% and flocculant density is 0.05%.

Figure 3-D shows sampling for the experiment. AMD of each site was pumped up to two plastic containers just before the experiment starts to avoid chemical changes by oxidation and transported by truck to the storage house installed the experiment equipment. Approximately 1.8 m³ AMD samples for each three sites were used for the experiments. Flow rate of the experiment was set at 5.0L/min. It took approximately 6 hours for each experiment. pH was set 4.0 at the 1st step and 7.0 at the 2nd step by PID.
Results

Results of the chemical analysis of each AMD is shown in Table 1. It is understandable that the water color of P-2 is pale greenish as Figure 3 shows. It is because of pH 4.6 which is relatively high. Besides, iron and aluminum content is very low compared to others. Details should be investigated more, however, it is thought that as the original AMD comes down by mixing with a river water through lime stone area, most of the iron and aluminum in the original AMD was removed along the stream. It can be said that P-3 and P-11 is almost same low pH value and higher content Cu and Fe. Mn should be noticed for all three AMD.

Results of the chemical analysis of Cu, Fe-total, Mn, As, Co and Ni of processed water and removal rate of metals of P-2 sample is shown in Table 2, results of P-3 sample is shown in Table 3, and results of P-11 sample is shown in Table 4. In case of P-2, only one step at pH 7.0 is applied, because the pH of P-2 is more than 4.0.

These results show that Fe and Cu can be removed separately by controlling pH at 4.0 and 7.0. Co and Ni behavior is similar to Cu behavior. It was not removed much at pH 4.0 but most of them are removed at pH 7.0. It is understandable considering the solubility product of these metals, and some amount of adsorption and/or precipitation phenomenon together with Fe sludge precipitation.

In case of Mn, removal rate at pH 7.0 are relatively low, such as 65.2% in P-2, 83.6% in P-3, 57.5% in P-11. At the 2nd step Cu, Total Fe-total and As are less than the limit value of the standard in both Serbia and Japan. However, it is necessary to lower the content of Mn to meet the effluent standard or limit value of water quality of Serbia.

Metal contents in the sludge generated by neutralization process of P-2, P-3 and P-11 are shown in Table 5, Table 6 and Table 7 respectively. Sludge was dried in Convection Ovens at temperature 40+ degree centigrade and analyzed by ICPAES for Cu, Fe, Mn, and by ICPMS for As, Co, Ni. These results suggest that Cu, Co and Ni in AMD can possibly recoverable in the sludge separately from Fe concentrated sludge generated by controlling pH conditions. The highest Cu content in the generated sludge was 7.8% at pH 7 from 75.11mg/L Cu contained AMD with comparably high content of Cobalt and Nickel. Highest Fe content in the sludge was 33.5% at pH 4 from 391.2mg/L Fe contained AMD. As behavior is more concordant with Fe.

Conclusions

The experiment results suggest that the two-step pH control neutralization and precipitation method is effective and practical to recover iron and copper separately in the sludge generated along the process and is reliable in processing the water quality to the required levels.

Sludge recovered from three AMD samples at pH 7 contains at least 1% copper with some amount of molybdenum and nickel. It is possibly recyclable considering that average Cu grade of the ore produced in this area is less than 0.5%.

The experiment equipment, which was developed this time, is useful to carry out researches to know the relationship between metal contents in sludge and AMD characteristics in a practical way.

It should be considered more whether this process will be practical and metal recycling from the sludge is economical.

Acknowledgements

This research is carried out as a part of the project titled “Research on the integration system of spatial environment analyses and advanced metal recovery to ensure sustainable resource development” planned from 2015 to 2019, conducted by Akita University, Japan Space System and Mitsui Mineral Development Engineering Co., Ltd. together with the Mining and Metallurgy Institute of Bor, funded by JST (Japan Science and Technology Agency) and JICA (Japan International Cooperative Agency).

Authors appreciate the researchers and technicians in the Mining and Metallurgy Bor for their supportive works on sampling, analysis and various kinds of experiments done in the field and the Institute.

References

H.Mongi, C.Kosaka, S.Matsumoto, Y.Hosoi
## Table 1: Chemical analysis of AMD samples at P-2, P-3, P-11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Cu (mg/L)</th>
<th>Fe-total (mg/L)</th>
<th>Mn (µg/L)</th>
<th>As (µg/L)</th>
<th>Co (µg/L)</th>
<th>Ni (µg/L)</th>
<th>Pb (µg/L)</th>
<th>Zn (µg/L)</th>
<th>Cd (µg/L)</th>
<th>Al (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-2</td>
<td>4.60</td>
<td>75.1</td>
<td>0.3</td>
<td>16.8</td>
<td>3.3</td>
<td>1121.1</td>
<td>280.1</td>
<td>0.2</td>
<td>3.5</td>
<td>21.6</td>
<td>71.0</td>
<td>529.7</td>
<td>226.2</td>
</tr>
<tr>
<td>P-3</td>
<td>2.67</td>
<td>187.1</td>
<td>506.6</td>
<td>20.5</td>
<td>290.1</td>
<td>654.0</td>
<td>1530.7</td>
<td>3.7</td>
<td>8.6</td>
<td>8.6</td>
<td>8.6</td>
<td>328.5</td>
<td>435.1</td>
</tr>
<tr>
<td>P-11</td>
<td>2.84</td>
<td>38.3</td>
<td>391.2</td>
<td>69.2</td>
<td>9.8</td>
<td>865.3</td>
<td>427.5</td>
<td>&lt;2.1</td>
<td>14.0</td>
<td>44.8</td>
<td>200.3</td>
<td>407.6</td>
<td>853.6</td>
</tr>
</tbody>
</table>

ICP AES ICP ICP ICP ICP ICP ICP ICP ICP ICP ICP ICP ICP

## Table 2: Chemical analysis of processed water and removal rate of metals of P-2 sample, and the Limit value of Serbia and Effluent standard in Japan.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (mg/L)</th>
<th>Fe-total (mg/L)</th>
<th>Mn (µg/L)</th>
<th>As (µg/L)</th>
<th>Co (µg/L)</th>
<th>Ni (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start pH 4.6</td>
<td>75.1</td>
<td>0.26</td>
<td>16.77</td>
<td>3.30</td>
<td>1121.1</td>
<td>280.1</td>
</tr>
<tr>
<td>1st step (pH 7)</td>
<td>0.21</td>
<td>0.07</td>
<td>5.83</td>
<td>&lt;1.0</td>
<td>100.50</td>
<td>49.20</td>
</tr>
<tr>
<td>Removal rate at 1st step (%)</td>
<td>99.7</td>
<td>75.3</td>
<td>65.2</td>
<td>100</td>
<td>91.0</td>
<td>82.4</td>
</tr>
<tr>
<td>Limit Value (Class V)-Serbia</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>100.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effluent standard - Japan</td>
<td>3.0</td>
<td>10.0</td>
<td>10.0</td>
<td>100.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Table 3: Chemical analysis of processed water and removal rate of metals of P-3 sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (mg/L)</th>
<th>Fe-total (mg/L)</th>
<th>Mn (µg/L)</th>
<th>As (µg/L)</th>
<th>Co (µg/L)</th>
<th>Ni (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start pH 2.67</td>
<td>187.07</td>
<td>506.58</td>
<td>20.46</td>
<td>0.29</td>
<td>653.97</td>
<td>1530.70</td>
</tr>
<tr>
<td>1st step (pH 4)</td>
<td>180.57</td>
<td>97.95</td>
<td>22.28</td>
<td>0.01</td>
<td>632.23</td>
<td>1363.30</td>
</tr>
<tr>
<td>2nd step (pH 7)</td>
<td>0.30</td>
<td>0.19</td>
<td>11.37</td>
<td>0.00</td>
<td>42.57</td>
<td>91.46</td>
</tr>
<tr>
<td>Removal rate at 1st step (%)</td>
<td>3.5</td>
<td>80.7</td>
<td>-8.9</td>
<td>96.9</td>
<td>3.3</td>
<td>10.9</td>
</tr>
<tr>
<td>Removal rate at 2nd step (%)</td>
<td>99.2</td>
<td>100.0</td>
<td>83.6</td>
<td>100.0</td>
<td>95.1</td>
<td>78.6</td>
</tr>
</tbody>
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## Table 4: Chemical analysis of processed water and removal rate of metals of P-11 sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (mg/L)</th>
<th>Fe-total (mg/L)</th>
<th>Mn (µg/L)</th>
<th>As (µg/L)</th>
<th>Co (µg/L)</th>
<th>Ni (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start pH 2.84</td>
<td>38.3</td>
<td>391.2</td>
<td>69.2</td>
<td>9.8</td>
<td>865.3</td>
<td>427.5</td>
</tr>
<tr>
<td>1st step (pH 4)</td>
<td>40.3</td>
<td>8.3</td>
<td>74.2</td>
<td>&lt;2.1</td>
<td>909.0</td>
<td>428.4</td>
</tr>
<tr>
<td>2nd step (pH 7)</td>
<td>0.31</td>
<td>0.044</td>
<td>29.4</td>
<td>&lt;2.1</td>
<td>134.1</td>
<td>79.1</td>
</tr>
<tr>
<td>Removal rate at 1st step (%)</td>
<td>-5.2</td>
<td>97.9</td>
<td>-7.3</td>
<td>100</td>
<td>-5.1</td>
<td>-0.2</td>
</tr>
<tr>
<td>Removal rate at 2nd step (%)</td>
<td>99.2</td>
<td>100.0</td>
<td>57.5</td>
<td>100</td>
<td>84.5</td>
<td>81.5</td>
</tr>
</tbody>
</table>

## Table 5: Metal contents in the sludge generated by neutralization process of P-2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Mn (%)</th>
<th>As (ppm)</th>
<th>Co (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7.0</td>
<td>7.8</td>
<td>3</td>
<td>0.76</td>
<td>6.4</td>
<td>628.8</td>
</tr>
</tbody>
</table>

## Table 6: Metal contents in the sludge generated by neutralization process of P-3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Mn (%)</th>
<th>As (ppm)</th>
<th>Co (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4.0 (3.8)</td>
<td>0.41</td>
<td>22.43</td>
<td>0.01</td>
<td>131.26</td>
<td>12.57</td>
</tr>
<tr>
<td>pH 7.0 (7.0)</td>
<td>3.89</td>
<td>3.55</td>
<td>0.44</td>
<td>5.97</td>
<td>186.38</td>
</tr>
</tbody>
</table>

## Table 7: Metal contents in the sludge generated by neutralization process of P-11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Mn (%)</th>
<th>As (ppm)</th>
<th>Co (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4.0 (3.8)</td>
<td>0.15</td>
<td>33.52</td>
<td>0.26</td>
<td>24.44</td>
<td>8.85</td>
</tr>
<tr>
<td>pH 7.0 (7.0)</td>
<td>1.24</td>
<td>0.47</td>
<td>1.67</td>
<td>14.50</td>
<td>373.55</td>
</tr>
</tbody>
</table>

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The Recovery Of Pd(II), Ir(III) And Rh(III) From Aqueous Solutions With Yeast-functionalised Zeolite

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Abstract

Wastewaters from platinum group metals (PGMs) processing plants can contain substantial amounts of metals including the very PGMs. The recovery of such metals from wastewaters can be of great value especially due to recent declines in commodity prices. The recovery of Pd(II), Ir(III) and Rh(III) by zeolite functionalised with spent yeast waste was studied and the effect of adsorbent dosage, pH, initial concentration, contact time and competing ions was determined. The significant recovery of Pd(II) and Ir(III) was achieved at pH 2, 2 mg L\(^{-1}\) and 10 g L\(^{-1}\) adsorbent dosage. The adsorption capacity of Rh(III) increased with pH whilst that of Pd(II) and Ir(III) decreased. The presence of competing ions led to an increase in adsorption capacity due to an adsorbent-Fe-analyte synergistic effect. The adsorbent is suitable for significant recovery of Pd(II), Ir(III) and Rh(III) from PGMs wastewater.

Keywords: adsorption capacity, platinum group metals, spent yeast, wastewater

Introduction

The readily increasing costs of platinum group metals (PGMs) and declining ore grades have been eroding the economic viability of PGMs mines around the world. As a result, some mining plants have closed whilst others are still facing closure. During the processing of minerals, large amount of wastewater is released into the environment and some studies have reported that it may contain traces of valuable minerals such as PGMs (Mosai et al., 2019). Since these metals are in very low concentrations, the current methods used for mining cannot be used to recover the lost minerals hence, a need for cheaper and more efficient methods for recovery. Zeolites are negatively charged aluminium-silicate clay minerals which have micro and mesopores located by water molecules and cations such as Ca\(^{2+}\) and Mg\(^{2+}\) (Guaya et al., 2015). Zeolites are readily available in different parts of the world and have been used as natural adsorbents for the removal of metals from wastewaters (Yuna, 2016). Other studies have indicated the efficiency of zeolite can be improved through functionalisation with ligands that have high affinity for target metals (Simsek et al., 2013; Bakatula et al., 2015).

In this study, the zeolite clay mineral was functionalised with spent brewer’s yeast waste and used to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions. Thus, this study seeks to come up with a very attractive and cheap material for the recovery of precious metals.

Materials and methods

Chemicals

The chemicals used were of analytical reagent grade and were purchased from Sigma Aldrich, South Africa. The 10 mg L\(^{-1}\) stock solution containing Pd(II), Ir(III) and Rh(III) was prepared and preserved with concentrated nitric acid. Working solutions were prepared daily from the stock solution which was stored in the refrigerator at 4°C when not used. The 0.01 mol L\(^{-1}\) HCl and NaOH were used to adjust the pH of the working solutions. The spent yeast waste was collected from the Wits Microbrewery, Johannesburg, South Africa using polypropylene plastic containers.

Functionalisation of zeolite with yeast

The collected yeast waste (40 mL) was added to 2 g zeolite in a 100 mL polypropylene bottle and mixed for 24 h using an elliptical
bench-top shaker at 25°C. The contents were filtered using suction and the unbound yeast was removed by shaking the functionalised zeolite for 5 min with deionised water. The contents were filtered again and the zeolite was dried at 25°C for 24 h.

**Characterisation**

The natural zeolite used was characterised with powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany) to determine the mineralogy of the adsorbent and X-ray fluorescence (XRF) (PAnalytical, Netherlands) for chemical composition. The functional groups of the natural and functionalised zeolite were determined using Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany). The amount of C, H and N on the natural and functionalised zeolite was determined using varioELcube V4.0.13 (Elementar, Germany). The surface area, pore size and pore volume were determined using TriStar 3000 V6.05A (Micrometrics, USA).

**Batch adsorption studies**

Batch studies were conducted to determine the effect of pH (2-9), initial concentration (0.5-10 mg L\(^{-1}\)), adsorbent dosage (5-50 g L\(^{-1}\)), contact time (0-540 min) and competing ions (Pt, Ru, Os, Hf, Au, Fe, Co, Ni, Ca, Mg, K and Zn) on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite. The raw zeolite was also used at the same conditions and the adsorption was not significant (p>0.05). The metals in the above conditions were shaken with the adsorbent to attain equilibrium and filtered. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany) was used to determine the concentration of the metals. The equilibrium adsorption capacity (qe (µg g\(^{-1}\))) and adsorption efficiency of the metals recovered by yeast-functionalised zeolite were determined using Eq. 1 and 2, respectively:

\[
q_e = \frac{(C_0 - C_e)}{M} \times 1000 \quad (1)
\]

\[
\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)
\]

where \(C_0\) and \(C_e\) (mg L\(^{-1}\)) are the initial and equilibrium concentrations of the metals, respectively, \(V\) (L) is the volume of the solution and \(M\) (g) is the mass of the yeast-functionalised zeolite.

**Data treatment**

**Adsorption isotherms**

The type of adsorption between the metals and yeast-functionalised zeolite was determined using the Langmuir, Freundlich and Dubinin-Radushkevitch (D-R) adsorption isotherms. The Langmuir isotherm describes the monolayer adsorption of metals onto a homogeneous surface with a fixed number of active sites. The assumption for this isotherm is that the active sites have equal adsorption energies (Latour, 2015). The Langmuir isotherm can be expressed as:

\[
\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \left( \frac{1}{K_L q_m} \right) \quad (3)
\]

where \(q_m\) (mg g\(^{-1}\)) is the maximum monolayer coverage and \(K_L\) (L mol\(^{-1}\)) is the Langmuir isotherm constant. The affinity of the metals for the adsorbent was determined using the separation factor (\(R_L\)) which can be determined from the Langmuir constant (\(K_L\)). The affinity can be expressed as favourable (0>\(R_L\) < 1), unfavourable (\(R_L\) >1), linear adsorption (\(R_L\) = 1) and irreversible adsorption (\(R_L\) = 0). The \(R_L\) is expressed as:

\[
R_L = \frac{1}{1 + C_0 K_L} \quad (4)
\]

The Freundlich isotherm model describes the adsorption of metals onto a heterogeneous surface where the active sites are assumed to have different energies (Bakatula et al., 2015). The Freundlich isotherm can be expressed as:

\[
q_e = K_f C_e^{1/n} \quad (5)
\]

where \(K_f\) ((mg g\(^{-1}\))/mol L\(^{1/n}\)) is Freundlich isotherm constant and \(n\) is adsorption intensity.

The Dubinin-Radushkevich (D-R) model is used to describe the adsorption between metals and adsorbents onto a heterogeneous surface with Gaussian energy distribution (Chen, 2015). The D-R model equation is as follows:

\[
\ln q_e = \ln X_m - K_D R e^2 \quad (6)
\]
where $X_m$ is theoretical isotherm saturation capacity (mg g$^{-1}$), $K_{DR}$ is the Dubinin-Radushkevich isotherm constant (mol$^2$ (kJ$^2$)$^{-1}$), $\varepsilon$ is the Polanyi constant which can be expressed as:

$$\varepsilon = R T \ln \left( 1 + \frac{1}{C_e} \right)$$  \hspace{1cm} (7)

where $R$ is the universal gas constant (J (mol K)$^{-1}$) and $T$ is temperature (K). The mean free energy of adsorption ($E_s$) can be calculated from $K_{DR}$ as shown in Eq. 8.

$$E_s = \frac{1}{\sqrt{2K_{DR}}}$$  \hspace{1cm} (8)

**Kinetics study**

The adsorption controlling mechanism between the metals and the adsorbent was determined using pseudo first- and second-order kinetic models. The pseudo first-order model has used to describe the rate of adsorption that is controlled by the rate of surface reaction in which case, the transition of metals from free to adsorbed state is considered (Rudzinski and Plazinski 2007). The pseudo second-order model is used to describe a reaction where the adsorption reaction on the surface of adsorbent is the rate-controlling step (Liu, 2008). The pseudo first and second-order kinetic models can be expressed by Eq. 9 and 10, respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (9)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (10)

where $q_t$ is the adsorbed amount (mg g$^{-1}$) at time $t$, $q_e$ is the adsorbed amounts (mg g$^{-1}$) at equilibrium and $k_1$ is the pseudo first-order rate constant (min$^{-1}$), $k_2$ is the pseudo second-order rate constant (g mg$^{-1}$ min$^{-1}$) and $k_2 q_e^2$ is the initial adsorption rate.

**Results and discussion**

**Characterisation**

The PXRD results showed that the dominant minerals of the zeolite were clinoptilolite ($(Na,K,Ca)_{2-3}\text{Al}_{1-3}\text{Si}_{2-4}\text{O}_{13}\cdot12\text{H}_2\text{O}$), quartz (SiO$_2$) and sanidine (KAlSi$_3$O$_8$). The results from XRF indicated that the zeolite was mostly composed of silica (SiO$_2$) (68.5%) and alumina (Al$_2$O$_3$) (11.6%). Since the yeast waste contains high amounts of amino acids, the possible interaction was through the oxides of the zeolite and these amino acids. The FTIR spectra of the natural and functionalised zeolite indicated that the functionalisation was successful since, there were N-H and C-N bands at 1535 and 1637 cm$^{-1}$, respectively on the functionalised adsorbent, indicative of the amino acid groups in the yeast. Due to the smothering of the zeolite pores by the spent yeast, the surface area and pore volume of the adsorbent decreased whilst the pore size increased. The amount of C, H and N increased after functionalisation due to high amount of amino acids.

**Effect of adsorbent dosage**

The effect of adsorbent dosage on the adsorption of Pd(II), Ir(III) and Rh(III) at pH 2 by yeast-functionalised zeolite was studied and the results are presented in Fig. 1. The adsorption capacity of the metals decreased as the dosage increased but, the adsorption efficiency increased with dosage due to increased amount of binding sites. The Pd(II) adsorption capacity was higher than that of Ir(III) and Rh(III) thus, the yeast functional groups on zeolite had high affinity for Pd(II) at pH 2. The adsorption efficiencies of Pd(II) were in the range of 69-91% as the dosage increased from 50 to 500 mg. The adsorption efficiencies of Ir(III) were found to be 33, 54, 59, 62 and 61% at 50, 100, 200, 300 and 500 mg of yeast-functionalised zeolite, respectively and those of Rh were found to be 17, 25, 35, 39 and 61%, respectively. The lower adsorption efficiencies of Ir(III) and Rh(III) can be attributed to high oxidation states and high atomic and ionic radii of the metals thus, only a few could be taken up by the active sites. The recovery of the metals with yeast-functionalised zeolite was in the order: Pd(II) $> \text{Ir(III)} > \text{Rh(III)}$.

**Effect of pH**

The effect of pH on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was studied and the results (Fig. 2) indicated that the adsorption capacity of Pd(II) and Ir(III) decreased as pH increased due to the change of species and adsorbent surface. At lower pH, the metals
exist as $\text{PdCl}_6^{4-}$ and $\text{IrCl}_6^{3-}$ due to high HCl concentration which was used to adjust the pH. The platinum mining wastewater has high concentration of HCl which is used during processing and thus, the metals exist in their chloride species (Mosai et al., 2019). Since these species are negatively charged, they will interact electrostatically with the positively charged surface which is due to high concentration of hydronium ions ($\text{H}_3\text{O}^+$). Thus at highly acidic regions, the amino acids will be positively charged and interact strongly with negatively charged species. The adsorption capacity of Pd(II) and Ir(III) decreased as pH was increased due to repulsions of the negatively charged hydroxide species and the negatively charged surface. However, the adsorption of Rh(III) increased with pH. A study by Labib et al. (2018) indicated that at higher pH, Rh(III) forms aqua/chloro complexes ([RhCl$_2$(H$_2$O)$_4$]$^+$ and [RhCl(H$_2$O)$_5$]$_2^+$) which are positively charged and would electrostatically interact with the negatively charged surface. Thus, to substantially recover Rh(III) from wastewater, pH should be adjusted.

**Effect of initial concentration**

The effect of initial concentration on the adsorption of Pd(II), Ir(III) and Rh(III) by the adsorbent at pH 2 was studied and the results are shown in Fig. 3. The adsorption capacity of Pd(II) increased with concentration from 0.5 to 10 mg L$^{-1}$ due to favourable adsorption. The adsorption capacity of Ir(III) and Rh(III) however, increased up to 2 mg L$^{-1}$ and remained fairly the same beyond this. This can be attributed to the limited binding sites for these metals which are swiftly occupied hence, no further increase in adsorption was observed. The adsorption efficiencies of Pd(II) were found to be 83, 83, 81, 74 and 64% at 0.5, 1, 2, 5 and 10 mg L$^{-1}$, respectively. The adsorption efficiencies for Ir(III) and Rh(III) were less than 25% beyond 2 mg L$^{-1}$.

The type of adsorption occurring between the metals and yeast-functionalised zeolite was determined using adsorption isotherms and the data is presented in Table 1. The correlation coefficients ($R^2$) were high for Langmuir isotherm, indicating that the adsorption of the metals to the adsorbent was through monolayer adsorption. The metals were removed from aqueous solutions through the metal-N interaction since, studies have indicated that PGEs have strong interactions with nitrogen (Mosai et al., 2019). The maximum adsorption coverage ($q_m$) of Pd(II) onto the adsorbent was higher than for Ir(III) and Rh(III) which can be attributed to high affinity of the active sites for Pd(II) hence, the adsorption capacity has been higher than that of the other metals. The correlation coefficients for Pd(II) were $>0.99$ for all isotherms, meaning that there is also a possibility of adsorption on different adsorption sites or different adsorption mechanisms leading to a heterogeneous adsorption. The mean adsorption energy (Es) of Pd(II) determined from D-R isotherm was 10.12 kJ mol$^{-1}$ meaning that the interaction with the adsorbent was through chemical ion exchange. The energies of Ir(III) and Rh(III) were greater than 16 kJ mol$^{-1}$ indicating that their interaction was possibly chemisorptive in nature (Youssef et al., 2008).
**Effect of contact time**

The effect of contact time indicated that there is at first a fast rate of adsorption of the metals which was observed within 10 min (Fig. 4). Beyond 90 min, the increase in adsorption of the metals was insignificant. Even though the adsorption of the metals was substantial within 90 min, a contact time of 6 h was selected for this study to obtain the maximum adsorption. The contact time data was used to fit in the kinetic models and determine the adsorption controlling mechanism. The results in Table 2 showed that pseudo second-order described the data better since the correlation coefficient \( R^2 \) was > 0.99 for all the metals, indicating that the interaction of the metals with the adsorbent is strong (Mosai et al., 2019). To further confirm that the data was better described by pseudo second-order, the experimental adsorption capacity \( (q_{exp}) \) was close to the pseudo second-order calculated adsorption capacity \( (q_{c}) \) of the metals. When the adsorption is described by pseudo second-order, the interaction between the metals and the adsorbent is so strong that the detachment of the metals is unlikely to happen, which is a good attribute of the adsorbent especially when it is handled from mining or waste sites.

**Competing ions**

The effect of competing ions on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was studied since, mining wastewaters contain substantial amounts of other metals. The results from this study give an indication of how the adsorbent will behave in real wastewater. The results (Fig. 5) showed that the adsorption capacity of the analytes increased in the presence of other ions and this can be attributed to the possible synergistic interaction of the analytes with other metals such as iron thus, leading to adsorbent-Fe-analyte interaction (Mosai et al., 2019). The percentage increments in adsorption were found to be 14, 27, 58% for Pd(II), Ir(III) and Rh(III), respectively. Other PGEs (Pt, Ru and Os) were substantially removed from the aqueous solutions which is a good attribute of the adsorbent. Thus, in the presence of metals such as Fe, there is a possibility of multilayer adsorption where the Fe is directly connected to the adsorbent and form bonds with the analytes. The ability of the adsorbent to remove metals such as (K, Ni, Co and Zn) means that the yeast-functionalised zeolite has dual efficacy and that is recovering precious metals whilst removing contaminants from wastewaters.

**Table 1 Adsorption isotherm parameters for the adsorption of metals by yeast-functionalised zeolite**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Dubinin-Radushkevich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q^* ) (mg g(^{-1}))</td>
<td>( K_L ) (L mol(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>0.99</td>
<td>53960</td>
<td>0.99</td>
</tr>
<tr>
<td>Ir(III)</td>
<td>0.15</td>
<td>1.10x10(^2)</td>
<td>0.99</td>
</tr>
<tr>
<td>Rh(III)</td>
<td>0.052</td>
<td>2.75x10(^0)</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Table 2 kinetic models parameters for the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite

<table>
<thead>
<tr>
<th>Metal</th>
<th>qe (exp) mg g⁻¹</th>
<th>k1 min⁻¹</th>
<th>qe (exp) mg g⁻¹</th>
<th>R²</th>
<th>k2 g mg⁻¹ min⁻¹</th>
<th>qe (exp) mg g⁻¹</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)</td>
<td>0.20</td>
<td>4.10</td>
<td>0.12</td>
<td>0.75</td>
<td>2.93</td>
<td>0.17</td>
<td>0.99</td>
</tr>
<tr>
<td>Ir(III)</td>
<td>0.080</td>
<td>1.98</td>
<td>0.17</td>
<td>0.81</td>
<td>4.13</td>
<td>0.12</td>
<td>0.99</td>
</tr>
<tr>
<td>Rh(III)</td>
<td>0.051</td>
<td>0.61</td>
<td>0.18</td>
<td>0.78</td>
<td>1.65</td>
<td>0.050</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**Conclusion**

The ability of zeolite functionalised with yeast waste to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions was studied. The results obtained were compared to those of the raw zeolite and the results were significantly different. The raw zeolite poorly adsorbed the metals but, there was a substantial change when the functionalised zeolite was used. The adsorbent was highly efficient at 2 mg L⁻¹ and a dosage of 10 g L⁻¹. The adsorbent will substantially recover Pd(II) and Ir(III) at highly acidic pH regions but the adsorption of Rh(III) will be more efficient at less acidic pH regions due to the formation of aqua/chloro complexes which are positively charged. The adsorption capacity of Pd(II) was highly preferred more than other metals due to the ability to adsorb onto different active sites of the adsorbent since, both Langmuir and Freundlich described the adsorption data well. The adsorption mechanism of all the analytes was best described by pseudo second-order kinetic model meaning that the interaction of the metals was strong due to chemical adsorption. The adsorption capacities of the analytes increased in the presence of other ions due to adsorbent-Fe-metal synergistic interaction. Desorption studies were not conducted since, the used adsorbent can be processed along with the new ore and thus, no extra chemicals required for recovery. Hence, this will be a very cheap process.

**Acknowledgements**

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Abstract

Although mine water could be useful, Aquamines Limited has pumped it out and discharged it. This study sought to establish the factors that have prevented the company from adopting mine water treatment technologies. A personal interview was used to collect cross-sectional data. The questions asked focused on knowledge, demand and institutions as influencers of adoption. It found out that the miner is not aware of such technologies and has not put any effort into seeking information about them. This study recommends the creation of awareness of the need to conduct mine water baseline surveys and acting on the results.

Keywords: Influencers of Adoption, Mine Water, Treatment Technologies

Influencers of Adoption of Mine Water Treatment Technologies in Taita Taveta County, Kenya – A Case of Aquamines Ltd

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Introduction

Water is necessary for the survival of the human race (Oki & Kanae, 2006). Human beings discharge water waste into the environment after utilising water for consumption and execution of socioeconomic activities (Scott, Daly, Hejazi, Kyle, Liu, McJeon, & Voisin, 2016). Scott et al. (2016) further advance that climate change will negatively affect the predictability of water supply. It is therefore paramount for man to properly harness water and seek alternative founts for the same. Kandiah, Binder and Berglund (2017) posit that reuse of water might be a substitute source of water that is sustainable. According to the Resolution adopted by the General Assembly of United Nations in 2015, Goal Six of the Sustainable Development Goals seeks to ensure availability and sustainable management of water and sanitation for all. It further underscores the need for international cooperation to encourage water efficiency and support for treatment technologies in developing countries.

Mine water could be advantageous or disadvantageous to the stakeholders of the areas where it is encountered during excavation. With the advent of mine water treatment technologies, it is natural to expect that all water found in mines is used to profit the mining company, community and the environment amongst others. While this may be the norm for Western and some African countries like South Africa, it is not the same for Kenya. Since 1974, Aquamines Limited, which mines Ruby and Tourmaline gemstones, has pumped out the water that it encountered underground and discharged it for fear that it is contaminated and that there isn’t a way of treating it. Thus, the question that begs is whether companies such as these are aware of existing mine water treatment technologies.

There exist several water treatment technologies. Adams, Anderson, Bless, Butler, Conway, Dailey & Hanley (2014) categorised these technologies into two; passive and active technologies. Examples of passive ones are Anoxic Limestone Drains, Aluminator, Constructed Wetlands, Biochemical Reactors, Successive Alkalinity Producing Systems (SAPS) and Phytotechnologies. The active ones include Fluidized Bed Reactor, Reverse Osmosis, Zero Valent Iron, Rotating Cylinder Treatment Systems, Ferrihydrite Adsorption, Electrocoagulation, Biological Reduction and Ceramic Microfiltration.

Literature Review

There are varied models of explaining the spread of a particular technology, key among them is the Diffusion of Innovations theory by Rogers (1962). Rogers defines diffusion as the process by which an innovation is
communicated through certain channels over time among the members of a social system. He also defined an innovation as an idea or practice that is seen as new by an individual or other unit of interest. Rogers (2010) postulates that members of a social system perceive the following characteristics of an innovation as having an effect on the rate of its adoption. The first one is relative advantage, which means that the innovation is technically superior to the technology it supersedes; the second is compatibility with existing values, skills, and work practices of potential adopters; third is complexity and refers to the extent to which the innovation is relatively difficult to understand and use; fourth is trialability and denotes the ability of the innovation to be experimented with on a trial basis without undue effort and expense; the last is observability, which is the capability of the benefits of the innovation to be seen and communicated to others.

The rate at which technology is adopted varies from one country to another. It is also different between organizations in the same country. This rate is influenced by a myriad of factors. The drivers of adoption of technology can be classified into three broad categories: knowledge, institutions and policies, and demand (Comin & Mestieri, 2014).

Knowledge may mean the formal know-how embodied in people (Nelson & Phelps, 1966). There’s a correlation between formal schooling and embracement of technology (Riddell & Song, 2012). Figuring out the kind of technology required to increase efficiency or effectiveness requires the person to be aware of the existence of such technologies (Comin & Hobijn, 2007). To this extent therefore, technology adoption is determined by the knowledge possessed by its subjects.

Beyond the knowledge held by individuals, there is organizational and sector knowledge which could positively influence the adoption technology by an organization through learning (Comin & Mestieri, 2014). They (Comin & Mestieri, 2014) further argue that similar organizations at close proximity may influence an organization into adopting the technology they are using. For instance, an organization may seek technological advice from those that have prior experience in the use of the technology in question. Organizations will tend to copy technology from neighbors especially when it is successful (Conley & Udry, 2010). In the same vein, the adoption potential of an organization could be affected by the technological experience of organizations that it has contact with even if they are geographically dispersed (Comin & Mestieri, 2014).

There’s a positive relationship between the technology used and the one that follows. In other words, adoption history influences future adoptions (Comin & Hobijn, 2004). Comin et al. (2010) showed that the technology currently in use in an organization has an effect on subsequent technology through factors like culture and institutions. The findings of their study suggest that the highly likely influencer of persistence in technology is the learning of sector-specific technological knowledge. This type of knowledge is an outcome of adopting and using new technologies.

The incentive of an agent to incur the costs of using new technology may be affected by political institutions (Comin & Mestieri, 2014). It is argued by Olson (1982) that the rents of producers that have invested heavily on human or physical assets in older technologies could be eliminated by new technologies, hence resistance. Acemoglu and Robinson (2000) underscore this resistance to new technology by emphasizing that the political and economic power of some elites may be reduced by the adoption of new technologies. The other way institutions affect the adoption of technology, is because they affect the policies implemented by government.

The adoption of technology is also affected by the level of demand for the products it produces. The higher the demand, the higher the rate of adoption and vice versa. Higher demand allows the adopters to recoup their investment (Comin & Mestieri, 2014). Research and development expenditures move in the same direction with output at business cycle frequencies (Comin & Gertler, 2006). The relationship between the variables discussed above and technology adoption may be conceptualized as shown in figure 1.1 on the next page:
This study conceptualizes the independent variables as knowledge, institutions and demand. The dependent variable is technology adoption. Of all the studies reviewed, none was found to have been conducted in the area of factors affecting the adoption of mine water treatment technologies. The studies that are close to this are ‘Adoption of biogas technology as an alternative energy source in Gakawa’ by Ikonya (2018) and ‘A systematic review of literature of the factors that affect sustained adoption of safe water, hygiene and sanitation technologies’ by Hulland, Martin, Dreibelbis, Valliant, and Winch (2015). Ostensibly thus, there is a knowledge gap in this space. The coastal region of Kenya, specifically Kasigau in Taita Taveta County is known for the challenge of encountering water while mining. This study, therefore, sought to answer the question, ‘What are the influencers of adoption of mine water treatment technologies in Taita Taveta County, Kenya?’

The general objective of the study was to establish the influencers of adoption of mine water treatment technologies in Taita Taveta County, Kenya. The accompanying specific objectives were:

a) To determine the influence of knowledge on the adoption of mine water technologies in Taita Taveta County
b) To determine the influence of demand on the adoption of mine water technologies in Taita Taveta County
c) To determine the influence of institutions on the adoption of mine water technologies in Taita Taveta County

### Methods

Research design has been defined by Cooper and Schindler (2006) as a blueprint for accomplishing research objectives. It is a plan for collecting, measuring and analyzing data. A research design cements the research project together (Trochim & Donnelly, 2005). It is the strategem of the inquiry conceived to find solutions to research questions or problems (Kumar, 2011). A case study approach was adopted to guide this study.

A case study design denotes approach of investigating one or a few units (Gomm, Hammersley & Foster, 2000). The unit of study for this case was Aquamines Limited. This company mines Ruby and Tourmaline gemstones. It has always used petrol-driven generators to pump out the water that it encountered underground to allow excavations to proceed. A personal interview was used to establish what influences adoption of mine water treatment technologies. The questions asked focused on the role of human capital, adoption history, geographic interactions and institutions on the adoption of these technologies. This data was collected from the manager of the company. The researcher did also visit the mining site and observed the dewatering process. Further, secondary data relating to mine water regulations was obtained from the Mining Act 2016, of Kenya.

### Findings and Recommendations

The study established that mine water is the main challenge to the mining activities of this company. Pumping out the water is considered a costly exercise in addition to the fact that the water is not utilized in any way save for consumption by wild animals and trees. The mining company does not have records of the chemical composition of the water. Mine-water treatment technologies have not been adopted at all and the interviewee is not aware that such technologies exist. No effort has been put into seeking information because of the fear of not being able to afford the technologies. The desire for use of mine water treatment technologies is present, but is not backed up
by ability to purchase the same. The fear of loss of economic rent by institutions does not apply in this case because no technologies are in use at the moment. The Mining Act 2016 of Kenya does not seem to have captured the interest of mine water treatment.

This study recommends the creation of awareness of the need to conduct water baseline surveys and acting on the results. Awareness is also required in the areas of the value of mine water and available mine water treatment technologies. There is also need for the government to include in the law matters of establishing the chemical composition of water found during excavation and management of the same. Stakeholders of the mine influenced water could also explore the use GIS-based environmental assessment to develop a robust water management plan. This kind of analysis was used to identify all probable springs of acid waters, circulation of pollutants and areas most threatened by the abandoned Kizel basin in Russia (Maksimovich, Pyankov & Khayrulina, 2017).

**Conclusion**

If a solution to this mine water problem is not found, the government will continue to lose would-be revenues, mining duration is unduly long and lots of man-hours are lost removing mine water. The output of this paper is important because it has brought to the fore the drivers of adoption of the technologies in Taita Taveta County, and by extension remote areas in Africa. The information shared will be invaluable to the crafting of strategies that will see mine water being put into better use.

Besides producing noteworthy results, this study was subject to some limitations which in turn provide avenues for further research. To begin with, the factors included in the conceptual model is not exhaustive. Elements like characteristics of government leaders could provide further insights into this area. Other limitations include the use of a case study design, relying on self-reported data mainly from the angle of the manager and restricting context to Taita Taveta County. Future enquiries could strive to address these limitations by using a survey research design and the establishment of the chemical composition of the water as well as varying the geographical context. This will augment the validity and generalizability of future research findings on influencers of adoption of mine water treatment technologies.

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Ikononye, S. N. U. (2018). Adoption of Biogas Technology as an Alternative Energy Source in
Gakawa Location, Nyeri County, Kenya.
Abstract
Biological treatment of selenium (Se) contaminated mining-influenced water (MIW) has gained popularity in recent years. Some commonly used bioreactor configurations include; constructed wetlands, fluidized-bed bioreactors (FBR), packed-bed bioreactors (PBR), hydrogen-based membrane biofilm reactors (H₂-MBR) and upflow anaerobic sludge blanket bioreactors (UASB). The successful operation of these bioreactors is dependent on seeding with mixed microbial consortium capable of removing selenium oxyanions without interference from competing co-contaminants. This review found that these bioreactors achieved widely varying selenium removal extents ranging from 59% – 99%. However, many of these technologies were studied under pilot and laboratory-scale conditions, with only a few implemented at full-scale operations.

Keywords: Selenium, mining-influenced water, biological treatment, bioreactor, microbial consortium

Introduction
Mining-influenced water (MIW) from some mining operations contains elevated concentrations of contaminants such as sulfate, nitrate, trace metals and metalloids such as selenium in some instances. Selenium, which typically occurs at concentrations lower than those of nitrate and sulfate in this complex MIW is a constituent of concern as it can have a disproportionate effect on receiving environments due to its extreme toxicity. When selenium is oxidized through exposure to air and water, it exists as oxyanions (SeOₓ); selenate (SeO₄²⁻) or selenite (SeO₃²⁻) depending on the level of oxidation and these species constitute the bioavailable (and thereby the most toxic) forms of selenium. Selenium can bio-accumulate in aquatic organisms with the potential to bio-magnify up the food chain. For example, lethal and teratogenic effects of SeOₓ in waterfowl (Ohlendorf et al. 1986) were attributed to SeOₓ bioaccumulation in aquatic life in San Joaquin Valley, Western United States (Lemly 1985). In other parts of the world, selenium contamination resulting in serious negative effects to aquatic life have been reported in many countries, such as China, Australia, Japan, South Africa, Russia, Argentina, and France. This is as a result of activities conducted by a wide variety of industries such as mining (coal, hard rock, uranium, phosphate), power generation (coal-fired power plants, oil refineries) and also agriculture (CH2M Hill, 2010; Lemly 2004). In many of these places, biological treatment processes have been implemented to remove selenium from their wastewater. However, there is a wide range of methods for selenium removal reviewed in (CH2M Hill, 2010).

The removal of dissolved selenium compounds from MIW is particularly challenging when: 1) dissolved selenium occurs at relatively dilute concentrations (for example, less than 1 mg/L) and must be removed to much lower concentrations (=1 µg/L in Canada, for instance) (Canadian Council of Ministers of the Environment, 2007) 2) it has a complex chemistry due to the possibility to exist in several oxidation states, 3) other contaminants in the MIW, such as nitrate and sulfate occur at concentrations much higher than those for dissolved selenium and thereby interfere with its removal. Dissimilatory reduction of soluble SeOₓ, the most common forms
of dissolved selenium found in MIW, to the less soluble elemental selenium Se⁰ through microbial biochemical metabolic pathways constitutes a promising approach to removal of dissolved selenium from MIW (Tan et al., 2016; Nancharaiah and Lens, 2015; Lenz and Lens, 2009). This paper reviews some of the challenges associated with some of the common biological treatment technologies used for the removal of selenium from MIW.

Selenium Oxyanion Reduction Pathways by Bacteria

There is ample evidence in the literature that microorganisms can reduce selenium oxyanions (SeOₓ) for a variety of purposes. These include dissipimilatory Se reduction, assimilatory Se reduction, and detoxification (Stolz and Oremland 1999). Certain heterotrophic bacteria are capable of dissipimilatory Se reduction, in which they couple SeOₓ reduction as electron acceptors to oxidation of organic compounds as electron donors for respiration. These bacteria that can be used to effectively remove selenium from MIW. Oremland et al. (1990) first reported evidence for dissipimilatory selenate reduction in experiments performed using sediment slurries sourced from a selenium-contaminated aquatic environment. The dissipimilatory reduction of selenate that was measured was linked to the production of stoichiometric amounts of elemental selenium, meaning that this was the only product of selenate reduction. Following this, Oremland et al. (2004) reported that dissipimilatory reduction of SeOₓ was performed by the bacterial species: Sulfurospirillum barnesii, Bacillus selenitireducens and Selenihalanaerobacter shriftii, all of which formed nano-sized elemental selenium particles that achieved removal of Se from soluble forms to an insoluble and immobilized form. Thauera selenatis was the first bacterium reported to carry out selenate respiration under anaerobic conditions (Macy et al. 1993). Schroder et al. (1997) purified and characterized a periplasmic selenate reductase from Thauera selenatis. The enzyme has high affinity for selenium and can reduce selenate at high percentage (98%) without nitrate inhibition (Macy et al. 1993). In another study at pilot scale, Cantafio et al. (1996) reported that, a packed-bed reactor using Thauera selenatis as inoculum was able to achieve complete (100%) selenate removal and almost complete denitriification (98%).

Assimilatory SeOₓ reduction occurs when Se is associated with cell biosynthesis of selenoproteins and this results in the accumulation of Se inside the cell biomass (Nancharaiah and Lens 2015). Microbial SeOₓ reduction is also performed in order to reduce the toxicity of these chemical compounds. In this case, methylated forms of Se most prevalently, dimethylselenide and dimethyldiselenide, are produced to reduce the toxicity of SeOₓ and, in some cases, cause them to be volatilized (Nancharaiah and Lens 2015).

Biological Processes used for Removal of Dissolved Selenium Oxyanions

Biological reduction was identified as the preferred technology for removal of SeOₓ from industrial effluents versus other physical or chemical methods (CH2M HILL 2010; USEPA 2014). Biological treatment technologies are broadly classified as passive or active process. Passive or semi-passive treatments rely on natural biogeochemical processes on the site and require few if any chemical reagents, special equipment, energy, maintenance or operation. Active treatment processes are highly engineered, high capital cost installations needing special reagents, energy and personnel to operate and maintain. Active treatment systems include process control to maintain optimum conditions, while passive treatment systems are subject to seasonal and other types of variability. Some common biological treatment systems are described below (Table 1). These biological treatment systems described were successful in achieving selenium removal at extents ranging from 59 – 99% for incoming total dissolved selenium concentrations ranging from 15 to 41800 μg Se L⁻¹. However, many of them were pilot- or laboratory-scale studies, with only a couple of commercial full-scale operations. Most active treatment processes consist of several reactors in series.
so as to deal with interferences from co-contaminants, such as nitrate, and to remove metabolic byproducts, such as ammonia and colloidal Se\textsuperscript{0}.

To remove nitrate, a pretreatment bioreactor is used as the first stage followed by selenium removal in subsequent bioreactors(s), which are then followed by aerobic bioreactors to eliminate metabolic byproducts produced in the upstream bioreactors. The number of bioreactors required for treatment of selenium containing MIW could be reduced if the bioreactor supports a microbial community with enzymatic systems that are specific for SeO\textsubscript{X} reduction and not inhibited by the presence of nitrate.

Regarding the process conditions that are required for selenium removal down to regulated levels, most active treatment
bioreactors need HRTs ranging from 6 - 48 hours. The required HRT is dependent on the selenium loading rate into the bioreactor and the loading rate of co-contaminants that could interfere with the rate of selenium removal. Another important parameter to control is pH, which must be near neutral since this is optimal for microbial SeOx reduction. For instance, Lortie et al., (1992) reported that no selenate reduction occurred at pH below 6.5 or above 9.5. These bioreactors also use mesophilic bacteria, which operate within the temperature range of 15 - 35°C and any changes in temperature could affect bioreactor performance. For instance, it was found that a drop in temperature from 15 to 7°C reduced selenate removal from 88% to 35% in a UASB reactor (CH2M HILL 2010). However, the ABMet® system has been operated successfully over a wide temperature range (3-38°C) (Staicu et al., 2017). An important concern regarding bio-treatment of selenium containing MIW is the formation of colloidal Se that needs to be removed from the effluent before discharged into receiving environment. Different post-treatment steps for solid-liquid separation of colloidal Se have been proposed including, media-filtration, coagulation and electrocoagulation (Staicu et al. 2017).

**Challenges with using Bioreactors for Removal of Dissolved Selenium from MIW**

Most of the bioreactors used for the removal of dissolved selenium have been tested at the laboratory- or pilot-scale, with the challenge of scaling-up most of these processes. Almost all of full-scale plants reported in the literature are located in Canada and US. However, most of these processes still experience performance deterioration and instability. As is typical for most biological processes, the success in reducing the contaminant of interest is dependent on creating the optimal conditions for the desired functional microorganisms to flourish, and maintaining these microbes throughout the treatment process. Briones and Raskin (2003) reported that, the stability of biological wastewater treatment systems is dependent on the functional redundancy of microbial communities in the bioreactor. Functional redundancy is having a diversity of functionally important groups of microorganisms that can perform desired treatment under a wide range of conditions. For mine water treatment, the challenge is the ability to maintain the functionally important microbial community members that can simultaneously remove selenate and nitrate in bioreactors. Selecting and maintaining the selenate-respiring specialists that can selectively remove selenium in the presence of other competing anions could reduce the amount of electron donor required for microbial respiration because the microbial reduction of the competing anions increases the electron donor proportionally. For instance, each mole of nitrate co-reduced with SeOx requires additional 5 electron equivalence to be reduced to N$_2$ gas. Organic carbon requirements are high for MIW treatment bioreactor operation, which increases the operating cost.

Constructed wetlands are useful when the wastewater is produced in large volumes but sensitive to temperature fluctuation and seasonal variation of vegetation, there is also the concern about gradual accumulation of selenium in vegetation and sediments in wetlands. Algae-bacterial process has the challenge of inability to consistently achieved selenate reduction to low levels unless nitrate is removed first (NSMP 2007, CH2M HILL 2010). The main operational limitation associated with ABMet® bioreactor process is its susceptibility to clogging (CH2M HILL 2010). When implementing FBR for full-scale mine water treatment, Sirivasan et al. (2014) reported that, the main operational challenges encountered was difficulty in controlling bed height in order to maintain bed expansion for selenium removal. For UASB bioreactor configuration, the challenges reported are; long acclimatization of the sludge, short-circuiting caused by accumulation of gas in the sludge, and variability in selenium removal efficiencies due to temperature sensitivity of the process (CH2M HILL 2010). When treating synthetic MIW under sulfate-reducing conditions in a UASB reactor, Lenz et al. (2008) observed that the removal of selenium is dependent of sulfate/selenate ratio with ratio greater than 8x10$^{-4}$ being the most
effective for selenate removal. However, this sulfate/selenate ratio is impossible to achieve in actual MIW. The main challenge associated with the use of pure cultures e.g. *Thauera selenatis* and *Bacillus sp*. SF-1 as inoculum in bioreactors is out-competition by other microorganisms entering with the feedwater since a sterile environment is impossible to maintain. The challenges associated with H$_2$-MBfR bioreactor are the expensive electron donor (hydrogen) membrane fouling especially from colloidal Se (Nancharaiah and Lens 2015) and presence of nitrate has inhibitory effect on selenate reduction (Lai et al. 2014).

**Conclusion**

Biological treatment is one of the popular methods for removing Se from MIW. Previous research has shown that, the major mechanism for selenium removal for this process is reductive precipitation based on microbial reduction of selenium oxyanions under anoxic conditions to particulate Se$_0$. Several active bioreactors have been developed and operated at laboratory-scale, pilot-scale and few at full-scale. These include UASB, FBR, PBR, H$_2$-MBfR. Passive and semi-passive bio-treatment system have been developed and used in certain cases. The effectiveness of these bioreactor systems is challenged by the presence of other co-contaminants especially nitrate and sulfate which occur at much higher concentration. Perhaps, it’s possible to overcome this challenge by using microbial community with enzymes that are specific for SeO$_x$ reduction. However, further research is needed to test this theory. Also, there is the need to optimize these bioreactor processes or develop new process to effectively treat actual mine water at full-scale. With further research, perhaps a combination of two different bioreactors could be a more effective strategy for removal of selenium from actual MIW at full-scale.

**Reference**


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Testing Iron Removal in a Trifurcated Pilot Plant for Passive Treatment of Circum-neutral Ferruginous Mine Water

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Abstract
A trifurcated pilot plant was implemented at an abandoned mine site for passive treatment of circum-neutral, ferruginous seepage water. Purpose of the composite system was to investigate the suitability of serially connected settling ponds, wetlands and sediment filters for passive iron removal in accordance with the strict compliance limit of 1 mg/L. After demonstrating reproducibility at equal flow rates in the three identical lines, hydraulic variation was used to develop comparison data for sizing of a full scale passive system. The multi-stage setup proved successful, reducing relatively low iron concentrations of app. 10 mg/L in the influent to compliance level in the effluent. System monitoring provided evidence that physico-chemical removal of suspended ferric hydroxides is a critical step in natural iron removal and may even become the rate-determining step for thoroughly oxygenated, circum-neutral mine waters. Area-adjusted removal rates were relatively low because of low hydraulic loading. Dependence of both treatment efficiency and area-adjusted removal on hydraulic loading was demonstrated during the variation period, showing direct and inverse relationships at graded flow rates, respectively. Ultimately, a more extensive and higher resolution database is necessary for pilot plant upscaling to full scale.

Keywords: passive treatment, iron removal, wetlands, hydraulic variation

Introduction
Contamination of water resources through mining activities is one of the most complex and costly environmental problems worldwide. Most prominent is the occurrence of acid mine drainage (AMD) as a result of sulphide mineral oxidation, which causes ferrous iron, acidity, sulphate and associated metals to be released into aqueous environments. Subsequent aeration and neutralisation lead to precipitation of ferric hydroxides, resulting in compromised usability of water resources and/or complete destruction of aquatic ecosystems. Ferruginous mine water can be treated in passive systems by utilising and enhancing natural (geo)chemical, biological and physical processes (Skousen et al. 2017). However, the scale of passive components (settling ponds, aerobic wetlands) is currently based on an empirical, area-adjusted removal rate by Hedin et al. (1994) that doesn't reflect the kinetic background of respective biogeochemical and physical iron removal mechanisms (Sapsford and Watson 2011; Tarutis Jr. et al. 1999).

A trifurcated pilot plant was installed for passive treatment of ferruginous seepage water from a former open-pit lignite mine. Whereas most multi-line (pilot) systems were constructed to test different materials or setups (e.g. Garcia et al. 2004; Nyquist and Greger 2009; Whitehead and Prior 2005), the innovative system in this study consists of three identical lines with multiple successive treatment stages each for natural iron removal. The system was designed to collect comparable hydraulic and hydrochemical data to investigate performance, kinetic relationships and critical influencing factors as a basis for upscaling. After providing evidence of reproducibility at equal flow rates in the three lines, hydraulic variation was used to investigate iron removal efficiency as a function of flow rate. Furthermore,
monitoring data is used to investigate kinetics and connexions of natural iron removal mechanisms with a focus on physico-chemical ferric iron removal processes such as aggregation and sedimentation/filtration.

**Pilot Plant**

The study site is located in the historic lignite district of Upper Palatinate (Germany) (fig. 1). For protection of surrounding aquifers, seepage water from a former open pit is pumped to a conventional treatment plant for iron removal via flocculation and coagulation. A small amount of the raw water is split off via a bypass and diverted to a distribution tank preceding the pilot plant.

The pilot plant for passive treatment of the mining influenced seepage water consists of three identical, parallel lines with multiple successive treatment stages each (fig. 2):

1. Preliminary treatment in settling ponds,
2. fine treatment in aerobic wetlands and
3. purification in sediment filters.

The composite setup was chosen to meet the very low compliance limit for total iron of 1 mg/L by successive iron removal with both treatment efficiency and maintenance requirements of the passive treatment components increasing along the flow path. Roll-off containers (7.00 × 2.35 × 1.25 m) were used for settling ponds and wetlands. Sediment filters are liner-sealed, approximately trapezoidal trenches (ca. 4.0 × 0.5 × 0.5 m) filled with granite gravel (8-16 mm). A total of ten sampling/measuring points numbered MP01-MP10 were installed in protected manholes with MP01 as inflow of the three parallel system lines, MP02-MP04 behind settling ponds, MP05-MP07 behind wetlands and MP08-MP10 behind sediment filters (fig. 2). The outflow of one component thus corresponded to the inflow of the subsequent component, with discharge from sediment filters (MP08-MP10) corresponding to system line outflows. Flow rates were adjusted by way of ball valves equipped with flowmeters in the three feeding pipes branching off MP01.

**Materials and Methods**

Monitoring of the pilot plant includes fixed sensors for continuous measuring of pH, conductivity and dissolved oxygen at the central line and all wetlands (MP01, MP03, MP05-MP07, MP09) and turbidity at all measuring points. Automatic measurements are double-checked weekly with hand-held meters (pH, SC, O₂, turbidity, redox potential). Water samples are collected once...
Laboratory analysis includes dissolved (<0.45 µm) ferrous and ferric iron, particulate (>0.45 µm) and total iron (Butler et al. 2008) as well as mayor elements. Operation of the pilot plant started in November 2017 and the first months were used as a test and adjustment period. In a first step, system inflow was distributed homogeneously across the three system lines to confirm similar performance at equal flow rates. A reference dataset was obtained between July and November 2018 (113 days) with evenly distributed flow rates ("reference period"). In a second step, comparison data was obtained between November 2018 and March 2019 (113 days) with flow rates incrementally varied (1st "variation period"). It should be noted that hydraulic fluctuations were inevitable in at least one system line (usually line 3) subject to filling level variations in the gravitationally drained distribution tank. Resulting average flow rates were 269±38 L/h, 277±8 L/h and 262±59 L/h during the reference period and 178±12 L/h, 276±16 L/h and 344±76 L/h during the variation period in system lines 1, 2 and 3, respectively.

Performance of individual treatment components was evaluated using typical performance indicators such as treatment efficiency (%-removal) and area-adjusted removal (areal mass removal per time interval) (Hedin et al. 1994, Tarutis et al. 1999). Flow rate and hydraulic (iron) loading in the pilot plant were directly proportional because of equal inflow iron concentrations in all system lines and may thus be used synonymously in the context of performance evaluation.

**Results and Evaluation**

Results of the entire operation period (including the test period) showed excellent system performance with effluent iron concentrations consistently below the compliance level of 1 mg/L (fig. 3). High-resolution monitoring of hydrochemical parameters revealed environmental factors (esp. seasonal and diurnal cycles) had a strong effect on ecology and hydrochemistry of the aerobic wetlands. For instance, plant growth and algae blooms in spring and summer resulted in substantial diurnal cycles of pH and dissolved oxygen in the wetlands. Besides, turbidity and conductivity were affected by discontinuous pump operation and concomitant filling cycles of the distribution tank, decreasing substantially during pump intermissions (e.g. weekends).

Inflowing iron was predominantly composed of suspended (particulate) ferric hydroxides (>90 %). As a consequence, iron removal occurred predominantly by way of physico-chemical processes such as aggregation and sedimentation/filtration. Iron analysis during the reference period (n=30) showed an overall iron removal efficiency of 97.8 % with most of the iron retained in settling ponds (72.8 %), followed by wetlands (19.6 %) and sediment filters (5.3 %) (tab. 1). Although the bulk of iron is retained in settling ponds, treatment efficiency is similarly high in subsequent treatment components despite substantially lower hydraulic iron loading.
decreased inflow concentrations (tab. 1), confirming expected superior treatment efficiency of wetlands and sediment filters.

Iron analysis during variation period 1 (n=30) also showed decreasing concentrations, yet with clear gradation according to flow rates (fig. 3, tab. 2). As expected, this corresponded to an inverse relationship between treatment efficiency and hydraulic loading in settling ponds and wetlands. The effect was, however, mostly offset by sediment filter efficiency, resulting in only marginally graded overall iron removal in system effluents during variation period 1 (fig. 4).

Whereas cumulative iron removal along the flow path of the three system lines is almost identical at similar flow rates during the reference period, distinct gradation according to flow rate is in evidence during variation period 1 as illustrated by fig. 4.

Area-adjusted removal based on estimated total mass removal over the reference period was similar in the three system lines at similar flow rates. Dependence of not only iron removal efficiency, but also area-adjusted removal on hydraulic loading was demonstrated during variation period 1. Line 2 showed similar results compared to the reference period at a similar flow rate, whereas lines 1 and 3 showed substantially decreased and increased area-adjusted removal at decreased and increased flow rates, respectively. Dependence of area-adjusted removal on hydraulic loading is illustrated for settling ponds in greater detail in fig. 5. Boxplots are based on all iron analysis with available flow measurements for both

### Table 1 Key figures for treatment components during the reference period

<table>
<thead>
<tr>
<th>Key figures</th>
<th>MP01</th>
<th>MP02</th>
<th>MP03</th>
<th>MP04</th>
<th>MP05</th>
<th>MP06</th>
<th>MP07</th>
<th>MP08</th>
<th>MP09</th>
<th>MP10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outflow c(Fe) [mg/L]</td>
<td>8.4±2.1</td>
<td>2.3±1.4</td>
<td>2.4±0.8</td>
<td>2.2±0.9</td>
<td>0.6±0.3</td>
<td>0.5±0.2</td>
<td>0.8±0.3</td>
<td>0.2±0.1</td>
<td>0.2±0.1</td>
<td>0.2±0.1</td>
</tr>
<tr>
<td>Treatment efficiency [%]</td>
<td>-</td>
<td>73.0</td>
<td>71.9</td>
<td>73.6</td>
<td>72.9</td>
<td>77.8</td>
<td>65.9</td>
<td>72.4</td>
<td>63.6</td>
<td>72.7</td>
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<tr>
<td>Area-adjusted removal [g/m²/d]</td>
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<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>0.6</td>
<td>0.7</td>
<td>0.6</td>
<td>1.0</td>
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<td>1.2</td>
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</table>

### Table 2 Key figures for treatment components during variation period 1

<table>
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<tr>
<th>Key figures</th>
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<th>MP03</th>
<th>MP04</th>
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</thead>
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<td>3.1±1.1</td>
<td>0.5±0.4</td>
<td>1.0±0.3</td>
<td>1.7±0.7</td>
<td>0.1±0.1</td>
<td>0.2±0.1</td>
<td>0.3±0.3</td>
</tr>
<tr>
<td>Treatment efficiency [%]</td>
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<td>79.0</td>
<td>69.1</td>
<td>63.1</td>
<td>71.2</td>
<td>60.9</td>
<td>45.9</td>
<td>71.1</td>
<td>80.4</td>
<td>83.4</td>
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<tr>
<td>Area-adjusted removal [g/m²/d]</td>
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<td>1.7</td>
<td>2.4</td>
<td>2.7</td>
<td>0.3</td>
<td>0.6</td>
<td>0.7</td>
<td>0.5</td>
<td>1.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Figure 4 Iron removal along the flow path with flow rates (Q)
reference and variation period with 26 and 29 data pairs, respectively. Flow rates were averaged over an interval of ±24h around the sampling time to compensate for hydraulic fluctuations as best as possible.

**Discussion and Outlook**

It should be noted that the datasets described above were subject to varied environmental influences with reference and variation period set in autumn and winter, respectively. Differences in temperature and vegetation development as well as variation of hydraulic retention time subject to pump operation or ice thickness were inevitable, yet potential effects on iron removal processes are difficult to quantify wherefore higher resolution data is necessary.

The composite system showed excellent treatment efficiency with iron removal consistently >95%. Settling ponds showed considerably higher area-adjusted removal rates than wetlands due to much higher hydraulic loading on the one hand and area-adjusted removal not correcting for lower hydraulic retention time due to lower volume at same surface area on the other hand. Ranges of area-adjusted removal for settling ponds were in accordance with >50% of passive systems investigated by Tarutis et al. (1999). Nevertheless, area-adjusted removal for both monitoring periods in the pilot plant was still orders of magnitude lower compared to (optimally) expected ranges for wetland sizing of 10-20 g/m²/d (Hedin et al. 1994). However, it is well-recognised that area-adjusted removal does not adequately reflect treatment performance with regard to non-linear overall iron removal kinetics as critically discussed by Tarutis et al. (1999) and Sapsford and Watson (2011). Low area-adjusted removal at relatively high pH in the pilot plant and particularly in wetlands is attributable to generally low hydraulic loading of the system. At the study site, catalytic processes such as heterogeneous oxidation of ferrous iron and homoaggregation of particulate ferric hydroxides take effect in the preceding seepage sump and water distribution system, where high (ferrous) iron concentrations in the range of 50-100 mg/L are effectively reduced to <15 mg/L before reaching the pilot plant. Therefore, little to no catalytic effects are to be expected within the actual pilot plant. Main purpose of the treatment system is the removal of residual suspended and, if present, dissolved iron for compliance purposes. Importance of efficient treatment components such as wetlands and sediment filters is clearly demonstrated by high treatment efficiency at (or despite) low inflow concentrations. Physico-chemical removal of suspended ferric iron clearly is the rate limiting step in the pilot plant and, based on the results of this study, there is a good cause to believe that the same may be true for other oxygenated and circum-neutral mine waters as previously suggested by Flanagan et al. (1994) and Mayes et al. (2009).

Available datasets clearly show decreasing treatment efficiency yet increasing area-adjusted removal with increasing hydraulic loading in accordance with findings of Tarutis et al. (1999). Future work will include further
variation periods with intermediate, higher and lower flow rates to expand the database. In addition, high-resolution mass balances will be generated using continuously monitored turbidity as a proxy for (particulate) iron in the pilot plant. Finally, overall data will be used for statistically adequate performance evaluation and calculation of suspended ferric hydroxide removal kinetics as a basis for upscaling from pilot to full scale.

Conclusions

- Combining multiple treatment components with successively increasing efficiency to a composite system proved successful, reliably reducing iron concentrations from about 8.4 mg/L in the influent to compliance level (<1 mg/L) in the effluent;
- Treatment efficiency and area-adjusted removal showed inverse and direct relationships with hydraulic loading, respectively. Area-adjusted removal is relatively low because of low hydraulic loading (concentration dependence of natural iron removal processes);
- System monitoring provided evidence that physico-chemical removal of suspended ferric hydroxides is a critical step in natural iron removal and may even become the rate-determining step in treatment of thoroughly oxygenated, circum-neutral mine waters;
- Hydraulic variation of the identical system lines provided excellent comparison data, yet a more extensive and higher resolution database is necessary for upscaling of the pilot plant to full scale.

Acknowledgements

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References


Abstract
The Cwm Rheidol-Ystumtuen metal mines discharge acidic waters adversely effecting 18 km of the River Rheidol to the sea. Collectively Adits 6 and 9 discharge c. 4.8 tonnes zinc, 160 kg lead, 11 kg cadmium and 4 tonnes iron into small ineffective limestone filter beds before reaching the river at the mouth of the Rheidol gorge. The Metal Mines Strategy for Wales has Cwm Rheidol ranked as the seventh most polluting. Previous Passive treatment trials confirm that such treatment would require a large area of unavailable flat land. Laboratory sono-electrochemistry trial success on Parys Mountain discharges indicated that magnesium electrodes could be trialled at Cwm Rheidol to produce magnesium hydroxide, raise the pH of the water and precipitating the metals as insoluble hydroxides. These highly successful electro-chemistry treatment trials (sono EC reactor, flocculator and lamella clarifier) identify that 99.5% of metals can be safely recovered using 1 kW/m\(^3\). Full scale treatment (32 m\(^3\)/hr flow rate) is now a viable Active treatment process that can be applied in NRW’s feasibility options for Cwm Rheidol at full scale, demonstrating an additional treatment tool to help failing water bodies achieve compliance with the EU Water Framework Directive (WFD).

Keywords: electrochemistry, WFD, AMD, sonification, treatment, zinc.
and 107% respectively, which continues to fail WFD for both metals to the tidal limit.

Results of ecological impact assessments have been equivocal with fish population studies showing salmon tolerance to zinc concentrations in the Rheidol, which average more than ten times WFD standards in places (NRW 2016).

Active Pilot Trial

The application of ©Soneco (Morgan 2014) sono-electrochemistry, with combined power ultrasound for treatment of acid mine drainage (AMD) using a magnesium anode to produce magnesium hydroxide in-situ. Using power ultrasound simultaneously with electrolysis removes the ionic boundary and passivation layers (Stern and Helmholtz layers) that can develop along the electrode surface during operation, making ‘fresh’ electrode material available for treatment. This reduces the electrical resistance of reactor circuit, reduces the power requirement and increases treatment efficiency and effectiveness. Other benefits include the cavitation and collapsing of oxygen formed at the anode, by removing the micro-bubble production. There is little or no chance of the contaminants binding to the oxygen bubble and rising to the surface, thus allowing for greater settlement characteristics.

The background and principles to the ©soneco process were detailed in an earlier paper on laboratory trials at Parys Mountain by the late Phil Morgan (Morgan 2017). The advantage of a pilot trial adopting electrochemistry and the successful adaption of sonification and magnesium electrodes at Cwm Rheidol limits the need for the land area required for passive treatment which simply does not exist in the Rheidol gorge. This trial was progressed in late 2017.

Additional development has highlighted several, previously unknown, benefits to the use of sono-electrochemical generation of magnesium hydroxide to treat acidic mine water, for example, Magnesium has the capability of pH neutralisation, whereby the pH will increase as a result of the cathodic half-reaction (Rybalka 2014) shown by the following equation:

\[ \text{Mg(OH)}_2(\text{s}) + 2e^- \rightarrow \text{Mg(s)} + 2\text{OH}^- \]

The rapid production and dissolution of hydroxide produced by the reaction results in an increase in the pH of the electrolyte (Martell 1974), in this case acidic mine water, in which the following reaction occurs:

\[ \text{Mg(OH)}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2(\text{OH})^-_{(\text{aq})} \quad \text{K}_\text{sp} = 10^{-11} \]

This increase of the pH enables the precipitation of metals and metalloids in their hydroxide form. It is further believed that the process by which the magnesium hydroxide reacts with sulphate ions found in mine water proceeds through a series of preferential leaching activities, this usually hinders contaminant removal rates but where magnesium is concerned, it benefits the treatment by a series of displacement reactions. “Sulfidic wastes commonly contain sulphides other than pyrite. If there is direct physical contact between at least two different sulphide minerals, electrons move between the sulphides and a galvanic cell is formed. During weathering the sulphide mineral with...

### Table 1 Average Results from 2010 to 2018 of sample points 81011 (Adit 6) and 35230 (Adit 9)

<table>
<thead>
<tr>
<th>Monitoring Data</th>
<th>Adit 6</th>
<th>Adit 9</th>
<th>Σ</th>
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</thead>
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<tr>
<td>Flow L/s</td>
<td>7.6</td>
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<td>8.3</td>
</tr>
<tr>
<td>pH</td>
<td>3.9</td>
<td>3.0</td>
<td></td>
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<tr>
<td>Zn (mg/L)</td>
<td>12.1</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>Pb (mg/L)</td>
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<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0.03</td>
<td>0.12</td>
<td></td>
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<tr>
<td>Fe (mg/L)</td>
<td>7.1</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>Mn (mg/L)</td>
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<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Zn (kg/yr)</td>
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<td>1,842</td>
<td>4,758</td>
</tr>
<tr>
<td>Pb (kg/yr)</td>
<td>161</td>
<td>0.4</td>
<td>161</td>
</tr>
<tr>
<td>Cd (kg/yr)</td>
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</tr>
<tr>
<td>Fe (kg/yr)</td>
<td>1,711</td>
<td>2,297</td>
<td>4,008</td>
</tr>
<tr>
<td>Mn (kg/yr)</td>
<td>137</td>
<td>83</td>
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</table>
the highest electrode potential is galvanically protected from oxidation, while the mineral with the lowest electrode potential is weathered more strongly. Selective oxidation of sulphide minerals occurs as one sulphide mineral is preferentially leached over another” (Nordstrom 1999).

A metal will always displace another based on its reactivity which, in this case, treatment utilising magnesium (which is higher in the reactivity series than all target species) will enable metals and metalloids to be forced out of its mineral compounds where it is then precipitated. The sono electrochemical process enhances this process as sonification modifies particle size, shape and surface morphology through high velocity interparticle collision which destabilises the contaminant, enabling enhanced rate of colloidal charge neutralisation and the formation of amorphous nanostructured adsorption sites resulting in a dense, dewatered sludge.

The reaction between magnesium hydroxide and the precipitation of metal and metalloid sulphides are known as a ‘Displacement Reactions’ occurring when one element is more reactive than another in solution e.g. the reaction between magnesium hydroxide and iron sulphate:

\[ \text{MgHO} + \text{FeSO}_4^{2-} \rightarrow \text{MgSO}_4^{2-} + \text{FeOH}. \]

As displacement reactions are competing for non-metal anions such as sulphate, which is found in mineral complexes that make up the mine water, the atoms of the reactive metal (in this case magnesium) put their electrons on to ions of less reactive metal.

Metal and metalloids from the often acid-producing sulphide minerals such as pyrite (or marcasite as FeS2), galena (PbS) and sphalerite (ZnFeS) can be precipitated before they are galvanically protected, which results in either prolonged or unsuccessful treatment. The galvanic protection process is the same as that for galvanised iron. The more electroconductive sulphide mineral oxidises at a slower rate than it would when not in contact with another sulphide e.g. Among the three most common sulphide minerals, pyrite has the highest electrode potential followed by galena and then sphalerite. If these minerals are in contact with each other, sphalerite will be preferentially weathered, and oxidation of pyrite is reduced. Hence, pyrite in direct contact with other sulphides does not react as vigorously as it does in isolation. Also, the oxidative dissolution of pyrite can be delayed, while other sulphides are preferentially oxidised (Lottermoser 2007).

Sulfidic wastes and AMD have been studied extensively and the chemical addition of MgOH has also been studied for its neutralising capabilities in the treatment of acidic mine water with successful results. The benefits of sono electrochemical treatment over chemical is its ability to produce an instantaneous, uniformed mass transport of highly mobile and active MgOH ions into solution, creating un-reversable REDOX reactions, precipitating metals as their hydroxide forms whilst substantially increasing the pH and preventing further acid producing oxidation reactions from occurring both during and after treatment.

Materials and Methods

During the three-month project at Cwm Rheidol, Power & Water segregated the project into two distinct sections. Both employing the ©Soneco process of electro generating Mg electrons for increased pH and removal of potentially toxic metals, but through two subtly different methods. Objectives were to confirm treatability in the field, generate data to demonstrate a full scale system could be sized, introduce flocculation, use recirculation to reduce magnesium take and increase precipitation, and identify optimum plate gap for energy demand.

Method 1 = Constant stirred tank electrode reactor (CSTER)

The CSTER is a shallow, cylindrical tank with externally mounted ultrasonic generators. The electrode plate is also cylindrical, but suspended internally via isolating guide rails within the tank itself. A stirrer motor is positioned centrally above the tank with variable speed drive (VSD) rotating an inert stirrer to keep the liquid and combined solids in suspension. This treatment method was employed for the first two months of the project.
Method 2 = Laminar flow fixed electrode reactor (DB1)

The DB1 reactor tank is a rectangular shaped tank, again with externally mounted ultrasonic generators, but this design includes a fixed, flat, electrode plate mounted internally via isolating guide rails. This design uses no moving parts, instead relying on the flow of liquid to promote laminar flow with both sides of the electrode plate utilised for proportional treatment without sacrificing efficiencies. This treatment method was employed for the last month of the project.

Process, Flow and Instrumentation

Liquid flowing from the inlet to the existing filter beds was captured within a small (above ground) sump and constantly pumped (via submersible pump) at a fixed flow rate (controlled via diaphragm valve and mechanical rotameter) through the Soneco reactor tanks. As the liquid passes through the Soneco reactor tank, the Power Supply Unit (PSU) comes into operation, gradually increasing the amount of power (treatment) required until a separate, yet integrated pH probe (Partech Instruments) achieves a reading of 10.00. The PSU constantly monitors and adjusts the amount of power commanded by means of integrated feedback from the pH controller. As the pH of the liquid fluctuates, so too does the amount of power demand, which ensures optimum use of power and consistent precipitation downstream.

Once the liquid has been treated (via electrolysis and ultrasound) within the Soneco reactor tank, the coagulated liquid passes into the clarifier tank. The potentially toxic metals precipitate, flocculate and settle into a hopper at the bottom of the clarifier, condensing through the weight of metals falling from above. Periodically a timed actuator valve releases the settled solids into a sludge capture tank whilst the clear water flows through the clean water outlet, into the existing filter beds, before exiting through the cascade into the River Rheidol.
Reaction time, pH, E_{\text{H}} (mV) (both Hanna Instruments) and amperages were noted during the treatment procedure. These were used along with the mechanical and electrical specifications of the Soneco® reactor to calculate Capex and Opex for a full-scale treatment plant.

**Results**

The average power consumption for treating 4m³/hr was 5kW, therefore 1.25kW/m³.

Difference between treated water metals and dissolved metals due to metal hydroxide precipitates:

TSS generated in system 126mg/L, the TSS in treated water was 11mg/L.

On site degassing and neutralization tests were conducted to establish if carbon dioxide was present in the mine water and ensure gypsum or calcium carbonate would not generate substantial unwelcome bi-products within the precipitates. Carbon dioxide was not present.

This method 2 system adopting the DB1 design had greater efficiency with more plate exposure and used an equivalent 1kW/m³/hr. Based on the above tests it is estimated that for 32m³/hr the magnesium (Mg²⁺) dissolution required to both pH neutralize and precipitate iron to less than 1 mg/l equates to is 26 mg/l or 20kg/day. Scaling this up identifies a use of 0.6 plates per day based upon a 31kg plate. Conversely for a system to last one month it will require an equivalent twenty plates.

Using the solids generation rate of 126mg/L, it is estimated using the flow of 32m³/hr that 4kg/hr of dried solids would be produced or 97kg/day. This equates to 9.7m³ of clarifier settled sludge at 1% total solids. Initial cake pressing tests indicate the solid matter can be increased to 10%w/w. The consequence being that sludge generation would be 1m³/day with a composition of 17.4% iron, 10.4% zinc, 29.3% hydroxide and 9.3% carbonate.

To estimate the clarifier tank volume, tests using settlement velocities have been conducted. Assuming an upper value of

*Figure 4 Pe-ID Method 2 – DB1.*
Table 2 Treatment Water Quality Method 1 (NRW filtered results. Metals in mg/L)

<table>
<thead>
<tr>
<th>Test</th>
<th>Untreated</th>
<th>Treated</th>
<th>Removal %</th>
</tr>
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<td>6.55</td>
<td>99.46</td>
</tr>
<tr>
<td>Cd</td>
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<td>7.98</td>
<td>0.040</td>
<td>99.48</td>
</tr>
<tr>
<td>Mg</td>
<td>11.45</td>
<td>29.32</td>
<td>-154.82</td>
</tr>
</tbody>
</table>

Table 3 Treatment Water Quality Method 2 Flow rate 1m³/hr (metals in mg/L)

<table>
<thead>
<tr>
<th>Test</th>
<th>Mine Water Total</th>
<th>Soneco Dissolved Post Treatment</th>
<th>Treated Total Metals</th>
<th>Removal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.3</td>
<td>8.3</td>
<td>8.5</td>
<td>90.2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.041</td>
<td>&lt;0.001</td>
<td>0.004</td>
<td>90.7</td>
</tr>
<tr>
<td>Zn</td>
<td>17.77</td>
<td>0.01</td>
<td>1.65</td>
<td>90.7</td>
</tr>
<tr>
<td>Pb</td>
<td>0.79</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>98.7</td>
</tr>
<tr>
<td>Fe</td>
<td>17.42</td>
<td>0.11</td>
<td>1.79</td>
<td>89.7</td>
</tr>
<tr>
<td>Ni</td>
<td>0.29</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>89.7</td>
</tr>
<tr>
<td>Al</td>
<td>4.05</td>
<td>0.42</td>
<td>0.51</td>
<td>87.4</td>
</tr>
<tr>
<td>Mg</td>
<td>11.67</td>
<td>32.32</td>
<td>31.25</td>
<td>-167.8</td>
</tr>
</tbody>
</table>

Table 4 The Outline Concept Design following the Pilot Trial

<table>
<thead>
<tr>
<th>Stage</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Usage</td>
<td>Theoretical Hydroxide Dose</td>
<td>635</td>
</tr>
<tr>
<td></td>
<td>Magnesium Use</td>
<td>680</td>
</tr>
<tr>
<td></td>
<td>Magnesium plate weight</td>
<td>kg 31</td>
</tr>
<tr>
<td></td>
<td>Plates per year</td>
<td>N° 20</td>
</tr>
<tr>
<td></td>
<td>Plates per month</td>
<td>N° 1.6</td>
</tr>
<tr>
<td>System Design</td>
<td>Sono EC Reactor</td>
<td>Name 2 N° DB4</td>
</tr>
<tr>
<td>Flash Mix</td>
<td>Retention min/Vol m³</td>
<td>1.5min/1m³</td>
</tr>
<tr>
<td>Floc Mix</td>
<td>Retention min/Vol m³</td>
<td>3.0 min/2m³</td>
</tr>
<tr>
<td>Rise rate</td>
<td>m/hr</td>
<td>0.6</td>
</tr>
<tr>
<td>Clarification area</td>
<td>m²</td>
<td>54</td>
</tr>
<tr>
<td>Lamella clarifiers</td>
<td>N°</td>
<td>2</td>
</tr>
<tr>
<td>Clarification area/clarifier</td>
<td>m²</td>
<td>30</td>
</tr>
<tr>
<td>Solids Generation</td>
<td>Solids generation</td>
<td>mg/L 126</td>
</tr>
<tr>
<td>Waste Sludge off clarifier</td>
<td>%ds</td>
<td>1.0</td>
</tr>
<tr>
<td>Dewatered sludge</td>
<td>%ds</td>
<td>10</td>
</tr>
<tr>
<td>Volume of dewatered sludge</td>
<td>%ds</td>
<td>0.9m³</td>
</tr>
<tr>
<td>Sludge dewatering</td>
<td>Type</td>
<td>Plate press</td>
</tr>
</tbody>
</table>

30mg/L for TSS a settlement velocity of 0.6m/hr is required, which equates to a total settlement area of 54m².

Conclusions

1. The predicted CapEx and OpEx of a sono-electrochemical treatment plant is attractive in comparison to other treatment / disposal options being considered for these adit discharges. Costs could be off-set by revenue earned by metals recovery from treated sludge. Power for a sono-electrochemical plant could also be sourced from renewable energy supplies.

2. This pilot study has achieved excellent results and confirmed that the ©soneco treatment process is a viable alternative treatment tool for AMD that lends itself particularly where renewables offset energy demands. Natural Resources Wales are considering feasibility options for metal mine water treatment schemes at Cwm...
Rheidol and three other sites.

3. Further research to enhance sediment harvesting to yield a cake with solids at 20%w/w and disposal/recovery options via resource recovery is required, as are communications with remote monitoring sensors to aid ongoing OpEx.

References


NRW (2016) Abandoned Mine Case Study: Cwm Rheidol Lead & Zinc Mine


Nordstrom DK, Alpers CN (1999) Geochemistry of Acid Mine Waters

Ecotoxicity with *Allium cepa* to determine the efficiency of conventional ARD treatment by neutralization/precipitation from a brazilian coal mine

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**Abstract**

ARD (acid rock drainage) represents a major problem in the mining industry worldwide due to the risk of water and soil pollution. The active treatment of ARD involves the addition of alkaline reagents to increase the pH and precipitate the dissolved metals as hydroxides. The ARD treatment plants in Brazil mostly use sodium hydroxide or lime for neutralization. However, even after the treatment the water contain substantial amounts of dissolved ions. The aim of this work was to assess the chemical and physical characteristics of the treated effluent and evaluate the toxicity using *Allium cepa* (onion) as the organism test. Onion as a bioindicator has been widely used in tests to examine effects caused by toxic metals present in wastewaters. The ARD studied came from coal mine located in Brazil, highly associated with pyrite. This wastewater is concentrated in iron, sulfate ions with the presence of aluminum, manganese, zinc and small amounts of lead and arsenic. The following treatment condition were tested accordingly the alkaline chemical reagent and neutralization pH: NaOH - pH 7.0 +/-0.1; NaOH - pH 8.7 +/-0.1; Ca(OH)₂ - pH 7.0 +/-0.1; Ca(OH)₂ - pH 8.7 +/- 0.1. All treatment conditions resulted in a considerable reduction of the concentration of the metals, although Mn an As still remained above or very near the maximum limits for discharge accordingly to the Brazilian legislation. Best results in terms of overall metal removal, including manganese and sulfate removal and final conductivity were achieved with Ca(OH)₂ at pH 8.7. Phytotoxicity tests were performed with *Allium cepa* in order to verify the efficiency of the adopted processes. The results showed that the raw ARD drainage was toxic, since it was able to cause total inhibition of root growth in the phytotoxicity assay. On the other hand, the treatments generated clarified water that does not present toxicity. There were no inhibition nor a delay in the growth of *Allium cepa* roots when compared to the control sample. Treatment Ca(OH)₂ at pH 8.7 presented a little bit better performance in terms of roots growth compare to the other conditions applied.

**Introduction**

Control of ARD (acid rock drainage) continues to be a major subject of interest in mining. Although new approaches are in development, conventional active treatment of acidic waters still remains as an efficient way to avoid water and soil pollution (Kefene et al., 2017; Masindi et al., 2018; Neculita e Rosa, 2019; Naidu et al., 2019; Skousen et al., 1996).

The active treatment of ARD involves the addition of alkaline reagents to increase the pH and precipitate the dissolved metals as hydroxides (Skousen et al., 1996; Kontopoulos, 1998; Matlock et al., 2002; Johnson and Hallberg, 2005). The choose of the best pH depends on the dissolved metals to be remove. Considering the acidic waters treatment plants in coal mining in Brazil, some prefer a circumneutral pH and others pH 8.7 when necessary remove manganese along with other metals. The reagents that are commonly used are the calcium hydroxide.
Calcium hydroxide is preferred since it is cheaper and allows partial removal of the amount of sulphate ions present in the wastewater (Silveira et al., 2009).

Assessment of the toxic potential of mining wastewater is very relevant. Test organisms such as *Daphnia magna*, *Lactuca sativa* (lettuce) and *Allium cepa* (onion) has been references in ecotoxicological studies of ARD. Sivula et al. (2018) evaluated the toxicity associated with an ARD by using the organism *Daphnia magna*, due to high sensitivity of the organism to environmental changes, especially regarding the toxicity of metals and variation of acidity. Steyn et al. (2019) has chosen to evaluate the effectiveness of treatment of ARD using organisms *Lactuca sativa* and *Allium cepa*, as they are quick and simple methods to evaluate phytotoxicity of substances based on seed germination and growth inhibition root, respectively. Geremias et al. (2012) evaluated the effectiveness of treatment of ARD using the organism *Allium cepa*, and justified your use highlighting advantages such as low cost, high sensitivity, reproducibility and high productivity. A series of other studies described the advantages of *Allium cepa* as bioindicator in detail, such as the works of Fiskesjö (1985), Rankand Nielsen (1994), Maluszynska and Juchimiuk (2005), and Arraes and Longhin (2012).

The aim of this work was to assess the chemical and toxicological characteristics of the treated effluent and evaluate the toxicity using *Allium cepa* (onion) as the organism test. The ARD studied came from coal mine located in Brazil, highly associated with pyrite. This wastewater is concentrated in iron, sulfate ions with the presence of aluminum, manganese, zinc and small amounts of lead and arsenic. The main variable studied were the alkaline chemical reagent (Ca(OH)$_2$ or NaOH) and pH (pH 7.0 +/-0.1 pH 8.7 +/-0.1).

**Materials and methods**

The sample of Acidic Drainage used in the development of this work was provided by Companhia Carbonífera do Cambuí LTDA, located in the municipality of Figueira, northeast of the State of Paraná, in the area of the Paraná sedimentary basin.

This work involves the treatment of acid rock drainage by means of the method of neutralization. The chemical and toxicological characteristics of the raw and treated effluent were analysed as illustrated in Figure 1.

The neutralization of the ARD through the addition of two gross reagents alkalizing (NaOH and Ca(OH)$_2$) in two situations different pH (pH 7.0 +/-0.1 pH 8.7 +/-0.1) under constant stirring. The slime formed by precipitation of metals was separated from the solution through filtration. Samples of ARD and the samples after neutralization were analyzed for pH, conductivity and concentration of the metals of Cu, Zn, Fe, Mn, Pb, Al and by issuing optical spectofotometer with Inductively Coupled Plasma (ICP-OES). The sulfate content was measured using the turbidimetric method. All analysis followed the procedures described in the “Standard Methods for Examination of Water and Wastewater” (Eaton et al., 2005)

Eighteen units of *Allium cepa* of the same origin of approximate diameters were selected. The experimentation were carried out in triplicate for each condition. After scraping shallow, this bulb was kept in touch with deionized water for 24 hours at room temperature (in all groups of samples.) After this period, the bulb was transferred to test substance and maintained contact with the same for 72 hours, adopting a control group in deionized water. The test was performed under the light and following the procedure of Fiskesjö (1985). For analysis of toxicity

![Diagram of the experimental procedure.](image1.png)

**Figure 1 Diagram of the experimental procedure.**
was measured number, mass and the length of the three largest roots in each bulb. The results of the test substances were compared with the control. The growth inhibition (phytotoxicity) was considered when there was a significant decrease between the test and control groups. Results of were assessed using analysis of variance (ANOVA) with significance level p ≤ 5% and Tukey Test to compare the differences between averages.

Results and discussion

Table 1 presents the results of the analysis of metals, conductivity and sulfate in raw and treated acid rock drainage, compared to the standard for discharge of wastewater in Brazil (CONAMA N° 430 of 2011 of the Ministry of Environment – Brazil). It can be observed that raw acid drainage has a low pH and a high concentration of metals and sulfate. Considering the treated water, it is possible to see that both reagents (NaOH and Ca(OH)₂) were equally effective in terms of metal removal, but Ca(OH)₂ allowed a higher removal of sulfate ions. Adjustment of pH to 8.7 allowed a higher removal of Fe, which can be explained by the presence of Fe²⁺. At this pH the removal of Mn was also more effective, however not attending yet the concentration for discharge in water courses in Brazil. Concerning the concentration of As, the procedures of neutralization/precipitation was also not effective to reduce the concentration for discharge. All this results are in accordance with the expected in terms of acid mine drainage chemistry (Skousen et al., 1996; Kontopoulos, 1998).

Table 2 shows the average results of growth of the roots of Allium cepa and Figure 2 depicts the bulbs of Allium cepa after the phytotoxicity test. Direct exposure of A. cepa bulbs to raw ARD configured in a complete inhibition of roots growth. However, after treatment, regardless of the reagent applied or the final pH adjustment, it was observed a good roots development with values close to that achieved in the control condition. It should be noted that the difference in length and by weight does not exceed 25% between the control condition and ARD after treatment.

The results statistical analysis is shown in Figure 3. There is a significant difference between the raw and the treated effluents. The control (contact made with deionized water) showed no significant difference with any treatments carried out. It should be mentioned that the analysis of variance (ANOVA) was applied for a 95% confidence level.

It is evident from the results that untreated acid rock drainage promoted phytotoxicity on plants, since it was capable of causing total root growth inhibition, when compared to the control sample (deionized water). Geremias et al. (2012) suggested that the phytotoxic effect would be associated with the low values of pH and a substantial concentration of (semi)-metals such as iron, aluminum, manganese, zinc, lead, and arsenic present in the effluent.

Table 1 Physical chemical characteristics of raw and treated ARD considering the alkaline reagent NaOH or Ca(OH)₂ and the final pH adjustment (pH 7.0 +/-0.1 pH 8.7 +/-0.1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw ARD</th>
<th>NaOH pH 7</th>
<th>NaOH pH 8.7</th>
<th>Ca(OH)₂ pH 7</th>
<th>Ca(OH)₂ pH 8.7</th>
<th>CONAMA 430</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.49</td>
<td>7.00</td>
<td>8.70</td>
<td>7.00</td>
<td>8.70</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>62.03</td>
<td>0.18</td>
<td>0.03</td>
<td>0.05</td>
<td>0.02</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>605.6</td>
<td>13.9</td>
<td>1.73</td>
<td>5.77</td>
<td>0.92</td>
<td>15</td>
</tr>
<tr>
<td>Mn</td>
<td>37.6</td>
<td>14.6</td>
<td>2.93</td>
<td>10.2</td>
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<td>1</td>
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<td>Pb</td>
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<td>0.13</td>
<td>0.20</td>
<td>0.26</td>
<td>0.50</td>
</tr>
<tr>
<td>Al</td>
<td>262.1</td>
<td>0.07</td>
<td>0.13</td>
<td>0.00</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>As</td>
<td>0.90</td>
<td>0.67</td>
<td>0.53</td>
<td>0.71</td>
<td>0.62</td>
<td>0.10</td>
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<tr>
<td>SO₄</td>
<td>7410.2</td>
<td>6443.7</td>
<td>5985.2</td>
<td>3124.8</td>
<td>2726.2</td>
<td>-</td>
</tr>
<tr>
<td>Conductivity (mS)</td>
<td>7.80</td>
<td>9.90</td>
<td>10.10</td>
<td>5.10</td>
<td>5.30</td>
<td>-</td>
</tr>
<tr>
<td>Sludge mass (g)</td>
<td>-</td>
<td>7.80</td>
<td>7.40</td>
<td>9.20</td>
<td>10.90</td>
<td>-</td>
</tr>
</tbody>
</table>

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Table 2 Average values (n = 3) of Allium cepa roots growth in raw and treated ARD considering the alkaline reagent NaOH or Ca(OH)₂ and the final pH adjustment (pH 7.0 +/-0.1 pH 8.7 +/-0.1).

<table>
<thead>
<tr>
<th></th>
<th>Length (cm)</th>
<th>Number of roots</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>5.1</td>
<td>28</td>
<td>0.7</td>
</tr>
<tr>
<td>Raw ARD</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>Treated with NaOH at pH 7.0</td>
<td>6.4</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>Treated with NaOH at pH 8.7</td>
<td>6.6</td>
<td>22</td>
<td>0.6</td>
</tr>
<tr>
<td>Treated with Ca(OH)₂ at pH 7.0</td>
<td>6.5</td>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td>Treated with Ca(OH)₂ at pH 8.7</td>
<td>6.9</td>
<td>20</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Figure 2 Bulbs of Allium cepa after the phytotoxicity test.

The effect of low pH is corroborated by the work of Fiskesjö (1985), which states that Allium cepa is not very sensitive to pH. Acceptable growth in water were found in the pH range between 3.5 and 11.0, since the roots of this species are able to change, to a certain extent, the pH to a level that allows its development. However, the very low pH of ARD of 2.49 falls outside of this range, which explain the absence of roots growth.

Treatment of the effluent allowed the pH adjustment and removal in great part the presence of metals. Despite of high conductivity of the treated water, Allium cepa showed a good development. This ecotoxicological did not showed differences between the chemical reagent applied and the differences of conductivity derived. Neither showed differences between the pH of metal precipitation - pH 7.0 or 8.7.

Considering the metals, copper and lead are indicated by Fiskejö (1985) as the main responsible for changes in the development of Allium cepa. However, these elements are present in low concentration in the effluent studied. Concentration manganese and arsenic, their concentration remains superior to the standards established by CONAMA 430. It is known that manganese concentrations above 18 mg L⁻¹ can cause effects on the growth of roots (Fiskesjö, 1985) and, based on this information, it is important to choose pH 8.7 at ARD treatment plants. The toxicity for arsenic is even greater than manganese, chronical effects are associated by the presence of this metal gives a well a decrease in mitotic index and generates chromosomal (Patra, 2004). The process of neutralization/precipitation applied in the conditions of this work was not suitable to remove this element to Brazilian standards of wastewater discharge, being a subject of future attention.

Conclusion

Acid rock drainage used in this work presented a pH of 2.5 and a high concentration of metals. Treatment through of neutralization/precipitation proved efficient, with removal of most metals. Even after treatment, the presence of Mn and As were above the standards established for discharge in water bodies in Brazil. The results of the tests of phytotoxicity with Allium Cepa showed that the raw ARD has a high degree of phytotoxicity, which caused complete inhibition of growth of the roots. Such inhibition was not evidenced in the post-treatment carried out, demonstrating no phytotoxicity roots growth for Allium
Allium cepa. The statistical evaluation of the results indicated that there is no significant difference for this toxicological test applied for anyone of the treated effluents (considering NaOH and Ca(OH)2 as reagents or precipitation pH at 7.0 or 8.7) compared to the control, proving the effectiveness of the treatment.

Acknowledgements
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References


Electrochemical Removal and Kinetics in the Removal of Fluoride from Underground Water in Kenya

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Abstract
The geology of Kenya makes it one of the countries in the World where Fluoride (F) occurs in high concentrations, in rocks, soil, surface and groundwater. Fluoride levels above 1.5 mg/L leads to skeletal and dental fluorosis which is evident in Rift Valley and Central Kenya. Electrochemical batch tests were conducted using standard NaF solution and aluminium anode to study the effects of; inter-electrode distance, supporting electrolyte, solution pH and Initial F concentration. The optimum inter electrode distance was 12 mm - 25 mm. Increasing surface area reduced F removal and current density with 20 cm² being optimum. Optimum pH ranged between 4 and 6 and was related to the amphoteric character of Al (OH)₃. Addition of NaCl supporting electrolyte increased F removal by 43.3 % and reduced specific energy by 44.6%. Adsorption process followed a second order reaction with the Lagegren model confirming that the rate constant increased with increasing fluoride concentration. The optimum results will be used to fabricate a prototype flow reactor that uses renewable solar energy.

Key words: Electrocoagulation, Kinetics, Lagegren, Amphoteric, Aluminium

Introduction
Fluoride occurs commonly in drinking water. Whilst fluoride was artificially added to drinking water for 210 million people [WHO, 1994] in industrial countries (Peterson 2004) to prevent caries, the fluoride concentration is exceeded to an unhealthy extent in at least 27 (Takdastan et al. 2014) developing countries. The concentration of fluoride between 0.8 mg/L and 1.0 mg/L is considered as healthy and as an effective prevention of caries. The WHO recommended limit of fluoride in drinking water is 1.5 mg/L. Long-term intake of water with higher concentration causes dental and skeletal fluorosis (WHO, 2018). Whereas dental fluorosis has only esthetical effect skeletal fluorosis leads to weakening of the bone frame due to accumulation over several years and finally to deformation of the whole skeleton. Furthermore, the damaged skeleton causes stiffness and pain in connecting joints.

Sources of exceeding fluoride concentration can be natural, e.g. volcanic (WHO 1994) as well as anthropogenic. The latter is caused by releasing untreated wastewater from industries like glass manufacturing, semiconductor production (Emamjomeh et al. 2011) and mining of fluorspar.

There are several conventional methods for treating wastewater to remove pollutants. However, the methods may not remove F to the desired levels. Electrocoagulation method that uses Aluminium anode will be investigated under different conditions in an electrolytic cell in a batch reactor to come up with optimum conditions

Methodology
The electrocoagulation reaction was carried out as batch tests in 250 mL polypropylene vessels. During the process, the treatment
solutions were stirred by a magnetic stirrer at 200 rpm. The treatment was carried out by a system of two or four electrodes provided with direct current. After the treatment the solution was filtered through cellulose round filters and analyzed.

During the experimental part the number of electrodes was increased from two to four which increases the active cell volume by three.

The parameters measured in raw and treated samples included: fluoride, aluminium ion concentration, conductivity and pH. Voltage was recorded in 10-min intervals.

Electrode distance was varied to 3 mm, 6 mm, 9 mm, 12 mm, 15 mm, 21 mm, 24 mm and 33 mm using an insulator. Initial fluoride concentration was varied to 4.5 mg/L, 11.3 mg/L, 17.1 mg/L, and 44 mg/L. Sodium Chloride Supporting electrolyte was varied to give 0, 10, 20, 30 and 50 mg/L NaCl. The initial pH of the solution was varied to 4.5, 6.7.8 and 9 using dilute solutions of either 0.1M NaOH or 0.1M HCl. Fluoride concentration was varied to 4.5 mg/L, 11.3 mg/L, 17.1 mg/L and 44 mg/L.

Conductivity and pH were determined by Fluorides were analyzed by the SPADNS spectrometric method using spectrometer MD 600

Results and Discussion

(a) Electrode distance

The amount of removed fluoride and produced aluminium ions at different times and same conditions except for the electrode distance was determined. The results are shown in Figure 2.

The fluoride removal efficiency along with the aluminium production increases at both treatment times with increasing electrode distance up to an optimum between approximately 12 mm and 25 mm. Non-conductive hydrogen bubbles cover the surface of the cathode and hence reduce the active area. Because of the small distance between the electrode plates there is only little mixing within the cell.

Therefore, hydrogen bubbles as well as formed aluminium hydroxide covering the plates cannot be removed. Also the change of already treated electrolyte between the
After passing the optimum the EC process is complicated because of the larger way the charge carriers have to cover. Takdastan (2014) also confirmed this correlation in his studies of influence of electrode distance on the EC of fluoride which confirmed less removal efficiency with increasing distance.

b) Supporting electrolyte

The amounts of removed fluoride and produced aluminium ions at different initial conductivities caused by addition of sodium chloride were determined. The results are shown in Table 2 and Figure 3.

Increased conductivity caused by a strong supporting electrolyte like sodium chloride increased the fluoride removal efficiency in a linear correlation. However, addition of 50 mg/L NaCl led to to 43.3% fluoride removal and 44.6% power reduction.

The results show that the addition of a supporting electrolyte decreases the power consumption of the process in an inverse relationship. The power consumption per removed amount of fluoride is decreased by 44.6 % at 50 mg/L added NaCl respectively 716 µS/cm. Hence addition of a strong electrolyte supports fluoride removal efficiency as well as energy consumption.

c) Initial pH

The amounts of removed fluoride and produced aluminium ions as well as the final pH at different initial pH were determined and the results are shown in Figure 4. The results show that the fluoride removal efficiency decreases with increasing initial pH. This behaviour is explained by the amphoteric character of aluminium hydroxide which reacts to tetra hydroxy aluminate beginning at pH above 6 (Eqn. 5).

According to Pearson the aluminium ion is a hard acid (trivalent, ionic radius 50 pm) and therefor has a tendency to react with hydroxide ions as a hard base. The hydrolysis

### Table 2 Fluoride removal and aluminium production at different NaCl concentrations

<table>
<thead>
<tr>
<th>Supporting Electrolyte</th>
<th>Initial conductivity [µS/cm]</th>
<th>Fluoride loss [mg]</th>
<th>Aluminium production [mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>646</td>
<td>1.50</td>
<td>13.8</td>
</tr>
<tr>
<td>10.00</td>
<td>654</td>
<td>1.88</td>
<td>15.0</td>
</tr>
<tr>
<td>20.00</td>
<td>666</td>
<td>1.90</td>
<td>15.6</td>
</tr>
<tr>
<td>30.00</td>
<td>684</td>
<td>2.08</td>
<td>17.1</td>
</tr>
<tr>
<td>50.00</td>
<td>716</td>
<td>2.15</td>
<td>18.1</td>
</tr>
<tr>
<td>Max. efficiency increase</td>
<td>--</td>
<td>43.3%</td>
<td>31.2%</td>
</tr>
</tbody>
</table>

Figure 3 Power Consumption per Removed Amount of Fluoride at different Initial Conductivities
of the aluminium ion depends on pH of the aqueous environment. Aluminium complexes are octahedral and hence have six ligands. At pH < 4 the dominant species is \([\text{Al(H}_2\text{O)}_6]^{3+}\) while at pH > 3 hydroxide ions begin to join the complex. The pH-dependent reactions whose describe the amphoteric character of aluminium hydroxide are listed in Eqsns. 2-4.

This ion cannot act as coagulant thus fluoride remains in the treatment solution. Furthermore, the pH is raised during the EC process due to its consumption of hydrogen ions respectively the formation of hydroxyl ions at the cathode (Eqn. 6).

In case of a high initial reaction, Eqn. 4 seems to be dominant and the consumption of hydrogen ions occurs hence pH drops. To ensure comparability between the different pH series the initial conductivity was maintained to the same value using NaCl. This step was necessary because the initial pH was adjusted using HCl.

d) Initial fluoride concentration

The amount of removed fluoride at different initial fluoride concentrations during the treatment process was determined. Therefore samples from the treatment solution were taken at different time intervals. The results are shown in Figure 5.

The fluoride loss is not linear to the reaction time because the complexation of aluminium fluoride hydroxide obeys a second order Lagergren model (Vasuderan et al. 2011; Zegwe 2017) (Eqn. 6) featuring time t, mass concentration of fluoride \(\beta(\text{F}^-)\), rate constant \(K_2\) and equilibrium mass concentration \(\beta_e(\text{F}^-)\)

\[
t/ \beta(\text{F}^-) = 1/k_2 \beta_e(\text{F}^-)^2 + 1/\beta_e(\text{F}^-)
\]

Therefore, the half-life period of fluoride depends on the initial concentration. This is shown in Figure 5 using the dotted 50 % line for the relative fluoride loss. Noticeably the half-life period between the initial fluoride concentrations from 4.5 mg/L to 44.0 mg/L increased from about 7 min to 16 min. The applied Lagergren model for all four concentrations is shown in Figure 7.

\[
pH 4 - 8: [\text{Al(H}_2\text{O)}_3\text{OH}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Al(H}_2\text{O)}_3\text{OH}]^{2+} + \text{H}^+ + \text{OH} \\
pH 4 - 9: [\text{Al(H}_2\text{O)}_3\text{OH}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Al(H}_2\text{O)}_3\text{OH}]^{2+} + \text{H}_2\text{O} + [\text{Al(H}_2\text{O)}_3\text{OH}]^{2+} + \text{H}^+ + \text{OH} \\
pH > 6: [\text{Al(H}_2\text{O)}_2\text{OH}]^{+} + \text{H}_2\text{O} \rightarrow [\text{Al(H}_2\text{O)}_2\text{OH}]^{+} + \text{H}_2\text{O} + [\text{Al(H}_2\text{O)}_2\text{OH}]^{+} + \text{H}^+ + \text{OH}
\]

Eqn. 3
Eqn. 4
Eqn. 5

Cathode reaction: \(3\text{H}_2\text{O} + 3\text{e}^- \rightarrow 3/2 \text{H}_2(\text{g}) + 3\text{OH}^-\)  

\[E^0 = 0\text{V (pH 0)}\]  
\[E^0 = -0.83\text{V (pH 14)}\]  

Figure 4 Fluoride removal and aluminium production at different initial pH values
This includes equilibrium concentration of fluoride \( \beta_e (F) \), rate constant \( k_2 \) and all second order terms \( t/\beta(F) \).

Figure 6 shows that the slope of the Lagegren function decreases with increasing initial fluoride concentration. As a result, the rate constant increases with increasing initial fluoride concentration as well as the equilibrium concentration of fluoride. Between 4.5 mg/L and 44.0 mg/L initial concentration, which is about tenfold higher, the slope decreased by 24 and the rate constant as well as equilibrium concentration increased by same margin. These results can be applied only for the treatment time of 30 min.

The functions of fluoride loss in Figure 22 assume that the reactions are not finished within this time interval. Vasudevan (2011) and Zewge (2017) determined the rate constants within 300 min and 1400 min respectively. Therefore, our resulting rate constants and equilibrium concentrations can only give a tendency about the influence of the initial fluoride concentration. To determine the exact parameters within our applied conditions, a longer treatment time has to be used.
Acknowledgements
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References
Resistance of Actinobacteria of the genus *Gordonia* to potentially toxic metals

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Abstract

Effects of potentially toxic metals (Cd, Cr, Cu, Mo, Ni, Pb, Zn) on the strains of alkanotrophic Actinobacteria of the genus *Gordonia* were studied. The strains were isolated from the samples of oil-contaminated soils and wastewater. Collection strains of *Gordonia* spp. highly resistant to potentially toxic metals (up to 40.00 mM) were selected. These strains are recommended for use in technologies for cleaning wastewater and water bodies contaminated with potentially toxic metals.

Keywords: *Gordonia*, Actinobacteria, bioremediation, potentially toxic metals

Introduction

According to N. Reimer’s classification, metals with a density of more than 8 g/cm³ and a weight of more than 50 atomic units should be considered as potentially toxic metals (PTMs). Environmental pollution by PTMs is one of the most common and environmentally hazardous types of anthropogenic pollution for living organisms. The production of many industries is accompanied by the uncontrolled supply of non-degradable and highly toxic wastes containing high concentrations of PTMs into natural ecosystems (Beretta 2018).

Industrial wastewater from chemical, textile, engineering, electrotechnical plants, non-ferrous metalurgy and other industries is contaminated with salts of non-ferrous and potentially toxic metals (Zaynutdinova 2013). Wastewater is most frequently polluted with zinc, cadmium, copper, chromium, nickel, mercu-ry, iron compounds, less often with cobalt and manganese. Contaminated wastewater generally contains a mixture of several PTMs (Berengarten 2008; Varaeva 2016).

Traditional ways of wastewater treatment from PTMs are based on the use of physicochemical methods (Sokolov 2015), which are not environmentally safe and do not provide complete removal of PTM ions from wastewater (Elizarova 2016). Modern approaches involve the use of biological methods of purification, such as aquatic plants, and bioreactors combined with immobilized microorganisms (Erum 2015; Shekhar 2015). In this connection, researchers are attracted by Actinobacteria with a wide range of functional capabilities, like utilization of natural and anthropogenic hydrocarbons as a carbon source, degradation of pharma pollutants, oil products and other emergent pollutants, as well as the production of active biosurfactants and complexes that facilitate mobilization and desorption of PTM ions.

The purpose of this work is to analyze the resistance of alkanotrophic Actinobacteria of the genus *Gordonia* to potentially toxic metals.

Methods

The working collection included 98 strains of Actinobacteria from the Regional Specialized Collection of Alkanotrophic Microorganisms (www.iegmcol.ru) representing the species *Gordonia alkanivorans* (2 strains), *G. amicalis* (8 strains), *G. rubripertincta* (59 strains), and *G. terrae* (29) (tab. 1). The strains were previously isolated from oil- and PTM contaminated soils and waters. The following salts were used in this work:
CuSO₄·5H₂O, (CH₃COO)₂Cd·2H₂O, K₂CrO₄, (NH₄)₂MoO₄·2H₂O, NiSO₄·7H₂O, Pb(NO₃)₂, ZnSO₄·7H₂O. Salt concentrations ranging from 0.08 to 80.00 mM in terms of pure metal. The degree of Actinobacterial resistance to PTMs was evaluated based on the minimum inhibitory concentrations (MICs) determined by the microwell method (Kuyukina 2001). For this, 100 μl of nutrient broth were aseptically applied to each well of a 96-well immunological plate, and aqueous solutions of PTM salts were serially diluted. As inocula, 48 h cultures of Actinobacteria pre-grown on the meat infusion agar were used. Bacterial suspensions (from 1.0 to 2.0 × 10⁹ cells/ml) were prepared in a sterile saline solution (0.5% NaCl solution) and added to the wells containing the limiting dilutions of HMs. The plates were incubated in a thermostat at 28° C for 48 h. Once the incubation period was over, 50 μl of 0.2% iodonitrotrosozolium chloride aqueous solution (Sigma, United States) was added to each well. This dye is known to act as a competitive oxygen acceptor of electrons in the electron transport chain of aerobic organisms. When the dye is introduced into the medium, it is reduced to water-insoluble formazan, which manifests itself in a few minutes as red-violet staining only in the presence of actively respiring microorganisms. The controls used were (1) a bacterial culture grown in the nutrient medium without adding the metals, and (2) a non-inoculated nutrient medium. The experiments were carried out in quadruplicates.

**Results**

According to our data, all cultures retained the ability to grow in the presence of PTM ions. MIC values ranged from 0.08 to 40.0 mM. Figure 1 presents the data obtained by the cluster analysis. They illustrate the distribution of the bacte-rial cultures in clusters depending on the degree of resistance to PTMs. As seen from the dendrogram, the strains tested are combined into four groups. Group D consists of strains with intragroup similarity up to 5 standard units, and the level of resistance ≤ 1.25 mM. Group C includes strains resistant to HMs in the range of 1.25 – 2.50 mM. Group B strains resist to PTM concentrations from 2.50 to 5.00 mM. Strains with the highest resistance are combined into group A (MIC ≥ 5.00 mM).

Based on the intraspecific degree of resistance to PTM ions, they can be presented in a row: G. amicalis > G. terrae > G. rubripertincta > G. alkanivorans, where the most resistant are G. amicalis, less re-sistant are G. alkanivorans. Table 2 presents the average data on intraspecific resistance to PTMs (mM).

### Table 1 Strains of Gordonia spp. used in the experiments.

<table>
<thead>
<tr>
<th>Species</th>
<th>Strains</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. alkanivorans</td>
<td>IEGM 748, 1269</td>
</tr>
<tr>
<td>G. amicalis</td>
<td>IEGM 726, 768, 1266, 1273, 1274, 1275, 1277, 1279</td>
</tr>
<tr>
<td>G. terrae</td>
<td>IEGM 108, 130, 136, 143Т, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 586, 735, 751, 1123</td>
</tr>
</tbody>
</table>

### Table 2 Resistance of Gordonia species to PTMs.

<table>
<thead>
<tr>
<th>Species</th>
<th>Cd²⁺</th>
<th>CrO₄²⁻</th>
<th>Cu²⁺</th>
<th>MoO₄²⁻</th>
<th>Ni²⁺</th>
<th>Pb²⁺</th>
<th>Zn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. alkanivorans</td>
<td>0.40±</td>
<td>2.82±</td>
<td>2.50±</td>
<td>1.57±</td>
<td>1.88±</td>
<td>10.00±</td>
<td>0.67±</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>2.19</td>
<td>0.0</td>
<td>0.94</td>
<td>0.63</td>
<td>0.0</td>
<td>0.59</td>
</tr>
<tr>
<td>G. amicalis</td>
<td>0.92±</td>
<td>4.69±</td>
<td>3.59±</td>
<td>2.34±</td>
<td>4.06±</td>
<td>16.25±</td>
<td>5.12±</td>
</tr>
<tr>
<td></td>
<td>0.44</td>
<td>2.32</td>
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<td>0.41</td>
<td>1.21</td>
<td>6.5</td>
<td>3.37</td>
</tr>
<tr>
<td>G. rubripertincta</td>
<td>0.51±</td>
<td>2.94±</td>
<td>2.34±</td>
<td>2.32±</td>
<td>2.21±</td>
<td>6.86±</td>
<td>1.42±</td>
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<tr>
<td></td>
<td>0.58</td>
<td>1.85</td>
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<td>1.36</td>
<td>1.77</td>
<td>6.0</td>
<td>1.12</td>
</tr>
<tr>
<td>G. terrae</td>
<td>1.20±</td>
<td>3.90±</td>
<td>1.55±</td>
<td>2.13±</td>
<td>3.49±</td>
<td>4.21±</td>
<td>2.20±</td>
</tr>
<tr>
<td></td>
<td>3.58</td>
<td>7.13</td>
<td>0.61</td>
<td>0.88</td>
<td>7.03</td>
<td>2.26</td>
<td>7.18</td>
</tr>
</tbody>
</table>
Figure 1 Dendrogram showing the resistance of the genus Gordonia strains under study to HMs.
Among the actinobacteria of the genus *Gordonia*, *G. terrae* strains had the highest resistance to PTMs. Compared with *G. rubripertincta*, their resistance to cadmium, chromium, and zinc was 8, 4, and 8 times higher, respectively (tab. 3).

Of 59 *G. rubripertincta* strains, *G. rubripertincta* IEGM 99, 730, and 733 showed high resistance to PTMs. Their MIC values were on average ≥ 10 mM (tab. 4).

Low resistance to PTMs was detected in strains belonging to *G. amicalis* and *G. alkanivorans*. Their resistance was significantly lower (from 2 to 32 times), compared with *G. terrae* strains. The most resistant strains of these species are presented in Tables 5–6.

**Conclusions**

In this study, the resistance of *Gordonia* spp. to PTMs was investigated. According to the degrees of toxic effects on the strains studied, PTM ions can be arranged in the following order: Cd$^{2+}$ > MoO$_4^{2-}$ > Zn$^{2+}$ > Cu$^{2+}$ > Ni$^{2+}$ > Pb$^{2+}$.

**Table 3** Resistance of *G. terrae* to HMs.

<table>
<thead>
<tr>
<th>Strains</th>
<th>PTM</th>
<th>MIC, mM</th>
</tr>
</thead>
<tbody>
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<td>IEGM 735</td>
<td>Cd$^{2+}$</td>
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</tr>
<tr>
<td>IEGM 735</td>
<td>CrO$_4^{2-}$</td>
<td>40</td>
</tr>
<tr>
<td>IEGM 143, 149, 154, 159, 735, 751, 1123</td>
<td>Cu$^{2+}$</td>
<td>2.5</td>
</tr>
<tr>
<td>IEGM 735</td>
<td>MoO$_4^{2-}$</td>
<td>5</td>
</tr>
<tr>
<td>IEGM 735</td>
<td>Ni$^{2+}$</td>
<td>40</td>
</tr>
<tr>
<td>IEGM 161, 735</td>
<td>Pb$^{2+}$</td>
<td>10</td>
</tr>
<tr>
<td>IEGM 735</td>
<td>Zn$^{2+}$</td>
<td>40</td>
</tr>
</tbody>
</table>

**Table 4** Resistance of *G. rubripertincta* to HMs.

<table>
<thead>
<tr>
<th>Strains</th>
<th>PTM</th>
<th>MIC, mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEGM 126, 730, 733</td>
<td>Cd$^{2+}$</td>
<td>2.5</td>
</tr>
<tr>
<td>IEGM 732</td>
<td>CrO$_4^{2-}$</td>
<td>10</td>
</tr>
<tr>
<td>IEGM 95T, 105, 730,733, 734, 747, 749</td>
<td>Cu$^{2+}$</td>
<td>5</td>
</tr>
<tr>
<td>IEGM 99</td>
<td>MoO$_4^{2-}$</td>
<td>10</td>
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<td>IEGM 721,733</td>
<td>Ni$^{2+}$</td>
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</tr>
<tr>
<td>IEGM 126</td>
<td>Pb$^{2+}$</td>
<td>40</td>
</tr>
<tr>
<td>IEGM 99, 124, 730</td>
<td>Zn$^{2+}$</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 5** Resistance of *G. amicalis* to HMs.

<table>
<thead>
<tr>
<th>Strains</th>
<th>PTM</th>
<th>MIC, mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEGM 1266, 1274, 1275, 1277, 1279</td>
<td>Cd$^{2+}$</td>
<td>1.25</td>
</tr>
<tr>
<td>IEGM 1273</td>
<td>CrO$_4^{2-}$</td>
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<tr>
<td>IEGM 1266, 1273, 1274, 1279</td>
<td>Cu$^{2+}$</td>
<td>5</td>
</tr>
<tr>
<td>IEGM 726, 768, 1273, 1274, 1275, 1277, 1279</td>
<td>MoO$_4^{2-}$</td>
<td>2.5</td>
</tr>
<tr>
<td>IEGM 768, 1266, 1273, 1274, 1277, 1279</td>
<td>Ni$^{2+}$</td>
<td>5</td>
</tr>
<tr>
<td>IEGM 768, 1266, 1274, 1275, 1277, 1279</td>
<td>Pb$^{2+}$</td>
<td>20</td>
</tr>
<tr>
<td>IEGM 1266, 1274</td>
<td>Zn$^{2+}$</td>
<td>10</td>
</tr>
</tbody>
</table>

**Table 6** Resistance of *G. alkanivorans* to HMs.

<table>
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<tr>
<th>Strains</th>
<th>PTM</th>
<th>MIC, mM</th>
</tr>
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<tbody>
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<td>IEGM 748</td>
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</tr>
<tr>
<td>IEGM 748</td>
<td>CrO$_4^{2-}$</td>
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<tr>
<td>IEGM 748, 1269</td>
<td>Cu$^{2+}$</td>
<td>2.5</td>
</tr>
<tr>
<td>IEGM 748</td>
<td>MoO$_4^{2-}$</td>
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<tr>
<td>IEGM 748</td>
<td>Ni$^{2+}$</td>
<td>2.5</td>
</tr>
<tr>
<td>IEGM 748, 1269</td>
<td>Pb$^{2+}$</td>
<td>10</td>
</tr>
<tr>
<td>IEGM 748</td>
<td>Zn$^{2+}$</td>
<td>1.25</td>
</tr>
</tbody>
</table>
CrO$_4^{2-}$ > Pb$^{2+}$, where cadmium is the most toxic, and lead is the least toxic. The collection strains of G. alkanivorans IEGM 748; G. amicalis IEGM 1266, 1274; G. rubripertincta IEGM 99, 126, 733; and G. terrae IEGM 149, 735 with high resistance levels to PTMs were selected. These strains are promising for the development of efficient processes for biotechnological treatment of wastewater and soil contaminated with PTMs.

**Acknowledgements**

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Abstract

About 8 million metric tons storage of cyanidation tailings from a former French gold mine produces a 10 m$^3$/h mine drainage that contains around 8 mg/L of As and 1 g/L of SCN– and is currently treated with a lime process. The existing treatment plant produces large amounts of sludge reflecting the large amounts of sulfate present in water and calcium from lime. The present study aims to developing a semi-passive mine water treatment process that would produce a lower amount of sludge and improve the treatment efficiency with a target discharge level under 100 µg/L of Arsenic.

Keywords: mine water treatment, arsenic

Introduction

As a first step, several options have been considered for arsenic and thiocyanate treatment whilst taking account the mine water characteristics.

Arsenic treatment:
Nowadays, arsenic treatment processes can be classified into four categories (Vu, 2003): Ion exchange, Membrane processes, Precipitation or Adsorption. Ion exchange and membrane processes have been excluded due to their cost and low efficiency. Precipitation can take place in acidic conditions, e.g. the precipitation of arsenic with sulphide forms Orpiment (As$_2$S$_3$) or Realgar (As$_4$S$_4$). As a real example, a large-scale precipitation bioassay has been implemented for heavily loaded arsenic (200 mg/L) water at the Trail site (British Columbia, Canada) (Evans, 2011). The pH of treated water rose from 5.8 initially to 6.5 and the arsenic concentration was reduced to 0.75 mg/L.

The lime treatment of arsenic waters is a precipitation process and has commonly been used in metallurgical production units (Riveros, 2001). Arsenic (V) co-precipitates to give calcium arsenate according to:

$$6\text{Ca(OH)}_2(s) + 4\text{H}_3\text{AsO}_4(aq) \rightarrow 2\text{Ca}_3(\text{AsO}_4)_2(s) + 12\text{H}_2\text{O}$$

This process generates large amounts of contaminated sludge, potentially able to release arsenic with time, thus it is not efficient at long term.

An alternative is the adsorption of arsenic on oxides of manganese (Hou 2017, Mishra 2016), aluminum or iron, and this has been widely studied to treat arsenic waters (Kaminski 2003) or on lanthanum compounds (Tokunaga, 1997, Haron 2001). At pH < 7.5, As (V) is more easily trapped than As (III). Concerning the adsorption of arsenic, several competing anions are identified: carbonates, bicarbonates and phosphates ions (Burnol 2007). Competition occurs mainly at low pH around 6. At pH 8 competition appears very limited (Burnol 2007). Finally, pH can limit adsorption of arsenate if pH is larger than 8 (Raven 1998).

Thiocyanate treatment:
Thiocyanate can be treated by chemical processes with strong oxidants like ozone or hydrogen peroxide (Gould 2012). However, these chemical processes are either ineffective, or too expensive, or generate one or more hazardous by-products, so they are usually not implemented in practice. Thiocyanate can advantageously be removed by bio-processes, based on its oxidation catalyzed by bacteria that use them as energy, sulfur, carbon and nitrogen sources. Some mining sites use this process at the industrial scale, such as the gold Homestake mine (South Dakota, United States) (Mudder 1984) and the Nickel Plate mine (British Columbia, Canada) (Gould 2012). Different technologies for enhancing
contact between bacteria and water can be used: simply agitated continuous reactors (suspended bacteria), ascending biofilters, trickle biofilters, fluidized supported beds. These are essentially active technologies whose kinetics of degradation of thiocyanates range between 15 mg SCN\textsuperscript{−}/L/h (Villemur 2015) and 194 mg SCN\textsuperscript{−}/L/h (Jeong 2006).

After considering potential processes used for arsenic and thiocyanate removal, the process retained here is based on the adsorption of arsenic on ferrihydrite precipitate combined with the biodegradation of SCN\textsuperscript{−}. In the present study, a semi-passive mine water treatment process is developed, in order to produce a lower amount of sludge and to improve the treatment efficiency (target discharge level under 100 µg/L of Arsenic).

**Background**

Water pollution caused by mine drainage is a modern concern that requires to be addressed in order to protect local ecosystems and fulfill the regulation. This study focuses on treatment of cyanide (CN\textsuperscript{−}), its derivate thiocyanate (SCN\textsuperscript{−}) and arsenic (As) in a water drainage originating from mine tailings of a former gold-mine site. In this site, 10 m\textsuperscript{3}/h (average) of water is produced by around 8 million metric tons storage of cyanidation residue. This water contains around 8 mg/L of As and 1 g/L of SCN\textsuperscript{−}, is rich in dissolved salts (Table 1) and has a pH close to 8. This water is currently treated within a lime process. The treatment plant produces large amounts of solid waste (sludge), mainly calcite (CaCO\textsubscript{3}), gypsum (CaSO\textsubscript{4}), and brucite (Mg(OH)\textsubscript{2}), reflecting the large amounts of sulfate present in water and the amounts of lime used in process.

In the lime process, arsenic is trapped as calcium arsenate. Process efficiency reaches 90 % on average, the outlet concentration being between 0.5 mg/L and 1 mg/L of arsenic when regulatory objective is generally 0.1 mg/L in discharge waters. However, calcium arsenate is an unstable product that reacts with atmospheric CO\textsubscript{2} to form soluble arsenic and calcite (Riveros, 2001). In addition, the current process does not remove thiocyanate from effluent. Instability of calcium arsenate, the large quantities of sludge produced and high operating cost of lime process brought the post-mining department (DPSM) of BRGM (the French geological survey, in charge of the site since 2006) to look for a more efficient process. This work implied lab experiments that ultimately aimed at designing an on-site pilot plant.

**Lab experiments**

In order to develop a pilot plant on-site, numerous lab experiments were performed: batch experiments, followed by continuous lab experiment with columns filled with pozzolana for both thiocyanate bio-oxidation and arsenic adsorption, and finally continuous lab experiments in which columns were replaced by a settling tank for arsenic adsorption and co-precipitation with iron.

First, batch experiments aimed to determine the optimal iron concentration (10 to 30 mg/L) and to test the relative efficiency of two sources of Fe III: Fe II sulfate (that is rapidly oxidized into Fe III) and Fe III chloride.

![Figure 1](image-url) shows results of this batch experiment. It is noticed that FeIII reacts faster than FeII. A few minutes are enough to reduce arsenic concentration. Nevertheless, FeII sulfate appears more efficient than FeIII chloride as it prevents the late release of arsenic after 24 h (figure 1).

Continuous lab experiments consisted in mixing ferrous sulfate solution (Fe\textsuperscript{2+} 20

<table>
<thead>
<tr>
<th>Substance</th>
<th>Conc. (mg/L)</th>
<th>Substance</th>
<th>Conc. (mg/L)</th>
<th>Substance</th>
<th>Conc. (mg/L)</th>
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*thiocyanate SCN excluded

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
Complete oxidation of ferrous iron was achieved and the effluent contained 2 mg/L of arsenic, indicating a 70% arsenic removal (figure 3a). Arsenic was present in soluble form (filtration at 0.45 μm) (50% of total As) and in particles form associated to iron oxides which were formed in the settling tank. A second experiment was conducted on settling tank (figure 3b), with a contaminated flow of 55 mL/h representing a residence time of 34.7 h and an input iron concentration of 25 mg/L. The goal was to enhance the sedimentation of particles via higher iron concentrations. Results (figure 3b) show a lower concentration of dissolved arsenic (300 μg/L average) in the effluent but it remains always around 2 mg/L of arsenic adsorbed on iron hydroxide particles. In conclusion, it is efficient and allows to reduce soluble arsenic concentration by 96%. This step should be followed by a filtering step to remove the iron particles and meet the target discharge level of 100 μg/L.

Regarding thiocyanate biodegradation, two bioreactors were implemented. Bio-oxidation of SCN⁻ was carried out in an aerated pozzolana bio-filter column functioning in a recycling mode in order to be in “batch” reactor conditions. Reaction rate was monitored over several batches. The first reactor had 440 mL of effective volume while the second had 3000 mL. The airflow was 100 mL/min for the first column and 1 L/min for the second one. The model reaction is the following:

**Figure 1** Batch experiment results with respectively 10 (a), 20 (b) and 30 (c) mg/L of Fe II and Fe III.
SCN$^- + 2\text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{NH}_4^+ + \text{SO}_4^{2-} + \text{H}^+$

Thiocyanate concentration effectively decreased from 1000 mg/L to below quantification limit in approximately 12 days (figure 4a). A linear degradation rate of $-4.5 \pm 1$ mg/L/h was observed repeatedly. Figure 4b shows results obtained when the column was switched in continuous mode. A $-2.5$ mg/L/h degradation rate was then observed. Dictor (1997) reached 81 mg/L/h over the course of 6 months of optimization. The short duration of the experiments could explain the observed low degradation rate. The lack of biofilm development is suspected to be the major factor limiting the degradation rate. At the end of batch experiments, ammonium was quantified in substantial proportions (half of the initial quantity of SCN) whereas nitrate remained under quantification limit.

**Design of the pilot plant for on-site experiments.**

An on-site experiment will be carried out in order to complement key data before final upscaling. According to lab scale experiments results, pilot plant will consist of two treatment steps. The pilot plant will treat a contaminated water flow of 0.100 m$^3$/h. In a first step, thiocyanate will be treated in a biofilter. According to the degradation rate found in literature (Dictor, 1997), a working volume of 1.3 m$^3$ is needed. Given the pozzolana porosity (40%), a 3 m$^3$ biofilter volume will be implemented. A second treatment step
could be an opportunity to identify the potential operational problems due to on-site environmental factors such as algae formation or undesired bacterial contamination.

**Conclusion**

This study was conducted in order to develop and build an optimized mine water treatment plant that will replace the current lime treatment plant. The goal is to develop a more efficient (reduced amount of sludge) and cost effective process. In order to achieve this goal, lab scale experiments were conducted and key data for process upscaling were obtained for the treatment of a mine water containing arsenic and thiocyanate.

As first results, this approach allowed us to design a treatment process for a contaminated mine water with its own characteristics. An in-situ pilot plant was designed. Pilot plant experiments will be conducted from first semester 2019. Key parameters will be followed and the effect of climate variability (temperature) and rainfall will be assessed. This "pilot plant" step must allow to design a treatment plant that will be as much as possible passive. For example, passive oxygenation could be achieved by taking advantage of the site slope using waterfalls. Only pumping of water and injecting ferrous sulfate solution will need energy.

**References**


![Figure 4](image-url)  
**Figure 4** Thiocyanate degradation on pozzolana column; (a) Batch experiments; (b) Continuous flow experiment.


Mishra T and Mahato DK (2016) A comparative study on enhanced arsenic (V) and arsenic (III) removal by iron oxide and manganese oxide pillared clays from ground water. Journal of Environmental Chemical Engineering 4 (1) pp. 1224–1230. dx.doi.org/10.1016/j.jece.2016.01.022


Figure 5 Process flow diagram of on-site pilot experiment.
Oyu Tolgoi is copper and gold mining project located in Gobi Desert region of southern Mongolia. The Oyu Tolgoi mine is situated in a desert-steppe ecosystem, where surface water, in the form of alluvial sub-surface flows and intermittent surface flows in dry river channels play an important role in supporting ecosystems and traditional herding practices. The Undai River (an ephemeral river) flows through the Oyu Tolgoi mine lease area and is close to the open pit. The development of the Oyu Tolgoi open pit and dewatering operations were going to affect Undai dry river bed, which required relocating a portion of the river channel mitigate effect to downstream water movement. Undai River diversion system was developed in 2012-2013 and consists of diversion dams, flood water diversion channel, and subsurface flow diversion. Thus subsurface and surface flows of Undai dry river bed were diverted from its original course, away from effect zone of the open pit, and rejoined the natural channel downstream of Mine Lease Area.

Upon completion of construction works in 2013, long term comprehensive environment monitoring has been conducted. Monitoring has included water level (in monitoring wells and herder wells), water laboratory analysis, surface and subsurface flow rates, flood monitoring and observations. Water quality has improved at the New Bor ovoo spring fresh water and water quality now complies with the Mongolian potable water standard parameters. Measured flow rate range at the New Bor ovoo spring have been 0.3 – 2.6 L/s, depending on summer-autumn rain events. No adverse effect on herders’ shallow groundwater wells and local water courses downstream of the diversion structure have been identified in five years of monitoring.

Heavy floods occurred in the summers 2017 and 2018 due to the heavy rainfall events. Surface flows successfully passed through the flood water diversion channel.

The Undai River Diversion Project has been successfully constructed and tested through high rainfall years of 2017 and 2018. The diversion has enabled the development and operation of the open pit, while maintain water levels in shallow wells downstream of the Oyu Tolgoi. The monitoring has demonstrated no change natural regime of downstream alluvial water levels and an improvement in water quality. An unexpected benefit has been the wide range of wildlife species and domestic animals that utilize the New Bor ovoo spring.
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The Oyu Tolgoi copper-gold mine is located in the southeast region of Gobi region of Mongolia, approximately 80 km north of China-Mongolian border. Oyu Tolgoi is a remote project and extensive infrastructure has been constructed including: Water Supply Borefield, Tailings Storage Facility, Concentrator, Waste Water Treatment Plant, Water Treatment & Bottling Plant, highways, housing, and Undai river diversion project.

It is situated in a desert-steppe ecosystem, where surface water, in the form of alluvial sub-surface flows and intermittent surface flows in dry river channels play an important role in supporting ecosystems and traditional herding practices.

Introduction

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Abstract

The effectiveness of water management in mining companies is largely controlled by mining, geological, natural and man-made conditions of the area. The use of dewatering and thickening of tailings of wet magnetic separation with installation of the process water circuits, and a reduction of wastewater discharge and seepage losses will be critical for ensuring the ecological efficiency of water balance management, which makes it possible to efficiently utilize the groundwater resources in the area for the establishment of water supply systems.

Keywords: water management, wet magnetic separation tails, thickening.

Rationale for study

The mining industry is a major contributory factor to the persistent environmental devastation and can have substantial geochemical effects on natural waters of the mining site and adjacent areas. Safety and environmental control of mining activity are largely dependent on the adopted water supply and wastewater disposal schemes. Minimizing the quantity of contaminated quarry wastewater inflow into the natural environment is a priority task for managing the water balance at a mining site. The order is to reduce industrial load on the environment and to maintain the ecological and resource potential of the territory.

According to the national waste management standards in the mining industry, special attention should be paid to the safety of tailings dams, tailings dewatering and thickening, dry storage of condensed wastes and minimization of the amount of discharge into natural water bodies (wastewater treatment with quality control) (GOST R 55100-2012).

EVRAZ KGOK (Kachkanar Mining and Processing Enterprise) is the largest mining company in Russia and the only company producing low-grade vanadium-titanium magnetite iron ores. The enterprise's annual output is approximately 55 million tons of iron ore (EVRAZ KGOK 2018; Vlokh 2016).

The high production efficiency of EVRAZ KGOK and low-grade sources of titaniferous magnetite iron ore generally require beneficiation. As a result of the use of large amounts of water, which generates substantial volumes of wastewater and tailings. In 2014-2016, the annual level of water use at EVRAZ KGOK amounted to 32.6-40.8 million m$^3$. About 50% of this volume has been discharged to the watercourses of with plant effluents (State Report 2017).

In addition to wastewater discharge, environment contamination from this site can be attributed to beneficiation tailings produced from wet magnetic separation. Beneficiation tailings in the volume of about 45 million tons are discharged to the tailings disposal site with an area of about 12 km$^2$ (Deryagina 2013). The disposal site is an aggradational tailings pond located on the slope of the Vyya River valley and Rogalevka River, its right-hand tributary.

The large proportion of all wastewater produced by the plant is accounted for by quarry wastewater and operational effluents pumped into the tailings pond, which stores tailings from magnetic beneficiation. About 3% (15.0 million m$^3$/year) of this volume is discharged through the foundation of tailings dams, directly seeping to the watercourses in the adjacent areas.

The chemical composition of natural waters depends on the geological environment of the area. The geology of the area is dominated by various metamorphic and igneous rocks overlain by a thin layer of loose...
Quaternary deposits. The confinement to the ore deposits is the main factor controlling the natural hydrochemical background of the area and results in the high iron, titanium, vanadium, chromium, manganese, cobalt, copper, zinc, and molybdenum content of natural waters (Ushakova, 2012). The absence of readily soluble rocks in the geological section leads to low TDS content of natural waters. The total amount of annual water inflows to open-pit areas is 7-8 million m³. The development of the deposit, promotes the transition of some of the chemical elements contained in the rocks into soluble forms. The compounds are discharged into surface water and groundwater with effluents and result in water contamination.

A substantial factor that causes changes in the chemical composition of natural waters is the use of blasting agents in mining operations. As a result, a high content of nitrogen compounds is recorded in wastewater and natural waters. Nitrogen compounds are nitrite, nitrate, and ammonium ions. The presence of ammonium ions (ammonium nitrogen) in open-pit drainage water is due to dissolution and leaching of ammonium nitrate during recharging of water-producing wells. Nitrite (nitrite nitrogen) contamination of drainage water is associated with absorption of nitrogen oxides during blasting, their subsequent percolation with atmospheric precipitates and release into drainage (open-pit) waters. The input of nitrate ions into drainage (open-pit) waters is associated both with the dissolution of ammonium nitrate in water-producing wells and leaching of absorbed nitrogen oxides with atmospheric precipitates. The amount of nitrogen compounds released into the drainage (open-pit) waters accounts for 3–4% of the total amount of nitrogen contained in blasting agents (Khokhryakov 2016). As a result, the concentrations of nitrogen compounds in surface water and groundwater substantially exceed the maximum admissible concentration (MAC), which results in the contamination of water bodies by the discharge of drainage waters.

Elevated concentrations of nitrogen compounds in watercourses would adversely affect the quality of water supplied to settlements via infiltration water intakes. Such water intakes are recharged by groundwater, the reserves of which are formed by river water. In particular, the development plan for the Ust-Vyya aquifer using infiltration water intake is prepared to ensure water supply to the town of Lesnoi located some 25 km downstream of the wastewater discharge point of EVRAZ KGOK. The proposed waste dump expansion will lead to the increase in concentrations of nitrogen compounds in the river water and groundwater if the cone of depression keeps expanding during water intake.

The results of monitoring observations conducted by ENI PGNIU since 2008 on the Vyya River, the main water stream receiving mine wastewater discharge, the river waters in the control section is 3.0 km downstream of the wastewater discharge point are fresh and ultra-fresh (174–333 mg/dm³), of calcium-bicarbonate and calcium-sulfate type. The concentration of nitrate ions in the river waters exceeds MAC for drinking and amenity water use (45.0 mg/dm³). Over the observation period, the concentrations of nitrate ions in the river waters varied within 29.5-130.6 mg/dm³ and did not exceed the MACs in certain periods downstream of the wastewater discharge point (Blinov 2016).

The contents of nitrite ions and ammonium ions do not exceed the MACs for drinking and amenity water use.

The concentrations of elements in groundwater in the vicinity of the tailings site commonly exceed the hygienic standards of total iron (up to 11.7 MACs) and manganese (up to 3 MACs). In individual wells are characterized by one-time maximum admissible concentrations for nitrate ion (up to 1.5-1.7 MACs) and vanadium (up to 2.6 MACs). The contents of other detectable components are substantially lower than the MAC values specified for drinking and amenity water use.

In view of the forthcoming large-scale projects to increase the productivity of EVRAZ KGOK, it is necessary to use environmentally and economically more efficient waste and quarry water management plans to reduce the industrial environmental load through installation of closed water intakes.
systems, the application of dehydration technologies and thickening of tailings of wet magnetic separation, minimization of wastewater discharge to water courses, and reduction of fresh water consumption to replenish the circulating water supply system.

**Justification of the environmental efficiency of the proposed open-pit and wastewater management plan**

The reconstruction of EVRAZ KGOK’s tailings facilities to ensure safe tailings storage is associated with the abandonment of the existing tailings dam and enhanced production efficiency of the enterprise. Taking into account the relatively small linear dimensions of the project area and the existing limitations, the main technical requirement for the design of a new tailings site is the thickening of tailings slurries.

Hydrocyclone thickeners have been used for thickening and efficient disposal of tailings in the tailing dam since the 1960s. The efficient disposal of tailings is achieved through the separation of tailings slurries, based on the particle size range and the pulp density of the slurry. Hydrocyclone thickeners were first used in Russia at the Achisai Polymetallic Plant for dam construction. Subsequently, hydrocyclone thickeners were applied at some tailings sites of the Almalyk, Afrikand, Mirgalimsai, Kamtaga, Khaidarkan and other beneficiation plants.

Cyclone thickeners were first used abroad for building tailings dams in the USA in the 1950s. Currently, this technology is widely used in Canada, Africa, Chile, Brazil, and South Africa. The construction of new and reconstruction of existing beneficiation plants always envision installation of the process water circuit. At the same time, the maximum use of process water was attained via thickening of tailings slurries (up to 30–70% solids) and recycling the clarified water back to the beneficiation process.

The environmental efficiency of the studied open-pit and wastewater management plan during the reconstruction of EVRAZ KGOK’s tailings site can be achieved by elimination of the possible influence of seepage water within a new portion of the site on the water intake within the Ust-Vyaaquifer located some 25 km downstream. The technical solutions for tailings facility reconstruction developed by MEKHANOBR ENGINEERING (St. Petersburg) envision engineering activities to ensure trapping of seepage water and effluents from the new and existing tailings dams.

The environmental effectiveness of the open-pit and wastewater management plan will depend on an equivalent maximization of the use of process water and a reduction of the wastewater volume discharged. This is achieved via tailings thickening and recycling the clarified water back to the process. This technology provides thickening of the initial tailings slurry of the enrichment plant from 7-11 to 75% in solids content using flocculants, which corresponds to current world best practice. The use of this technology will result in a more than 4-fold decrease in the tailings dam area (up to 10.5 million tons/year), a reduction of the volume of the pumped slurries thus reducing energy costs for pumping.

The volume of wastewater pumped to the tailings dam as part of wet magnetic separation tailings is decreased by 40 times (to 12.19 million m$^3$/year). This is lower than the volume of the observed seepage losses through the foundation of the embankment dams. The water content in the thickened tailings at 75% solids is 0.33 m$^3$ per 1 ton of solids, which is approximately equal to the pore volume of the dumped tailings. Small amounts of water may seep through the dumped tailings and enter the drainage system and then the process water circuit. In accordance with the developed flow diagram, the water seeping from the existing tailings storage is also collected and pumped back to the process water circuit. Reducing the volume of a liquid component in the dumped tailings and removal of seepage water will cause the pressure drop on tailings dams. Thus preventing emergency situations and, as a result, contamination of the adjacent areas.

The use of the dewatering and thickening of wet magnetic separation tailings technology, the creation of water recycling systems and minimization of the discharge of wastewater seepage losses will ensure the environmental efficiency of the plant's water systems, the application of dehydration technologies and thickening of tailings of wet magnetic separation, minimization of wastewater discharge to water courses, and reduction of fresh water consumption to replenish the circulating water supply system.
balance management. The implementation of these actions is important to reduce the industrial load on the environment, to prevent contamination of natural waters by nitrogen compounds, and to more effectively use the groundwater resources for establishment of a water supply system.

**Conclusions**

The analysis of existing natural, industrial, and geological conditions in the operation area of EVRAZ KGOK confirmed the maximum ecological efficiency of the proposed water balance management plan.

Overall reduction of the technogenic influence on the ecosystems in adjacent areas is achieved through the application of tailings thickening and dewatering systems, the maximum use of recycled process water, and reduction of the volume of discharged wastewater.

The proposed actions will decrease the probability of contamination of natural waters and provide the opportunity for the augmentation of groundwater resources of the area. The water quality allows to organize safe domestic and drinking water supply by attracting surface water to infiltration water intakes of settlements.

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Assessment of Water Quality in the Witwatersrand Basin using Inorganic Contaminants

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Abstract
This study evaluated the quality of the surface water resources in the East Rand. Multivariate statistical tools (principal component analysis and hierarchical cluster analysis) were used to investigate how mining and other factors negatively influence the surface water quality. The water quality index (WQI) was used to assess how suitable the water is for domestic use. The results obtained indicate that in addition to mining activities, sewage discharges and industrial effluents also have a negative effect in the surface water quality. Poor water quality from anthropogenic sources should be properly treated before being discharged into the surface water resources.

Keywords: mining, water quality index, principal component analysis, hierarchical cluster analysis

Introduction
Economically, South Africa has benefited greatly from mining, resulting in one of the major economic hubs (Johannesburg) in Africa to be developed from gold mining activities. However, this economic development left a polluted environment due to improper disposal of mine waste such as mine residues and acid mine drainage (AMD) (fig. 1).

Mining activities have a negative effect of deteriorating the water quality. This is a problem that is being faced in the Witwatersrand Goldfields of South Africa such that these can lead to shortage of usable water in the future (Humphries et al. 2017). Anthropogenic activities such as mining, industrial effluent and sewage discharge may result in an elevated levels of metals such as Fe, Al, Mn, Pb, Cu, Co, U, Zn (Humphries et al. 2017) and anions (such as SO₄, NH₃, NO₃) in the water bodies. Enrichment of such metals in the water leads to the water being unsuitable for domestic use as well other uses such as agriculture (Wang et al. 2017). Polluted water may pose a potential risk to human health and livestock or aquatic ecosystems (Giri and Singh 2013). Mines often deposited tailings close to water bodies such as the Blesbokspruit in the East Rand Goldfield,

Figure 1 Mine dump in West Rand Goldfield generating acid seepage
The Wonderfonteinspruit in the West Rand and the Russell Stream in the Central Rand. Therefore leaching of the potentially toxic elements could negatively affect the quality of surface water. It is therefore crucial to protect water resources from contamination, mostly by anthropogenic activities (Wang et al. 2017). This study evaluates the effect of mining on the current water quality resources in the East Rand Goldfield. Multivariate statistical tools and water quality index were used to assess the surface water quality and the effecting factors.

**Methods**

**Study area**

Water samples were collected in the East Rand of the Witwatersrand Goldfields in South Africa as shown in fig. 2.

**Sample collection and preparation**

A total of 19 sites in the East Rand were sampled for the inorganic chemistry analysis. Samples were collected using 100 ml polyethylene bottles. Duplicate samples at each site were collected for quality control. Samples to be analysed for cations were preserved by adding 3 drops of concentrated HNO$_3$. Both cation and anion samples were preserved at 4 °C before being analysed using inductively coupled plasma mass spectrometry (ICP-MS) and ion-chromatography (IC) respectively.

**Water quality index**

Surface water quality in the East Rand Goldfield was evaluated using a comprehensive water quality index (WQI) tool. This reflects the integrated effect of different water quality variables as shown in Equation 1 below (Meng et al. 2016).

\[
WQI = \sum W_i \times \left( \frac{C_i}{S_i} \right) \times 100
\]

Where $W_i$ = the weight of each parameter $i$ and was obtained on the basis of the eigenvalues for each principal component.

![Figure 2 The sampled points in the East Rand of the Witwatersrand Goldfields (Van Ryn Canal (VRC), Van Ryn Ponding (VRP), Van Ryn Downstream (VRD), Gravelotte Canal (GC), Gravelotte ponding @N12 (GP@N12), Gravelotte Sewage Canal (GSC), Gravelotte Sewage Canal Ponding (GSCP), Gravelotte outside Clay Quarry (GCQ) Gravelotte Ponding (GP), Leeupan (LP), Blesbokspruit at Esselen Street (B@ES), Blesbokspruit at Grootvlei (B@G), Blesbokspruit at Daggafontein (B@D), Blesbokspruit at Marievale (B@M), Blesbokspruit at Welgedacht (B@W), Largo Sinkholes (LSH), Alexander Dam (AD) and Cowles Dam (CD)
and factor loading for each parameter from the PCA results, and represents the relative importance of each water quality parameter for drinking purpose. $C_i$ = concentration of the element in the water sample and $S_i$ = drinking water limit obtained from South African water quality guideline and the World Health Organisation (DWAF 1996 and WHO 2011).

According to Meng et al. (2016), the WQI classify water into five categories: WQI < 50 means that the water is of excellent quality; 50 ≤ WQI < 100 means that the water is of good quality; 100 ≤ WQI < 200 means that the water is of poor quality; 200 ≤ WQI < 300 means that the water is of very poor quality and WQI ≥ 300 means that the water is of extremely poor quality.

**Statistical analysis**

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used to investigate how mining and other factors influence the surface water quality in the basin. PCA places the principal components in a way that the ones contributing most in the variance of the dataset are classified as the first and the ones that contribute less are taken as the last principal components (Kura et al. 2013). HCA groups variables into clusters in terms of how closely related they are to each other and how different they are from the rest of the groups (Kura et al. 2013). Data processing was done using Microsoft Excel 2010 and the Statistical package for social sciences (IBM SPSS 22).

**Results and discussion**

**Water quality assessment**

Surface water quality was assessed by comparing the concentrations of all the parameters in the water with their respective drinking water standards according to DWAF (1996) and WHO (2011) as shown in tab. 1.

It was noted that NH$_3$ concentrations at sites B@D sewage, GSC, GSCP and GC are above the drinking water limits. Also, B@M, LSH and B@D dam and B@D sewage had concentrations that exceeded the drinking water quality standards for SO$_4^{2-}$ and Fe respectively. Maximum permissible limit of sulfate in drinking water as described by WHO (2011) is 250 mg/L with high SO$_4^{2-}$ concentrations in water potentially causing laxative effects (Annapoorna and Janardhana 2015). Conversely, >0.3 mg/L concentrations of iron gives water a bad taste and odour and it stains laundry (DWAF 1996 and WHO 2011). Levels of ammonia in drinking water should be below 1 mg/L (WHO, 2011) such that concentrations above may change the taste and odour of the water (DWAF 1996).

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<td>609.50</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>0.01</td>
<td>0.02</td>
<td>NO$_3^-$</td>
<td>11.00</td>
<td>0.05</td>
<td>7.85</td>
</tr>
<tr>
<td>Cu</td>
<td>2.00</td>
<td>0.01</td>
<td>0.01</td>
<td>F</td>
<td>1.50</td>
<td>0.20</td>
<td>0.58</td>
</tr>
<tr>
<td>Fe</td>
<td>0.30</td>
<td>0.04</td>
<td>0.48</td>
<td>NH$_3$</td>
<td>1.00</td>
<td>0.10</td>
<td>23.00</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>700.00</td>
<td>264.00</td>
<td>1643.00</td>
<td>Alkalinity</td>
<td>300.00</td>
<td>0.17</td>
<td>109.46</td>
</tr>
<tr>
<td>pH</td>
<td>9.20</td>
<td>7.50</td>
<td>9.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 1 Drinking water quality limits (DWAF, 1996; WHO, 2011) and descriptive statistics for the parameters*
Water quality index

Weights ($W_i$) of each parameter were calculated on the PCA as shown in tab. 2. Using the $W_i$ from tab. 2 and the limits obtained from South African water and WHO water guidelines, the WQI was calculated for the East Rand Goldfield. Results obtained are depicted in fig. 3.

Results in fig. 3 show that the water quality in East Rand Goldfields is generally poor with exception AD, B@ES, GCQ, VRC, VRP and VRD that showed a good water quality. B@ES is at the uppermost upstream of the Blesbokspruit, and the water samples did not seem to show substantial elevation in any ions. Similarly, water sampled at VRC, VRP and VRD, flows from Kleinfontein Lake, and is currently not vulnerable to contamination by sewage or mining activities. This is because the surface water in the Van Ryn area is diverted from the mining sites by a canal. Therefore all this water is potable and can be used for domestic purposes.

There are sites that displayed poor water quality (fig. 3) due to increasing concentrations of $SO_4^{2-}$ and $NH_3$. Sites that displayed high $NH_3$ concentrations are B@D sewage, GC, GSCP and GSC because of either water mixed with sewage or direct sewage sampled for analysis. The presence of ammonia in the water may be from agricultural and industrial processes or sewage pollution (WHO 2011). LSH, B@D, and B@M showed an increase in $SO_4^{2-}$ concentration. This can be a result of mining activities in the area since $SO_4^{2-}$ rich mine water from the Eastern Basin Mine Water Treatment Plant is released to the Blesbokspruit after treatment and leachates from mine residues pollute water in this catchment. This water therefore pollutes Largo Sinkholes towards the downstream of the Blesbokspruit. Surface water quality deterioration was observed from midstream of the Blesbokspruit and this may also be influenced by mining activities since the spruit passes close to the gold mine tailings. Water in the CD and GP also showed deterioration in its quality because of sewage mixing that was happening in these areas.

Principal Component Analysis

Tab. 2 shows PCA results (variables, loading values and eigenvalues) as acquired from SPSS. This technique shows that $SO_4^{2-}$, Cl, Ca, Mg, Li, Ti and Na contributes a total variance of 33.5% in altering the surface water quality. Component 2 with a variance of 28.2% displayed Fe, Mn, $NH_4$, Cu, Co, Al and Zn to be the second highest contributing group to the water quality change. As obtained from the PCA results, metals and ions that appeared under PC1 and PC2 could be related...
to mining, industrial and sewage discharges. This is because these were assumed to be the most influencing anthropogenic sources to the surface water quality. However, concentrations of ions such as Ca and Mg could be related to weathering of the rocks that interacts with water along its flow path, in particular the dolomite which outcrops and suboutcrops extensively in the study area. Nonetheless, these ions do not have a negative effect to the water quality since their concentrations are within the drinking water standards.

**Hierarchical cluster analysis**

The dendrogram shows four groups as indicated by fig. 4. Group 1 is composed of sites that displayed good water quality as calculated by the WQI. This is the water that is not influenced negatively by the mining activities and can therefore be used for domestic purposes. Group 2 on the other hand shows sites that are highly contaminated by sewage since they showed an increase in NH$_3$. This water fell within the poor water quality as displayed by fig. 3.
Sites that showed deterioration in their water quality were clustered together as group 3. Lastly, group 4 is composed of sites that displayed poor water quality because of their high $\text{SO}_4^{2-}$ concentrations as a result of mining activities and industrial wastes. Contamination of these sites occurs from one site to the next along the river flowpath.

**Conclusions**

Multivariate statistical tools (PCA and HCA) and the WQI were used to investigate the main influences of surface water quality. This study indicates that mining activities, industrial effluents and sewage discharge around the East Rand Golffield have an effect in the surface water quality. This was noted from elevated concentrations of $\text{SO}_4^{2-}$, Fe and $\text{NH}_3$ in the water. PCA results also indicated that metals such as Al, Co, Cu, Mn as well as Cl and Ca had an effect in altering the water quality. However, as confirmed by the tools, there are other sources within the basin that still indicated good water quality signature for domestic use. The WQI results showed one site with extremely poor water quality due to contamination by sewage. To improve the surface water quality in this basin, tailing dumps that are next to the water bodies needs to be removed. Also, treatment plants should avoid discharging treated water back to the streams, unless it is of good quality. Lastly, proper sewage channels from human settlements must be installed to avoid raw sewage water mixing with surface water.

**Acknowledgements**

The authors would like to thank the Department of Mineral Resources for funding the project.

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influencing the groundwater chemistry in a small tropical island of Malaysia. Int. J. Env. Res. & Publ. Health, 10(5):18611881


Mine Water Management under Seasonal Rainfall Condition

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Abstract

Almost all hard coal mines of Vietnam are situated in Quang Ninh Coal Basin in the North East of Vietnam, near the coast of Ha Long Bay. Mine water discharged from coal mines has caused negative effects on Ha Long Bay’s ecology as well as the quality of surface water resources. The primary reason is the seasonal mine water variation in both quantity and quality. Identifying a sufficient capacity for mine water treatment and managing the surplus volume of mine water during rainy season are two important solutions for designing mine water treatment plants (MWTPs).

Keywords: mine water, Quang Ninh Coal Basin, mine water treatment plant, seasonal mine water variation, rainy season

Introduction

Almost hard coal mines in Quang Ninh Coal Basin are under the management of Vietnam National Coal and Mineral Industries Holding Corporation Limited (VINACOMIN). Coal mining has been conducted by both open-pit (O/P) and underground (U/G) mining. Water running into mines is mainly surface water (rainwater) and groundwater.

Mine water is acidic and contains coal sludge (TSS), iron (Fe) and manganese (Mn) which are considered to be major pollutants (Kurtz 2009, Bilek et al. 2011, U+Ö 2015). The total volume of mine water is about 120 million m³ per year which is treated in 44 MWTPs (VITE 2014). The quality of treated mine water needs to meet The National Standard on Industrial Wastewater (QCVN 40:2011/BTNMT) which is pH = 5.5 – 9; TSS ≤ 100 mg/L; Fe ≤ 5 mg/L; Mn ≤ 1 mg/L accordingly. These values are adjusted further depending on the water supply purpose and volume parameters of the receiving water body and the wastewater flow (MONRE 2011).

There are four seasons in the North of Vietnam. However, a year can be divided into two main seasons for the mining industry regarding the rainfall: rainy season that lasts

Figure 1 Diagram of the rainfall in Hon Gai area and the mine water drainage of Ha Tu O/P Coal Mine in 2016
from May to October and dry season that lasts from November to the following April. The annual rainfall in Quang Ninh varies from 2,200 mm to 2,400 mm and mainly concentrates in July, August, September. The variation of rainfall affects both the quantity (fig. 1) as well as the quality of mine water (Tran Mien 2017).

For U/G coal mines, the most important pumping time for mine water drainage in a year often coincides with the period of rainy season. For O/P coal mines, the mine water is accumulated in the pit bottom. The pumping time for mine water drainage concentrates in October, November and December in order to drain off water from the mining pit and to prepare the mining field for the following year. Due to the seasonal variation of mine water, the capacity of MWTPs is not stable as designed which leads to overflow in the rainy season and lack of inflow in the dry season as well as discrepancies from the technical norms in the discharged water. These are the biggest challenges for the mine water management of coal mines in Vietnam.

Before 2014, when designing MWTPs, two methods for determining the treatment capacity were used. Either the highest monthly average volume of mine water in a year was used with the aim to thoroughly complete the treatment of mine water (“full treatment” viewpoint) or in case of limited investment budget (“economical” viewpoint) the average annual volume of mine water was chosen. Both methods resulted in undesirable effects on the economic and technical efficiency of MWTPs. The performance survey among 34 MWTPs operating in the period of 2013 – 2014 in Quang Ninh Coal Basin shows that in 2013 up to 60% of them operated less than 75% of their designed capacity, 30% of them achieved their designed capacity; the corresponding figures in 2014 are 29% and 42% (VITE 2014). Those treatment plants which exceeded their design capacity produced low quality of treated water.

The cause of the above-mentioned problems originates in the decision of design capacity without considering the seasonal variation of mine water which means that the volume of mine water greatly decreases in dry season and contrary in rainy season. The feature of the seasonal variation of mine water requires a method to identify a sufficient design treatment capacity for MWTPs in order to ensure their cost-effectiveness as well as an effective management of surplus mine water volume in rainy season.

Methods

Seasonal mine water management for coal mines in Vietnam includes a set of following solutions:

- Identification of treatment capacity for the MWTP projects by taking the seasonal variation of mine water volume into consideration but keeping the investment costs at a suitable level and achieving conformance to national standards for industrial wastewater;
- Effective management of increased mine water volumes in rainy season;
- Installation and operation of the flexible multi-line treatment systems adjusted to mine water quantity at the operation time.

The identification of treatment capacity for MWTP projects by taking the seasonal variation of mine water volumes into consideration is based on the analysis of the seasonal variation of the mine water volumes (SMWA) in a number of consecutive years (3 years at minimum). The order of the steps is as follows.

Collecting, editing, analyzing the development of mine water drainage

Data of mine water drainage in coal mines can be managed and provided by some various relevant sections in the same mine depending on their respective management roles. Therefore, it is necessary to execute the verification, comparison, editing, correction and validation of data. The accuracy of data provided will determine the precision of MWTP designs.

Identifying capacity parameters

Data of mine water drainage in a year will be processed into 4 different volumes: i/ monthly average; ii/ quarterly average; iii/ (dry and rainy) seasonal average and iv/ annual average. Usually, the monthly average is the highest value and the annual average is the lowest. This is in accordance with the
methods of treatment capacity identification as used before, therefore the values will be used for reference. The quarterly average and the seasonal average (rainy season) are used for analysis and evaluation in accordance with SMWA. Depending on rainfall in the year, the value of seasonal average volume in rainy season is calculated according to the actual period of rain.

Verifying the capacity of mine water equalization in rainy season

The equalization of mine water in rainy season is an important factor which decides on the effective management of mine water of coal mines in Vietnam. This is realized by a reservoir system called “equalizing reservoirs”.

In rainy season, parts of the mine water are stored in them. The volume of the equalizing reservoirs should be sufficient to store the surplus mine water after a rain event in order to prevent an overflow of untreated mine water into receiving water courses. At the same time, the reservoirs support settling of coal sludge in mine water during its retention time there (Tran Mien 2017).

In dry season, when the volume of mine water is greatly decreased, equalizing reservoirs are to collect and maintain its stable supply of mine water for treatment modules in correspondence with the volume of mine water at operation time.

The relevant parameters to be identified include: surplus mine water (increased mine water volume) in rainy season; available volume of equalizing reservoirs; real pumping time for storage meeting mine safety regulations, especially the ones for underground coal mines.

It is necessary to reuse available objects that are not used any more, such as sedimentation ponds of coal preparation plants, sections of abandoned stream for the establishment of equalizing reservoirs.

Identifying the appropriate number of parallel treatment modules in correspondence with the volume of mine water in season

As a design solution, parallel treatment modules are used to mobilize treatment capacity of a MWTP in accordance with mine water quantity existing at operation time. The number of parallel treatment modules is identified by the difference or ratio between the 3rd quarterly average volume or the rainy season average volume and the remaining other values of the same parameter in the same year.

Making the decision for a capacity alternative

A capacity alternative for any MWTP design will be decided based on analysis, evaluation and comparison of the above-mentioned factors. The capacity alternative chosen for the MWTP design is the lowest one among those and must satisfy the demand of full treatment of mine water volume in the year.

A decision on treatment capacity usually should be based on supplementary information such as: i) planned investment cost based on investment experiences from similar MWTPs which have been installed previously; ii) available conditions for design implementation (area, location of the area for equalizing reservoirs and other conditions related to the mines infrastructure).

SMWA method is currently used by VITE in making new MWTP designs and verifying the treatment capacity for MWTPs under operation.

Results

The results of SMWA method are shown in the verification of the treatment capacity for Ha Tu Open-pit (O/P) Coal Mine MWTP, Quang Ninh as an example.

Ha Tu MWTP treats mine water from mining field V.16 of Ha Tu O/P Coal Mine, designed with the capacity of 1,500 m³/h into two stages. In the 1st stage, the capacity of 300 m³/h has been installed with 3 parallel treatment modules that have been put into operation in June 2013. In the 2nd stage, an additional capacity of 1,200 m³/h has been installed with 2 parallel treatment modules that have been put into operation in January 2016. Their working regime is 300 days per year; 30 days per month; 3 shifts per day (or 20 operating hours per day). The total volume of 2 equalizing reservoirs is 25,000 m³. Current status: Capacity of Ha Tu MWTP
is insufficient for treating its mine water volume in rainy season, therefore an overflow of untreated mine water into the receiving water course often occurs. It is necessary to verify its real capacity (for the year of 2018).

Figure 1 shows a resemblance between the developments of rainfall in Ha Long area and mine water drained from Ha Tu O/P Coal Mine.

Figure 3 shows the developments of treatment capacity in 2016, 2017, 2018 of Ha Tu MWTP. The volume of mine water increases from May to October and reaches its peak in July, August and September.

The performance of treatment in 2016, 2017 and 2018 is shown in table 1.

**Development of verification:**
Development of mine water drainage in 2018 is shown in table 2.

Results of calculation of capacity parameters are shown in table 3.

From the results of table 3, two capacity alternatives which have been offered to verify are the quarterly average volume of 2,400 m$^3$/h and the rainy season average volume of 1,800 m$^3$/h. The treatment capacity which has to be verified is the design capacity of 1,500 m$^3$/h.

Table 4 shows calculations of the developments of treatment capacity in accordance with the quantity of mine water supplied to Ha Tu MWTP in the year. The results of table 4 indicate the lack of treatment capacity in months of rain ( - sign) and the surplus in months outside rainy season.

Table 5 shows the results of verification on treatment capacity in months after rainy season.

**Conclusions from the results of verification:**
The design capacity of 1,500 m$^3$/h is insufficient for treatment demand during and after rainy season. Therefore, overflow of untreated mine water into receiving water

<table>
<thead>
<tr>
<th>Year</th>
<th>Drained volume, m$^3$</th>
<th>Treated volume, m$^3$</th>
<th>Overflow volume, m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2016</td>
<td>9,508,512</td>
<td>2,492,293</td>
<td>7,016,219</td>
</tr>
<tr>
<td>2017</td>
<td>8,009,430</td>
<td>6,927,644</td>
<td>1,081,786</td>
</tr>
<tr>
<td>2018</td>
<td>7,427,038</td>
<td>6,623,130</td>
<td>803,908</td>
</tr>
</tbody>
</table>
courses often occurs.

The capacity alternatives could be considered for Ha Tu MWTP are the quarterly average capacity of 2,400 m³/h or the rainy season average capacity of 1,800 m³/h, of which the rainy season average capacity follows the economic viewpoint while the quarterly average capacity is oriented towards high safety.

Between two these alternatives, the rainy season average capacity of 1,800 m³/h is preferred because this alternative satisfies two prerequisite criteria which are i) its available capacity for the surplus of mine water volume higher than the same criteria of the capacity alternative of 2,400 m³/h and ii) but with a lower investment scale.

Effective management of the surplus volume of mine water in rainy season is the accumulation of mine water in the pit bottom and treatment in the months after the rainy season.

The enlargement of capacity for Ha Tu MWTP needs to be considered.

### Conclusions

The seasonal variation of rainfall in Vietnam has important effects on the management and the treatment of mine water. The management of surplus mine water in rainy season is an obligatory factor for reducing bad effects on the environment but, at the same time improving the economical and technical effectiveness of MWTPs at Quang Ninh Coal Basin.

SMWA method has being applied for designing MWTPs in coal mines under the management of VINACOMIN, as well as verifying the design capacities of existing MWTPs.

SMWA method together with the installation of equalizing reservoirs and parallel treatment modules have made up a set of solutions for the seasonal mine water management under the features of tropical rain in Vietnam (fig. 4).

SMWA method still has limitations due to the lack of data and their low confidence level. According to legal regulations of The

### Table 2 Development of mine water drainage in 2018

<table>
<thead>
<tr>
<th></th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity, m³/h</td>
<td>992</td>
<td>379</td>
<td>246</td>
<td>222</td>
<td>284</td>
<td>681</td>
<td>2,589</td>
<td>2,810</td>
<td>2,342</td>
<td>1,132</td>
<td>370</td>
<td>331</td>
</tr>
</tbody>
</table>

### Table 3 Capacity parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monthly avg.</td>
<td>992</td>
<td>379</td>
<td>246</td>
<td>222</td>
<td>284</td>
<td>681</td>
<td>2,589</td>
<td>2,810</td>
<td>2,342</td>
<td>1,132</td>
<td>370</td>
<td>331</td>
</tr>
<tr>
<td>Quarterly avg.</td>
<td>539</td>
<td>396</td>
<td>2,580</td>
<td>611</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seasonal avg.</td>
<td>423</td>
<td>1,640</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual avg.</td>
<td>1,032</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>

### Table 4 Developmets of treatment capacity

<table>
<thead>
<tr>
<th>Inflow, m³/h</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment potential by alternatives:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2400 m³/h</td>
<td>1,408</td>
<td>2,021</td>
<td>2,154</td>
<td>2,178</td>
<td>2,116</td>
<td>1,719</td>
<td>-189</td>
<td>-410</td>
<td>58</td>
<td>1,268</td>
<td>2,030</td>
<td>2,069</td>
</tr>
<tr>
<td>1800 m³/h</td>
<td>808</td>
<td>1,421</td>
<td>1,554</td>
<td>1,578</td>
<td>1,516</td>
<td>1,119</td>
<td>-789</td>
<td>-1,010</td>
<td>-542</td>
<td>668</td>
<td>1,430</td>
<td>1,469</td>
</tr>
<tr>
<td>1500 m³/h</td>
<td>508</td>
<td>1,121</td>
<td>1,254</td>
<td>1,278</td>
<td>1,216</td>
<td>819</td>
<td>-1,089</td>
<td>-1,310</td>
<td>-842</td>
<td>368</td>
<td>1,130</td>
<td>1,169</td>
</tr>
</tbody>
</table>

### Table 5 Balance of treatment capacity in months after rainy season

<table>
<thead>
<tr>
<th>Alternative of 2,400 m³/h</th>
<th>Total of capacity needed for the surplus mine water volume, m³/h</th>
<th>Total of capacity operated in months after rainy season, m³/h</th>
<th>Total of available capacity for the surplus mine water volume, m³/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alternative of 1,800 m³/h</td>
<td>-2,341</td>
<td>1,832</td>
<td>3,568</td>
</tr>
<tr>
<td>Designed capacity, 1,500 m³/h</td>
<td>-3,241</td>
<td>1,832</td>
<td>2,668</td>
</tr>
</tbody>
</table>
Government of Vietnam, since 2018 all MWTPs in Quang Ninh Coal Basin need to install an automatic monitoring system. For this reason, the confidence level of data will be ameliorated in the coming time.

**References**


VITE (2014) Project “Evaluation of the effectiveness of technology, techniques and management for existing mine water treatment plants and orientations of application for the next ones” (Vietnamese)

VITE (2016) F/S of Ha Tu Mine Water Treatment Plant Project – 2nd Stage (Vietnamese)
Abstract
This study evaluates the potential for biological treatment methods to achieve a good quality status for water bodies in Saxony (Germany). Generally suitable methods were classified in engineered ecosystems, technical reactors and subsurface in-situ technologies. These utilize either iron oxidation or sulfate reduction as the core microbial process. Broad application to mitigate the long-lasting and widespread mining impact in Saxony seems limited. Some of the delineated obstacles are: economic limitations due to the amount of carbon source necessary to stimulate sulfate reduction at the affected scale; long term instability of sulfides in naturally aerobic systems; low reaction rates in winter.

Keywords: Water Framework Directive, good status, sulfate reduction, iron, metal(iod-)-s, Saxony

Introduction
Mining has a century-old tradition in Germany’s federal state of Saxony (Kugler 2008). Till today this affects the quality of surface waters and groundwater. Caused by the accompaniment of the mined raw materials with sulfidic minerals, the contamination is typically characterized by acidic conditions, elevated concentrations of sulfate, iron, other metals or arsenic.

With the adoption of the European Water Framework Directive (WFD, European Parliament 2000) the priority of water protection increased for the member states of the European Union. Using a cross-border approach, catchments of groundwater and surface water were divided in so-called water bodies, which must achieve a good chemical and ecological status latest by 2027. By the reference year 2015 this was not met for 59 % of the groundwater bodies (related to the surface area) and 99 % of the streams (related to stream length) in Saxony.

In this study the applicability of biological treatment methods for mining impacted water was assessed on typical Saxon conditions. For this purpose the work was structured in the following tasks: a) delineation of legal standards that relate to mining activity in Saxony, b) characterization of the state of surface and groundwater bodies for these quality components in Saxony, c) review of biological treatment methods for these components, d) review and assessment of already existing biological mine water treatment in Saxony.

Methods
As stated above, the presented work can be divided in four tasks with the following approaches: In order to determine which parameters are affected by mining at one hand and are potentially responsible for the poor status of water bodies in Saxony at the other hand, the relevant legal basis was assessed and brought together with the general geological and geochemical conditions in the region.

In a second step mining affected water bodies were characterized regarding to long-term concentrations of these mining related compounds. Concentrations at 1908 surface water and 3026 groundwater observation points were provided by the Saxon State Office for Environment, Agriculture and Geology (LfULG). First a temporal aggregation was conducted for all observation points by calculating average long-term concentrations (1990-2017 for groundwater, 2000-2017 for surface water). Subsequently a spatial aggregation on these average concentrations...
over the water bodies was performed by calculating average values and percentiles. As the number of observation points in surface water bodies often does not exceed five, only average values were calculated for them. To characterize hot-spots of contamination, where a treatment would be potentially located, 90 percentiles were used for the groundwater bodies. Maps were created that visualize these concentrations and in which degree they exceed legal standards and later used to group surface and groundwater bodies in so called ‘stress groups’.

For Saxony’s mining related contaminants derived above, the international literature on biological treatment methods was surveyed. Focus was set on real treatment applications and their economic feasibility. Promising biological treatment methods were described, classified and evaluated with respect to their specific applicability under conditions in Saxony.

In a last step available literature about already existing biological mine water treatment in Saxony was evaluated. Technical and economic key performance parameters were compiled as well as the reasons for eventual termination.

**Mining related water contamination spectrum in Saxony**

Provisions of the WFD are transposed into federal German legislation by the Groundwater Ordinance (Grundwasserverordnung, GrwV) and the Surface Waters Ordinance (Oberflächengewässerverordnung, OGewV).

In these ordinances limiting concentrations for hazardous components are defined. These are to consult to determine the good or bad status of water bodies. In order to select those quality components that are related to mining activities in Saxony the following criteria were applied: Raw materials mined in Saxony comprise lignite (Lusatian and Middle German district), hard coal, and ores of e. g. silver, uranium, zinc (Ore Mountains region). As lignite is accompanied by iron sulfides and as ores are mostly sulfidic minerals, mining caused formation of acid mine drainage (Blowes et al. 2014). Especially in the Ore Mountains region acid mine drainage also contains non-iron metals and metalloids. Figure 1 summarizes quality components in the two ordinances that can be attributed to mining effects in Saxony.

**Figure 1 References for mining related quality standards of surface and groundwater in German legislation.**

<table>
<thead>
<tr>
<th>Groundwater Ordinance (GrwV)</th>
<th>Surface Water Ordinance (OGewV)</th>
<th>Good Chemical Status (§ 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good Chemical Status (§ 5)</td>
<td>threshold values (annex 2):</td>
<td>GOOD CHEMICAL STATUS (§ 5)</td>
</tr>
<tr>
<td>arsenic: &lt; 10 µg/L</td>
<td>arsenic: &lt; 10 µg/L</td>
<td>GOOD CHEMICAL STATUS (§ 5)</td>
</tr>
<tr>
<td>cadmium: &lt; 0.5 µg/L</td>
<td>cadmium: &lt; 0.5 µg/L</td>
<td>GOOD CHEMICAL STATUS (§ 5)</td>
</tr>
<tr>
<td>lead: &lt; 10 µg/L</td>
<td>lead: &lt; 10 µg/L</td>
<td>GOOD CHEMICAL STATUS (§ 5)</td>
</tr>
<tr>
<td>sulfate: &lt; 250 mg/L</td>
<td>sulfate: &lt; 250 mg/L</td>
<td>GOOD CHEMICAL STATUS (§ 5)</td>
</tr>
</tbody>
</table>

a mean annual EQS: checking compliance with the environmental quality standard by annual mean concentrations.

b General physico-chemical quality elements are to consult supportingly to determine the ecological status.

c suspended matter fraction < 63 µm

d general physico-chemical quality elements (annex 7):

| Iron: < 0.7...1.8 mg/L |
| Silver: < 0.02 µg/L |
| Zinc: < 800 mg/kg |
| pH-value: 5.5...8.5 |

**Characterization of surface water and groundwater bodies**

By the year 2015, 24 of the 83 Saxon groundwater bodies and 122 of the 746 surface water bodies were in a bad chemical or ecological status due to mining related contamination. Their location correlates to the three main mining regions: Lusatian lignite district, Middle German lignite district and Ore Mountains region. Additionally, surface water transports contamination northward with the main flow direction. Figure 2 and figure 3 show the location of the mining affected water bodies with their mining related contamination spectrum (stress groups). Whereas in the lignite mining areas the legal...
Figure 2 Groundwater bodies in Saxony grouped by their contamination with mining related compounds. The 90 percentile of long term annual mean concentrations (1990-2017) of all monitoring points in a groundwater body exceeds the threshold value of the GrwV.

Figure 3 Surface water bodies in Saxony grouped by their contamination with mining related compounds. Long term average concentrations (2000-2017) of all monitoring points in surface water body exceed threshold values of the OGewV. Me: metals including copper, nickel, lead, cadmium, zinc.
standards of sulfate and metals are exceeded, water bodies in the Ore Mountains are mainly only contaminated with metal(loid)-s. Arsenic exceeds environmental quality standards in surface water bodies rather evenly.

**Review of biological mine water treatment methods**

Biological mine water treatment methods were defined to include all methods whose core process rely on the direct utilization of (micro-)biological metabolic processes or, indirectly, their geochemical effect. Above delineated mining related contaminants are all inorganic and thus, with the exemption of sulfate, cannot be degraded, but only be transformed into less mobile forms (immobilization).

With respect to utilizable biological core processes, microbial sulfate reduction (heterotrophic or autotrophic) and microbial iron oxidation are to consider. By stimulating one of these metabolic processes an often complex network of geochemical reactions is induced, including mineral dissolution/precipitation, sorption or further redox reactions. Also purely physical processes support remediation (e.g. filtration). The specific manifestation is strongly dependent on site specific conditions.

For further handling, the assessed mine water treatment methods were grouped by their core technology. Regarding those biological treatment methods that are potentially applicable under Saxony's conditions, these three groups comprise:

a) **Engineered ecosystems** have contact to the atmosphere and are unprotected against climatic influences (constructed aerobic or anaerobic wetlands).

b) **Technical reactors** are constructively closed reaction rooms for a (micro-) biologic community under more controlled conditions (reactors for microbial auto-/heterotrophic sulfate reduction or iron oxidation).

c) **Subsurface reactors** are installations, that supply a reactive medium to the aquifer and use the downstream aquifer as reaction room for the initiated microbial processes (reactive barriers including funnel-and-gate concepts, reactive zone technologies).

No standardized nomenclature for these methods exists. The majority of literature sources published lab scale or bench scale experiments, which were not assessed for this study. Only few publications show performances of existing treatment plants and even less specify figures on (long term) economic feasibility or pitfalls.

**Experiences and perspectives for biological mine water treatment in Saxony**

Until today seven pilot treatment plants were operated in Saxony that utilize biological treatment methods. At the current state none of them will be further developed to full scale by the remediation agencies. Table 1 summarizes location, treatment target, technology and, as far as known, the reason for termination.

Six of the plants listed in Table 1 are located in the lignite mining districts with the focus on treatment of iron and sulfate. Many of them base on heterotrophic sulfate reduction as core process and therefore depend on the supply of a carbon source. The ratio of carbon to sulfate is determined by reaction stoichiometry and therefore limits economic feasibility at the current price of utilizable and regulatory approvable carbon sources. A further characteristic for treatment attempts in the lignite mining areas is the focus on treatment of groundwater flowing into surface streams or water at discrete lake discharges. This reflects the effort of the responsible remediation agency, LMBV mbH, to lower contaminant fluxes into surface streams. Treatment of mining affected groundwater itself on larger scale is not emphasized, as the area of former groundwater draw down altogether covers about 3000 km².

In the Ore Mountains region, with its stronger metal contamination, only one biological pilot plant was operated (Pöhla). Presently the responsible remediation agency, WISMUT GmbH, operates six chemical treatment plants for mine water (mainly heap leakage and waters from pit flooding). Their economic feasibility and secure process control outcompete biological treatment options so far.

<table>
<thead>
<tr>
<th>Site Source</th>
<th>Target contaminants</th>
<th>Technology</th>
<th>Status and period of operation</th>
<th>Reason for termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skado called</td>
<td>Fe, SO(_4)</td>
<td>funnel-and-gate, in-situ injection of glyc erin, hSR</td>
<td>pilot plant 2008-2010</td>
<td>economic feasibility</td>
</tr>
<tr>
<td>Ruhlmühle</td>
<td>Fe, SO(_4)</td>
<td>in-situ injection of glyc erin, nutrients, hSR</td>
<td>pilot plant 12/2014-07/2017</td>
<td>economic feasibility</td>
</tr>
<tr>
<td>Burghammer</td>
<td>Fe, SO(_4)</td>
<td>on-site bioreactor for aSR with generation of H(_2)</td>
<td>on-site test 01/2011-01/2013</td>
<td>realization of pilot test suspended</td>
</tr>
<tr>
<td>Hainer Lake</td>
<td>SO(_4)</td>
<td>on-site fixed-bed reactor with gravel and granular iron, molasses, hSRa</td>
<td>on-site test 06-12/2011</td>
<td>strong T dependence, increased effluent iron concentrations</td>
</tr>
<tr>
<td>Senftenberger Lake</td>
<td>Fe, SO(_4)</td>
<td>in-situ injection of methanol, nutrients, hSR</td>
<td>pilot plant 09/2000-12/2003</td>
<td>not known</td>
</tr>
<tr>
<td>Pöhla</td>
<td>As, Fe, Mn, U</td>
<td>aerobic constructed wetland, FeOx</td>
<td>pilot plant 2004-2014</td>
<td>failed to meet target concentrations; high maintenance and costs</td>
</tr>
</tbody>
</table>

Generally, most of the biological treatment methods could reduce concentrations of target contaminants. Each of the methods has its specific capabilities and limitations that are further restricted if effluent concentrations are to meet regulatory limits for the good status (Figure 1). To summarize, the following perspectives and limiting conditions were derived from experiences in biological mine water treatment in Saxony:

1. Related to chemical treatment, specific space requirement is increased due to lower reaction rates. Further, biological reaction rates show higher temperature dependencies. Especially in the Ore Mountains region, this may bring surface water treatment to cease during winter.

2. Biological mine water treatment methods do not per se have lower maintenance costs than chemical treatment methods have.

3. Immobilization of metal(oid)-s creates sludges, sediments or geological bodies enriched in these contaminants. Long term possibilities for utilization, disposal or protection against redissolution must be found. This limitation also affects non-biological treatment methods.

4. All treatment methods based on hetrotrophic sulfate reduction need a microbially utilizable and regulatory approved carbon source. For flown through solid media these should also be long-term permeable for years. Economically feasible substances, for which durable discharge into water is expected to be regulatory permitted, are not known at the present time. As a rule-of-thumb the costs for carbon source alone account for 0,5…1 € per kg sulfate.

5. Microbial sulfate reduction requires absence (or if not given, removal) of oxygen and nitrate in the water to treat. Surface waters and partly groundwater in Saxony are naturally aerobic which implies additional effort to implement sulfate reduction.

6. All in-situ methods utilizing sulfate reduction are perceptible for redissolution of sulfidic precipitates as soon as anaerobic conditions cease after treatment (Vandenbohede et al. 2019).

7. Treatment of contaminated rivers or streams offers another constraint: Most of the contaminants considered here (metals, metalloids) are sorbed at particular matter of the stream bed. Dynamic equilibrium between dissolved and sorbed metal(oid)-s would obliterate any treatment of water alone.

Potential application of biological treatment for mining impacted water in...
Saxony is seen for local hot-spots, as for example heap leachate with constructed wetlands or in-situ methods for highly contaminated groundwater streams. Layout of the treatment technology as well as economic feasibility depend on the specific site conditions at one hand and future development of official regulations and prices at the other hand.

**Conclusions**

There are numerous examples for successful biological mine water treatment worldwide (e.g. Skousen et al. 2017). However, in summary the following obstacles hinder broad application of biological mine water treatment under conditions in Saxony: a) economic boundary conditions (e.g. price for approvable carbon source), b) often lower process control compared to chemical treatment, and last but not least c) the sheer extend of contaminated water volumes, with often no distinct contamination hot-spot; where the latter point is valid for any treatment technology.

**Acknowledgements**

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Hydraulic-economic optimal management model of mine water resources: an example is Suancigou Coal Mine in western China

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Abstract
A majority of coal mines, located in arid and semi-arid areas of western China, are facing the challenges among mine water resource supply, drainage and ecological environment. Numerical models of groundwater movement in aquifers are built in Suancigou Coal Mine, which are based on hydrogeological conditions analysis and characterization of mine water filling factors. According to the specific requirement of mine water users for water quantity and quality, mine water is treated in tertiary (sewage) treatment. The optimized hydraulic-economic management model is analyzed by control, treatment, utilization, recharge and ecological environmental protection of mine water. The model solves the mine water resource problems in Suancigou Coal Mine, and supports it to realize the sustainable development and utilization of groundwater resources, which would contribute to tremendous economic benefits.

Keywords: mine water, numerical model, treatment and utilization of mine water resource, hydraulic-economic optimal management model

Introduction
Mine water, not only threatens coal mine production safety, but potentially leads to environmental pollution and a great waste of water resources due to unscientific discharge (Qian and Miao et al. 2007). At present, China’s coal production is about 3.7 billion tons per year, while mine water drainage is up to 7.2 billion tons annually (Wu 2014), which strongly proves that mine water resource is one of largest associated resources during coal mining (Wu and Li 2009). In recent years, with awareness-raising of protecting water resources and environment, and driving by maximization of enterprises’ interests, the utilization rate of mine water has increased gradually (He and Yang et al. 2008). However, value of utilization rate is still low in China, which is of huge differences between different regions, and far from the goal set by the government. Optimizing the combination model of mine water control, treatment, utilization, recharge and ecological environment protection in Suancigou Coal Mine is to treat and utilize mine water in order to maximize of economic benefits on the premise of ensuring mine safety production. Based on the analysis of mine hydrogeological variations and mine water filling factors, the numerical model of mine groundwater is established and the characteristics of the groundwater flow field under the current mining conditions are simulated. Mine water treatment technology coordinated by ground and underground is put forward according to water quality and quantity requirement of users. Finally, the hydraulic-economic optimal management model of mine water control, treatment, utilization, recharge and Eco-environment protection is established.

General situation of mine
Suancigou Coal Mine, located in Junggar of Inner Mongolia, China (Fig. 1), is developed by inclined shaft with a face of about 49.8
km². At present, the main mining areas are the 4th coal seam of the Lower Permian Shanxi Formation and the 6th coal seam of the Upper Carboniferous Taiyuan Formation. The landscape of the mining area belongs to the erosive hilly landform of the plateau, and the branched valleys are well developed in the Ordos Loess Plateau. The topography is generally high in the north and low in the south. Further more, it shows a trend of high in the middle and low in the East and west. The climate of Ordos is dry semi-desert plateau continental arid climate. Large temperature difference between day and night, and the annual average temperature is between 5.3 and 7.6 °C. Rainfall mostly concentrated from July to September, which making for 60% to 70% of the total precipitation.

Groundwater aquifers in Suancigou Coal Mine mainly include porous aquifers of Quaternary loose rocks, fractured aquifers of Carboniferous-Permian clastic rocks and karst aquifers of Ordovician carbonate rocks. The hydrogeochemistry analysis results and environment isotope test values show that the hydraulic relationship between different aquifers is weak.

Mine water control

By analyzing the mine water filling factors and the current mine production, the main mine water source in Suancigou is the sandstone fissure water in coal roof and the goaf water respectively. It enters the underground mine mainly in three ways: (1) borehole drilling, exploring and drainage water holes in mine; (2) water drainage boreholes in goaf; (3) faults and water-conducting fissure zone. Based on both “upper three zones” model (Ma and Wu 2008) and empirical formula that take the water-conducting fracture zone height into account, risk assessment of roof water-inrush is obtained by characterization of roof rock assemblage and water-rich analysis of roof aquifer formation. Firstly, risk assessment results show that the fissure water in the aquifer formations of the Carboniferous Taiyuan Formation, Permian Shanxi Formation and Lower Shihezi Formation can flow into the mine through the water-
conducting fissure zone. Secondly, not only water yield property of water-bearing rock groups affected by water-conducting fissure zones are very weak, but water yield property of water-bearing rock groups not affected by water-conducting fissure zones are with similar features. In addition, water yield property is relatively strong about the pore aquifers of loose rocks in Quaternary valleys which are not affected by water-conducting fissure zones. Moreover, the aquicludes underlying Quaternary pore aquifers have better integrity and continuity, and their thickness is fairly large. Hence, water inrush from the roof will not occur in general.

According to mine geology and hydrogeology condition, the numerical model of groundwater movement in Suancigou Coal Mine is established by MODFLOW module in Groundwater Modelling System (GMS) in order to better shown the groundwater movement. The hydrogeological parameters of the model are calibrated and evaluated according to the dynamic data of karst water level with observation boreholes. Then the groundwater flow field under current mining conditions are simulated. The results show that the fissure water in both Shanxi Formation aquifer of Permian Lower Shihezi Formation and Carboniferous Taiyuan Formation aquifer of Permian Shanxi Formation finally forms a cone when groundwater seeps into the mining area through the water-conducting fissure zone.

**Mine Water Treatment, Utilization and Recharge**

Whenever groundwater flows into the water filling aquifer in mines, it will be reacting with surrounding rocks and coal seams by a series of chemical reactions. Meanwhile, mining activities will pollute water quality as well. Therefore, the characteristics of mine water quality are almost same with the hydrochemical characteristics of water-filled water source, and probably be infected by other factors as well.

The combined process of pretreatment, primary treatment and secondary treatment is adopted in mine water treatment system. Pretreatment, including diversion of clear water and waste water, and goaf purification, is a type of underground treatment. Primary treatment is processed above ground, which includes clarification and disinfection. Secondary treatment, effectively remove dissolved salt, colloid, bacteria, viruses, bacterial endotoxins and most organic substances in mine water, is a reversing osmosis membrane treatment technology.

Users of mine water in Suancigou mine, power plants, underground dust removal and drilling (underground production I), bathhouses, underground equipment cooling (underground production II), ground recharge, coal washery and mining area greening, are determined based on water requirement of Suancigou Mine and its surrounding enterprises, and the principle of water supply by mine water quality.

Mine water that under ground can be used in coal washing plant after processed by the ground horizontal flow sedimentation tank; primary treatment water mainly roles as greening or dust removal; secondary treatment water mainly acted as water source of bathing, power plants, and underground equipment cooling. Ground recharge plays the role as artificial storage, where redundant mine water source, processed by secondary treatment that meets the requirement of water quality for water recharging, can be recharged to groundwater aquifers.

To protect and adjust the utilization of mine water resources, a karst water pumping borehole is selected as injection well which is 560 m deep and exposed high permeability karst aquifer formation about 200 m. In groundwater injection test, the injection rate ups to 1440 m³/h with natural pressure condition (water pressure is about 3 MPa in natural state). Thus, the recharge borehole works well, and is well suitable for adjusting mine water resources under current mine water inflow condition.

**Ecological environment protection**

Discharge rate of mine water in Suancigou Coal drops to zero after the above treatment, and neither threaten or damage the hydro-environment of surface rivers, soil and groundwater surrounding the mine. As karst water acts as the mainly water source for industrial and residential water supply in...
this region, mine water resources utilization cannot only reduce the consumption of the water source, but also supplement the water source by surface water injection. Therefore, it would be benefit to the local ecological and hydrological environment protection, and conducive to the sustainable use and development of karst water resources at the same time (Gunson and Klein et al. 2012).

**Hydraulic-Economic Optimal Management Model**

In view of the mine programming of Suancigou Mine, management periods are divided into two 2.5-years. Under the premise of ensuring the safety of mine production (that is, no mine water hazard occurs), the hydraulic-economic optimal management model, based on both demands of users for mine water resources and water quality, and various quality cost of mine water treatment, is established in Suancigou Coal Mine aiming at maximizing economic benefits by groundwater dynamics theory and operation research, including mine water resources control, treatment, utilization, recharge and environmental protection (Wu and Wang et al. 2010).

The optimal management model is composed of objective function and constraint conditions. First of all, the water supply price of users is formulated specially according to regulations of regional industrial water price. Then, customized water quality requirements of various users to determine their water quality treatment cost separately. After that, mine water transmission cost from sewage plant to various users is calculated accordingly. Finally, followed objective functions are set up with the maximum economic benefit of the coal mine.

Where $N_1, N_2, N_3, N_4, N_5, N_6, N_7$ are the number of water supply wells for the power plant, underground production I, bathhouse, underground production II, surface recharge, coal washery, and greening of the mining area, respectively.

$Q_{a(i,j)}, Q_{b(i,j)}, Q_{c(i,j)}, Q_{d(i,j)}, Q_{e(i,j)}, Q_{f(i,j)}, Q_{g(i,j)}$ indicates the single well water supply rate for power plant, underground production I, bathhouse, underground production II, surface recharge, coal washery and greening of mining area in the first and second periods. $g_{f1}$ denotes water supply price of power plant; $g_{f2}$ denotes water supply price of underground production I, bathhouse, coal washery, underground production II and greening of mining area respectively; $g_{f3}$ represents water supply price of ground recharge; $t_{f1}, c_{f1}, c_{f2}$ respectively represents the cost of extraction and first treatment and second treatment of mine water; $s_{f1}$ represents water transmission cost of power plant; $s_{f2}$ represents water transmission cost of underground production I, ground recharge and underground production II; $s_{f3}$ is water conveyance cost of bathhouse; $s_{f4}$ is water conveyance cost of coal washery; $s_{f5}$ is water conveyance cost of greening, and $C(i,j)$ is the days of planning period.

\[
\begin{align*}
\text{Max } Z &= \sum_{i=1}^{N_1} \sum_{j=1}^{C(i,j)} C(i,j)(g_{f1} - t_f - c_{f1} - c_{f2} - s_{f1})Q_{a(i,j)} + \sum_{i=1}^{N_2} \sum_{j=1}^{C(i,j)} C(i,j)(g_{f2} - t_f - c_{f1} - c_{f2} - s_{f2})Q_{b(i,j)} + \sum_{i=1}^{N_3} \sum_{j=1}^{C(i,j)} C(i,j)(g_{f2} - t_f - c_{f1} - c_{f2} - s_{f3})Q_{c(i,j)} + \sum_{i=1}^{N_4} \sum_{j=1}^{C(i,j)} C(i,j)(g_{f2} - t_f - c_{f1} - c_{f2} - s_{f4})Q_{d(i,j)} + \sum_{i=1}^{N_5} \sum_{j=1}^{C(i,j)} C(i,j)(g_{f2} - t_f - c_{f1} - c_{f2} - s_{f5})Q_{e(i,j)} + \sum_{i=1}^{N_6} \sum_{j=1}^{C(i,j)} C(i,j)(g_{f2} - t_f - c_{f1} - c_{f2} - s_{f6})Q_{f(i,j)} + \sum_{i=1}^{N_7} \sum_{j=1}^{C(i,j)} C(i,j)(g_{f2} - t_f - c_{f1} - c_{f2} - s_{f7})Q_{g(i,j)}
\end{align*}
\]
The constraint conditions include both the drawdown value or range of groundwater level in aquifers disturbed by coal seam mining, and the specific water demand values of each user. Regarding to the area where the mine has been exploited, the groundwater drawdown of the controlled observation points satisfies the following constraint conditions:

\[ \sum_{i=1}^{N_1} \beta(k, i, 1) Q_a(i, 1) + \sum_{i=1}^{N_2} \beta(k, i, 1) Q_b(i, 1) + \sum_{i=1}^{N_3} \beta(k, i, 1) Q_c(i, 1) + \sum_{i=1}^{N_4} \beta(k, i, 1) Q_d(i, 1) + \sum_{i=1}^{N_5} \beta(k, i, 1) Q_e(i, 1) + \sum_{i=1}^{N_6} \beta(k, i, 1) Q_f(i, 1) + \sum_{i=1}^{N_7} \beta(k, i, 1) Q_g(i, 1) = s(k, 1) \]  

(2)

\[ \sum_{i=1}^{N_1} \beta(k, i, 2) Q_a(i, 1) + \sum_{i=1}^{N_2} \beta(k, i, 1) Q_a(i, 2) + \sum_{i=1}^{N_3} \beta(k, i, 1) Q_b(i, 1) + \sum_{i=1}^{N_4} \beta(k, i, 1) Q_b(i, 2) + \sum_{i=1}^{N_5} \beta(k, i, 1) Q_c(i, 1) + \sum_{i=1}^{N_6} \beta(k, i, 1) Q_c(i, 2) + \sum_{i=1}^{N_7} \beta(k, i, 1) Q_d(i, 1) + \sum_{i=1}^{N_8} \beta(k, i, 1) Q_d(i, 2) + \sum_{i=1}^{N_9} \beta(k, i, 1) Q_e(i, 1) + \sum_{i=1}^{N_{10}} \beta(k, i, 1) Q_e(i, 2) + \sum_{i=1}^{N_7} \beta(k, i, 1) Q_f(i, 1) + \sum_{i=1}^{N_{11}} \beta(k, i, 1) Q_f(i, 2) + \sum_{i=1}^{N_7} \beta(k, i, 1) Q_g(i, 1) + \sum_{i=1}^{N_{12}} \beta(k, i, 1) Q_g(i, 2) = s(k, 2) \]  

(3)

To the planned mining area, groundwater drawdown of the controlled observation points satisfies the following constraint conditions:

\[ \sum_{i=1}^{N_1} \beta(k, i, 1) Q_a(i, 1) + \sum_{i=1}^{N_2} \beta(k, i, 1) Q_b(i, 1) + \sum_{i=1}^{N_3} \beta(k, i, 1) Q_c(i, 1) + \sum_{i=1}^{N_4} \beta(k, i, 1) Q_d(i, 1) + \sum_{i=1}^{N_5} \beta(k, i, 1) Q_e(i, 1) + \sum_{i=1}^{N_6} \beta(k, i, 1) Q_f(i, 1) + \sum_{i=1}^{N_7} \beta(k, i, 1) Q_g(i, 1) \leq s(k, 1) \]  

(4)

\[ \sum_{i=1}^{N_1} \beta(k, i, 2) Q_a(i, 1) + \sum_{i=1}^{N_2} \beta(k, i, 1) Q_a(i, 2) + \sum_{i=1}^{N_3} \beta(k, i, 1) Q_b(i, 1) + \sum_{i=1}^{N_4} \beta(k, i, 1) Q_b(i, 2) + \sum_{i=1}^{N_5} \beta(k, i, 1) Q_c(i, 1) + \sum_{i=1}^{N_6} \beta(k, i, 1) Q_c(i, 2) + \sum_{i=1}^{N_7} \beta(k, i, 1) Q_d(i, 1) + \sum_{i=1}^{N_{11}} \beta(k, i, 1) Q_d(i, 2) + \sum_{i=1}^{N_9} \beta(k, i, 1) Q_e(i, 1) + \sum_{i=1}^{N_{10}} \beta(k, i, 1) Q_e(i, 2) + \sum_{i=1}^{N_7} \beta(k, i, 1) Q_f(i, 1) + \sum_{i=1}^{N_{12}} \beta(k, i, 1) Q_f(i, 2) + \sum_{i=1}^{N_{13}} \beta(k, i, 1) Q_g(i, 1) + \sum_{i=1}^{N_{14}} \beta(k, i, 1) Q_g(i, 2) = s(k, 2) \]  

(5)

The customized amount of mine water required by each user meets the following constraint conditions:

\[ Q_1 \leq \sum_{i=1}^{N_1} Q_a(i, 1) \leq Q_2, \quad Q_1 \leq \sum_{i=1}^{N_2} Q_a(i, 2) \leq Q_2, \quad Q_3 \leq \sum_{i=1}^{N_3} Q_b(i, 1) \leq Q_4, \quad Q_3 \leq \sum_{i=1}^{N_4} Q_b(i, 2) \leq Q_4, \]
\[ Q_5 \leq \sum_{i=1}^{N_5} Q_c(i, 1) \leq Q_6, \quad Q_5 \leq \sum_{i=1}^{N_6} Q_c(i, 2) \leq Q_6, \quad Q_7 \leq \sum_{i=1}^{N_7} Q_d(i, 1) \leq Q_8, \quad Q_7 \leq \sum_{i=1}^{N_8} Q_d(i, 2) \leq Q_8, \]
\[ Q_9 \leq \sum_{i=1}^{N_9} Q_e(i, 1) \leq Q_{10}, \quad Q_9 \leq \sum_{i=1}^{N_{10}} Q_e(i, 2) \leq Q_{10}, \quad Q_{11} \leq \sum_{i=1}^{N_{11}} Q_f(i, 1) \leq Q_{12}, \quad Q_{11} \leq \sum_{i=1}^{N_{12}} Q_f(i, 2) \leq Q_{12}, \quad Q_{13} \leq \sum_{i=1}^{N_{13}} Q_g(i, 1) \leq Q_{14}, \quad Q_{13} \leq \sum_{i=1}^{N_{14}} Q_g(i, 2) \leq Q_{14} \]  

(6)
\( \beta(k,i,1) \) represents the unit impulse response function in the first period, and \( \beta(k,i,2) \) represents that in the second period. \( Q_s(i,1), Q_s(i,2), Q_s(i,1), Q_s(i,1), Q_s(i,2), Q_s(i,2), Q_s(i,1), Q_s(i,2) \) are the single well water supply for power plant, underground production I, bathhouse, underground production II, surface recharge, coal washery and mining area greening in the first period, separately. \( Q_s(i,2), Q_s(i,2), Q_s(i,2), Q_s(i,2), Q_s(i,2), Q_s(i,2), Q_s(i,2), Q_s(i,2) \) denote that in the second period. \( s(k,1) \) is the water level drawdown value of the control observation point in the first period, and \( s(k,2) \) is the water level drawdown value of the control observation point in the second period. \( Q_s, Q_s \) show the upper and lower limits of water demand for the power plant. \( Q_s \) and \( Q_s \) form the upper and lower limits of water demand for underground production I. \( Q_s, Q_s \) respectively indicate the upper and lower limits of water demand for the bathhouses. \( Q_s, Q_s \) represent the upper and lower limits of water demand for underground production II. \( Q_s, Q_s \) indicate the upper and lower limits of water demand for surface recharge. \( Q_s, Q_s \) are the upper and lower limits of water demand for coal washing plant. \( Q_s, Q_s \) indicate both the upper and lower limits of mining area greening.

**Conclusions**

The relationship between the optimal combination of mine water control, treatment, utilization, recharge and ecological environment protection is systematically researched by taking prevention and control of mine water disaster, mine water decontamination, and water resources utilization as the goal in Suancigou Coal Mine. A groundwater movement numerical model is established based on hydrogeological conditions analysis and mine water filling factors characterization. By tertiary (sewage) treatment of mine water resources, specific water supply for different users is realized, and the injection test shows that recharge well can realize the function of mine water resources adjustment in coal mine. The optimal hydraulic-economic management model of mine water control, treatment, utilization, recharge and eco-environmental protection in Suancigou Coal Mine is established, which scientifically improves the management level in coal mines, in order to realize zero discharge rate of mine water, protection of ecological and hydrological environment, and achieves maximum economic.

**Acknowledgments**

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MINE WATER HYDROGEOLOGY
Spatial water interaction in radium/uranium mines – a Portuguese case study

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Abstract

The extraction of radioactive ore produces tailings and large volumes of waste rocks accumulated in the dumps. The abandoned Picoto radium mine area is located close to Vilar Seco village (Portugal). The mineralization occurs in quartz veins, with torbernite, meta-torbernite and uranophane, and some U-bearing minerals. The mine is in a soft slope area, with altitudes ranging from 360-380 m, included in the Cagavaio river catchment.

The mining works were developed in surface and underground. First radium exploitation was carried out between 1917-21, in two open pit mines. Later, from 1950-53, the exploitation was reactivated, in underground galleries, to produce uranium. This mine was closed in 1953 and never has been restored. A local growing area was developed, mainly for vineyards and agricultural products. Three dumps contain about 35000 tonnes of wastes and is slightly covered by vegetation.

A total of ten surface water and groundwater samples were collected. Most waters have pH values from 4.7 to 6.3 and are poorly mineralized (EC=45-224 µS/cm; TDS=17-150 mg/L). However, some waters are contaminated with NO₂⁻, Fe, Mn, As and U. The drainage waters must be controlled within a temporal and spatial monitoring.

Keywords: radium/uranium mines, water, contamination, remediation, central Portugal

Introduction

Mine activities have a potentially harmful effect in surface water and groundwater. The extraction of radioactive ore produces tailings, large volumes of contaminated waste rocks and heap-leach residues accumulated in the dumps at mine sites. Associated sulphur bearing minerals are oxidised, causing acidification of water and the release of metals. The erosion and weathering of dumps cause contamination of surface water and groundwater (e.g. Gómez et al. 2006; Antunes et al. 2018) leading to contamination of stream sediments and soils (e.g. Lottermoser et al. 2005; Lottermoser and Ashley 2006; Kipp et al. 2009). Particularly, in the wet season and wet climates, acid mine drainage development and leaching of dumps are dominant pathways of contaminants into the surrounding environment.

Uranium mining within Europe reached its height between 1960 and 1990, after which the deposits became depleted and mines closed (Dittmar 2013). Consequently, there are about 150 uranium mines in the EU (Raeva et al. 2014; Falck 2015). In Portugal, about 60 radioactive ore deposits were exploited, between 1908 and 2001, to produce radium and uranium (Carvalho 2014). These mines were abandoned, and local areas were studied to assess the influence of environmental radioactivity and potentially toxic elements

The main purpose of this study is to characterize the spatial water interaction in a radium/uranium mine area and temporal variability of some chemical proprieties and trace element contents in surface water and groundwater associated with the old Picoto mine, 65 years after the closure.

**Methods**

The abandoned Picoto mine area is located at the Central Iberian Zone of the Iberian Massif (ZCI), close to Vilar Seco village, southeast of Viseu, central Portugal. The area is included in the catchment of the Cagavaio river, with dominant drainage NE-SW, and in a soft slope topography, with altitudes ranging between 360 and 380 m (Fig. 1).

In this area, a Variscan porphyritic biotite > muscovite granite (late- to post-D3) occurs and intruded the Beiras Group complex (previously called Schist-greywacke Complex), containing phyllites and metagreywackes (Oliveira et al. 1992; Azevedo et al. 2005). The medium- to coarse -grained porphyritic granite, with biotite > muscovite, contains up to 9-17 mg/L U, in uranium bearing minerals, such as uraninite, zircon and monazite (Cotelo Neiva 2003). Granite is affected by different episiensitization degrees (Teixeira et al. 2010).

The mineralization occurs mainly in quartz veins intruding the granite. These quartz veins fill faults and fractures trending N37°-45° E and N50°-70° E, locally brecciated (Cotelo Neiva 2003). The metatorbernite and uranophane, together with some U-bearing minerals such as chlorite and Fe-Mn-hydroxides, and pyrite, occur in the quartz and disseminated microfractures (Teixeira et al. 2010).

The mining activity took place in open pits and underground. Between 1917 and 1921, an inicial radium exploitation was developed in two open-pit mines (NE Rio Cagavaio). After that, between 1950/53, uranium was exploited in underground galleries, about 150 m long. The mine ceased its activity in 1953, leaving three waste heaps, with about 35 000 tonnes, without any intervention and rehabilitation measures. Nowadays, the area is occupied by local crops, especially vineyard and agricultural products mainly to local human consumption.

![Figure 1 Geographic setting of the Picoto mine area and location of water sampling points (Surface water: ● – stream water; groundwater: X - spring; ▲ - well).](image)
A total of ten sampling points was chosen to collect surface water (samples: 5, 6, 8 and 10) and groundwater (samples: 1, 2, 3, 4, 7 and 9), twice in a hydrological year, representative of the dry (summer) and raining period (winter). The water samples 8 and 9 were collected upstream the mine area, located outside the mine influence, and representing the local background (Fig. 1). Waters were collected about 20 cm below the surface of the water level. Temperature, pH, Eh, dissolved oxygen (DO), Total Dissolved Solids (TDS), Electrical Conductivity (EC) and alkalinity were determined “in situ”. The samples were filtered through 0.45 µm pore size membrane filters. Those for the determinations of cations were acidified with HNO₃ at pH 2 and analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using a Horiba Jovin Yvon JV2000 2 spectrometer with a monochromator. Anions were determined in non-acidified samples by ion chromatography with a Dionex ICS 3000 Model. Duplicate blanks and a laboratory water standard were analysed for quality control. The validation of the precision of the analytical results was performed according to the methodologies of Xuejing (1995) and Min et al. (2014). The determinations were carried out in the Department of Earth Sciences, University of Coimbra, Portugal.

**Results**

The abandoned mine area of Picoto is located close to a rural area, in the vicinity of Vilar Seco, and some of its water is used for agricultural irrigation.

In general, the waters are acidic or near neutral, with pH values ranging from 4.7 to 6.3, with the most acid value obtained in the surface water receiving drainage from the Picoto mine area (water sample 6; Fig. 1). Most waters are poorly mineralized (EC=45-224 µS/cm), which is supported by the values of total dissolved solids (TDS), ranging from 17 to 150 mg/L. According to the Piper classification, the dominant hydrochemical water facies is of undefined type or Na-Cl-HCO₃ water type.

The water samples have high metal contents and are classified as acid to near-neutral in the Ficklin diagram (Fig. 2). There is no significant difference between the chemical composition of the waters collected outside the mine influence (water points 8 and 9, Fig. 1) and the waters located inside the mine influence (Fig. 2).

During the dry period, the waters tend to be more acidic and have higher EC values, particularly groundwater (springs and wells). Sulphide oxidation of the mineralized veins, now accumulated in the tailings and heaps, produce the most acid water, and increase the leaching and solubility of potentially toxic elements (e.g. Antunes et al. 2016, 2018).

In general, in the dry period, there are higher NO₂⁻, Fe, Cu and As water contents than in the rainy period, probably due to a concentration effect (Fig. 3). Most of the waters does not present significant variation in U contents between the dry and rainy period. Otherwise, Th contents tend to have higher values in the rainy season (Fig. 3), probably due to dissolution in favourable pH-Eh conditions.

However, most waters are contaminated with NO₃⁻, Fe, Mn, Cu, As and U and should not be used for human consumption or agricultural activities (Fig. 3). The Fe and Cu water contamination occurs preferentially in the dry period, associated with lower pH values, which promotes an increase of chemical species dissolution, with the release of the metals. The water contamination is mainly associated with the old radium mine and human activities.

The results of external gamma radiation show high values, particularly near waste...
dumps from the mine exploitation (0.61 μGy.h⁻¹), surpassing the regional background value for the Oliveira do Hospital region; being an indicator of radiological contamination due to mining activity (EDM 2007).

**Conclusions**

In the studied area, water contamination is mainly associated with old mine activities for radium/uranium exploitation.

The drainage waters must be controlled with spatial and temporal monitoring.

The obtained results in surface and groundwater associated with the Picoto abandoned radium/uranium mine reinforce the evidence of environmental and human health risks associated with old abandoned mine areas and the definition and application of adequate remediation and/or rehabilitation methodologies.

**Acknowledgements**

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**Figure 3** Seasonal chemical variation in waters from the Picoto mine area. Dry period (summer) - light gray; rainy period (winter) - black. Water points: st – stream water; w - well; s - spring. VP - parametric value (Portuguese Decree 1998, 2007, WHO 2011).
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Oliveira JT, Pereira E, Ramalho M, Antunes MT, Monteiro JH (Coords.) (1992) Geological map of Portugal, 1/500 000 (5th Ed.), SGP, Lisboa
Abstract
The Iberian Pyrite Belt is one of the largest metallogenic province in the world. The characteristics of this region have a reflection on the existence of Acidic Mine Drainage (AMD) discharged into the river network affecting the water quality.

A several number of surface and groundwaters in the Iberian Pyrite Belt (south of Portugal) was collected in different water environments. Mine water is highly acid with medium-high to extreme metal contents, while surface and groundwater are neutral with low metal contents. Mine waters are the most contaminated with a maximum EC value (27570 µS/cm) and SO$_4^{2-}$ (80691 mg/L), As (141 mg/L), Cu (1445 mg/L), Fe (41023 mg/L), Zn (841 mg/L) contents.

A numerical index of acid mine drainage (AMDI) has been calculated. The group of mine water environment had a mean AMDI of 20.0 reflecting a little or no dilution of direct mine water drainage. River network could be indicated as an affected river downstream mine drainage (AMDI 80.2), while groundwater (AMDI 92.2) is uncontaminated by AMD. The groundwater composition will be strongly controlled by natural geochemical processes, from the geology of the ore deposits and water rock interaction.

Keywords: surface, groundwater, acid mine indexes, contamination, monitoring

Introduction
The incessant mining activity since Roman times promoted numerous abandoned and active mine sites that are an important source of water contamination. Nowadays, there are more than 4800 ha occupied by waste dumps, open pits, tailing dams, and mining facilities (Grande et al. 2013). Some of these mines can be considered representative of the paragenetic diversity as well as of mining history and environmental framework of the Iberian Pyrite Belt (IBP), in southwestern Europe, one of the most important metallogenic provinces in the world. In this metallogenic province, which covers a large area of cross-border territory between Portugal and Spain, most of the mines were closed without environment guidelines and without preventive or corrective measures to protect the environment (Rodrigues 2011; Grande et al. 2013).

Water is a key resource for human living, especially for drinking and irrigation purposes and its quality is one of the most critical factors influencing human health (Zhang et al. 2012). Water protection is a major management concern, particularly in scenarios of water scarcity and water contamination, especially in mining regions with semi-arid climates. The studied area is one of the driest regions of southwestern Europe, with precipitation occurring mostly in the winter months, and droughts frequently occurring during the summer (Gomes et al. 2018).

One of the most serious problems of environmental contamination worldwide is the formation of acid mine drainage (AMD) in mining regions. The general process of AMD formation results from a series of
interconnected steps that are primarily accomplished by oxidation of sulphides (Lottermoser 2010). Sulphide minerals are exposed to weathering, which generates acidity, sulfate and potentially toxic elements (e.g., Valente et al. 2015; Gomes et al. 2016; Soyol-Erdene et al. 2018). The leachates emerging from waste dumps, tailings dams, and other mining facilities are discharged into the river network, being responsible for the contamination of the receiving water courses (Valente et al. 2013; Gomes et al. 2018).

There is a considerable difficulty in comparing temporal and spatial variation of AMD wastewaters, and affected surface and groundwaters, using individual chemical and physical parameters. The effect of AMD on the different water systems is also complex due to the multi-factor nature of the effects (Kelly 1988). Slight variations in environmental conditions can cause substantial differences in individual parameter flux rates. Therefore, acid mine drainage index (AMDI) is very important to detect, quantify and categorize water quality and to monitor the recovery of contaminated sites (Kuma et al. 2011).

The present study aims to study the occurrence of some potentially toxic elements in different spatial water environments in the semi-arid climate Portuguese metallogenic province of the IPB and the application of the acid mine drainage index. This index allows for the contamination detection and its quantification from acid mine drainage and consequently to monitor the recovery of receiving waters.

Methods
The study area is in the southwest region of the Iberian Peninsula, covering the Portuguese sector of the Iberian Pyrite Belt (IPB). This region is part of a geological formation with a high density of polymetallic sulphide deposits which extends from Seville (Spain) to the coast of Portugal (Fig. 1).

The IPB is subdivided into several tectono-stratigraphic units including the Phyllite-Quartzite (PQ) Group and the volcano-sedimentary complex (VSC) (Sáez et al. 1999). The presence of more than 90 polymetallic sulphide deposits associated with the volcano-sedimentary complex gives to the Pyrite Belt a status of being a world-class metallogenic province (e.g., Relvas et al. 2002). The massive sulphide deposits contain predominantly pyrite, sphalerite, galena and chalcopyrite, and are associated with many minor phases (Sáez et al. 1999). The geological and mineralogical characteristics of the region reflect the existence of AMD-producing wastes that are dispersed by the numerous mining complexes and once discharged into the river network, and may affect the quality of water bodies (Gomes et al. 2018).

A total of twenty-one surface and groundwater samples in the IPB (south of Portugal) was collected and analysed for physico-chemical properties and selected trace elements. Water sample sites were categorized into three similar groups based on source classification: mine water environments (10 samples), river network (6 samples) and
groundwater (5 samples). Temperature, pH, redox potential (Eh), Total Dissolved Solids (TDS) and Electrical Conductivity (EC) were measured “in situ”. The collected samples were transported to the laboratory and the anions were determined by ion chromatography, while metals and arsenic were analysed by inductively coupled plasma optic spectrometry (ICP-OES).

Numerical indices of the severity of acidic mine drainage have been calculated for the three different water environments of the study area. The acid mine-drainage index (AMDI; Gray 1996) is calculated using a modified arithmetic weighted index utilizing seven parameters (qi) which are most indicative of acid mine-drainage contamination, i.e. pH value, sulphate, iron, zinc, aluminium, copper and cadmium. Weighting (wi; Table 1) express the relative indicator value of each parameter, estimated by consideration of (a) the concentration of parameters in raw and diluted AMD, (b) their sorption properties, (c) the effect of neutralization on concentration, (d) the relevance of concentration to ADM formation, and (e) detection limits of the analytical procedures used (Nieva et al. 2018). The pH and sulphate are considered to be of highest indicator value as they were unaffected by sorption processes, while sulphate was also unaffected by neutralization processes and by natural neutralization (Gray 1996). The AMDI score is calculated according to the equation: 

\[ \text{AMDI} = \left(\frac{\sum (q_i w_i)}{100} \right) \]

where qiwi are the water quality ratings of the seven parameters.

The water quality (q) for each parameter is measured on a scale from 0 to 100, with values closer to 0 corresponding to the raw AMD or to highly contaminated waters and 100 to the best possible quality. However, the problem with this approach is that it lacks sensitivity in the effect which a single bad parameter value will have on the water quality index (Gray 1996).

**Results**

Mine water is highly acid (pH 1.8-3.6) with medium-high to extreme metal contents, while surface water (pH 6.6-7.7) and groundwater (pH 7.2-8.0) are neutral with low metal contents (Fig. 2). There is no significant difference between the chemical composition of surface and groundwater suggesting a low residence time, therefore surface waters show a high metal content (Fig. 2).

However, all the waters are extremely mineralized with an electrical conductivity mean value of 8926, 1262 and 1136 µS/cm, in mine waters, surface water and groundwater, respectively. Mine waters are the most contaminated with a maximum EC value of 27570 µS/cm and SO\(_4^{2-}\) (80691 mg/L), As (141 mg/L), Cu (1445 mg/L), Fe (41023 mg/L), Zn (841 mg/L) contents. These waters are contaminated and cannot be used for human consumption or agricultural irrigation according to the Portuguese parametric values (Portuguese Decree 1998; 2007).

The piper classification shows a set of samples that are mainly sulphate waters (magnesium and mixed sulphate-types), corresponding to the AMD-affected waters (Gomes et al. 2018). Surface freshwaters present higher variability and are mainly mixed chloride and sulphide. Groundwaters are mixed chloride suggesting a water rock interaction.

### Table 1. Parameters and weightings used in the calculation of ADMI (Kuma et al. 2011).

<table>
<thead>
<tr>
<th>Parameter identifier (i)</th>
<th>Parameter</th>
<th>Weighting (wi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>Sulphate (mg/L)</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>Iron (mg/L)</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td>Zinc (mg/L)</td>
<td>0.12</td>
</tr>
<tr>
<td>5</td>
<td>Aluminium (mg/L)</td>
<td>0.10</td>
</tr>
<tr>
<td>6</td>
<td>Copper (mg/L)</td>
<td>0.08</td>
</tr>
<tr>
<td>7</td>
<td>Cadmium (µg/L)</td>
<td>0.1</td>
</tr>
<tr>
<td>Total weighting</td>
<td></td>
<td>1.0</td>
</tr>
</tbody>
</table>
The ADMI index was calculated considering the most indicative parameters of AMD contamination ($q_i$ – pH, $SO_{4}^{2-}$, Fe, Zn, Al, Cu and Cd) and their respective weightings ($w_i$) of the water from mine water environments, river network and groundwater (Table 2). The group of mine water environments had a mean AMDI of 20.0 (1.7 – 39.7) reflecting a raw ADM with little or no dilution of direct mine water drainage, mainly seepage from spoil collecting in surface ponds. According to the classification of contaminated and uncontaminated waters by AMDI (Gray 1996), river network could be indicated as an affected river downstream of the mine drainage (AMDI: 74.0 - 86.5), while groundwater (AMDI: 88.4 – 96.0) is uncontaminated by AMD. The groundwater composition will be strongly controlled by natural geochemical processes, from the geology of the ore deposits and water rock interaction.

**Conclusions**

The acid mine-drainage index is designed to detect and quantify contamination from acid mine drainage, and to help categorize samples, quantify effect and to monitor the recovery of receiving waters. The ADMI index is a tool to discriminate between sources and types of AMD and assessing the degree of effect on surface and groundwaters.

ADMI is also a useful method to quantitatively assess the relative intensity of contamination and effect of acid mine drainage, over time and space, that must be considered in environmental risk assessment of active and abandoned mine sites, before and along remediation and monitoring processes.

**Acknowledgements**

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References


Abstract
The sagging water outburst was firstly noticed in China in 1980s. On the basis of actual cases happened in China, the paper investigated the mechanism and prevention measures of this kind of hazards. The prerequisites to form a sagging void space include: upper hard rock strata, lower soft aquifuge and long water accumulating process. Static water head/pressure and rockbursting energy are the two main forces to trigger the ourburst of ’sagging wate bulb’. It was summarized that the patterns/passages of sagging water outburst included rockburst-induced passage, extra-high water-connected zone passage, re-activated faults passage and Neozoic faults passage. The comprehensive prevention measures involve in: pre-dewatering the interlayer-sagging water body via underground drilling, pre-dewatering the aquifers which may potentially recharge the sagging water body, increasing the size of working face to limit the development of sagging strata, etc.

Keywords: mining-induced sagging water, mechanisms, diversion-based drilling, roof

Introduction
As the movements of coal roof are controlled by full caving mining at a coal mine, the normal tensile may cause the overburden, which are composed of hard and soft formations, to yield uncoordinated sagging deformations, or even to leave a large interlayer lenticular-like void space. Further, when the interlayer void space in the sagging zone is continuously expanded and water accumulates to a certain amount, the rockburst of the upper hard rock might cause a sudden outburst of the interlayer sagging water into the stope, causing a mine water accident like what the goaf water inrush usually does.

Initially, this kind of inrush was noticed in China in 1980s. It was with the aids of a paper by a former Suviet expert that the Chinese practitioners first knew the concept of sagging and further inferred that, under a certain circumstance, the sagging zone might form a huge void space, gradually be flooded by neighbour aquifers and finally induce an unexpected inrush hazard. They judged that the inrush occurred at a Nantong coal mine (Sichuan, China) in 1980s were actually the outburst of flooded sagging void. From the year of 1990 to 2000, there were some Chinese investigating the occurrence, mechanism, prevention of sagging zone. However, not all sagging zone might leave enough void space and not all void space could get flooded. It happened under a certain conditions. The accidents of sagging water outburst were not fairly common.

But after 2000, this kind of accidents were frequently reported in China again. For example, on May 21 of 2005, a sagging water inrush accident happened at the Haizi coal mine (An’hui, China) and caused a huge property and safety loss. The void sagging space were formed under the thick intrusive sill. Especially in the recent years, this kind of accidents were more reported occurring in the Ordos Jurassic coalfields. In general, sagging water burst was always being neglected and easily being misjudged. So, the purpose of the paper is to investigate the mechanisms of and precaustions against sagging water outburst…
Interlayer sagging void

As the caving method being adopted, there will be developing the caving zone, fractured zone and sagging zone in the overburdens at the goaf side. For the roof pattern of soft strata overlain by hard strata (shortly as ‘upper hard and lower soft’), the normal tensile may cause uncoordinated sagging deformations, or even to leave a large interlayer lenticular-like void space. In caving zone and fractured zone, the deformation void is soon damaged again; but in the sagging zone, the void may be remained, expanded and enlarged (Figure 1).

The prerequisites to form a sagging void space include:

1. Upper hard rock strata
   Indispensably, in the vertical upper part of the sagging zone, there must be a certain thickness of hard igneous, sedimentary, metamorphic rocks, like limestone, sandstone, conglomerate, intrusive sill, etc. In most cases, this kind of hard rocks carry almost no groundwater, and are always ignored their potential threat.

   Case 1: At Haizi coal mine (An’hui, China), it was the intrusive sill 76.3-88.7m in thickness that cantilevered in the sagging zone and left a huge void space full of water. On May 21 of 2005, the sagging void space suddenly bursted, the violent inrush of water mixed with debris instantly peaked at 4000 m³/h, and the process last for 3.5 hours.

   Case 2: At Xinji coal mine (An’hui, China), it was the excessively thick and expansive gneiss nappe that hung over the upper part of sagging zone to yielded a big void space. As the gneiss cantilever eventually was broken, the big ‘water bulb’ in sagging zone suddenly bursted. At an inrush rate of 400m³/h, the longwall face was soon inundated.

2. Lower soft aquifuge
   Beneath the upper hard rocks, a lower soft aquifuge is needed to wrap up the void space to hold seepage water. It could be either the inact aquifuge in the sagging zone or the re-united aquifuge in the fractured zone.

   For example, from September of 2009 to March of 2010, there happened 4 times of inrush accidents at the Hongliu coal mine in the Ordos Coalfield (Ningxia, China), the maximum inrush rate rose up to 3000 m³/h and the working face was twice flooded. It was judged that strata of silt enriched in expansible clay re-formed a layer of secondary aquifuge in the fractured zone, which formed a kind of secondary sagging water body.

3. Long water accumulating process
   The sagging void space usually got recharged by a traditionaly neglectable aquifer. A long water accumulating process was always observed. It could be reasonably inferred that the harder the upper rock is, the longer the cantilever of hard strata hanged over, the larger the void space develope, the more the water is accumulated and the more serious the outburst hazard would be. At the case of the Guojiuhe coal mine (Shanxi, China), the longer water accumulating time at the 3rd sagging water inrush led to a total drainage of 22.6 × 10⁴ m³, much larger the former two inrush accidents.

   Forces to trigger sagging water outburst
   There are two kinds of forces to trigger the
ourburst of ‘sagging wate bulb’. One is static water head/pressure of the recharging aquifers and the other is the rockbursting energy of the upper hard rocks. The magnitude of rockburst energy depends on the strength, fissures, thickness and cantilever of the upper hard rock strata. Most of the sagging water outburst were triggered by a mixture of them.

Patterns of sagging outburst

On the basis of actual cases happened in China, we sum up the patterns/passages of sagging water outburst as:

(1) Rockburst-induced passage. For this pattern, common forces of rockburst and static water pressure directly pierce through the ‘water bulb’ in the sagging zone. Most of the sagging water outburst accidents in China, like the ones in Haizhi coal mine, Honglou coal mine, Jining coal mine, Dafuosi coal mine, Yuhua coal mine, Huoshizui coal mine, Cuimu coal mine, etc., belong to this pattern.

(2) Extra-high water-connected zone passage. For this pattern, water interconnected zone elevates surprisingly higher than as expected to induce the outburst of flooded sagging void. For cases where the multi-coal-seams are sequentially excavated, the water connected zone would reach an extra-height. The sagging water outburst happened in the Nantong coal mine in 1996, Yutianbao coal mine in 1985, Datong coal mine in 2008, etc., were all induced by extra-water-connected height.

(3) Re-activated faults passage. For example, the sagging water outburst sequently occurred at Xinji coal mine in December of 2001 and in January of 2003. It was due to the under fault being re-activated by the rockburst of the upper hard rock, which resultantly damaged the flooded ‘water bulb’ in the sagging zone.

(4) Neozoic faults passage. The cases of this kind of pattern include: the sagging water outburst at Guojiaste coal mine with a total inrush of $22.6 \times 10^4$ m$^3$ and the one at Dalu coal mine with a maximum inflow rate of 430 m$^3$/h. Apart from the ‘flooded bulb’ in the sagging zone, the Neozoic faults even pierce up into the regional Cretaceous water-enriched sandstone aquifers, thereupon causing a big and steady inrush flow rate.

Precautions against sagging hazards

A comprehensive preventions measures involve in: (1) pre-dewater the interlayer-sagging water body via underground drilling; (2) Pre-dewater the aquifers which may potentially recharge the sagging water body; (3) Increasing the size of working face to limit the development of sagging strata; (4) strengthen the capacity to buffer and eliminate water inrush in a short time. Practice proves that the method is correct and the effect is great.Occur.

Acknowledgements

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Abstract

Hydrochemical analysis is one of the most efficient and simple methods to distinguish the source of mine water inrush. However, in reality, its applicability has been restricted hugely due to the mine water inrush source are usually the mixed one. In this study, taking Jinggezhuang mining area as an example, the hydrochemical characteristics of the mixed mine water (the mixture of the ordovician limestone water, k6-coal 12, coal 9-coal 7, coal 5 roof sandstone water and the alluvial loose aquifer at a ratio of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1, respectively) were firstly investigated by the water quality test; secondly, the mixed reaction mechanism was rapidly obtained using the irreversible reaction simulation model of PHREEQC, and also established a water mixed reaction model applied for Jinggezhuang mining area by the error analysis of hydrochemical compositions of water bursting point and the standard values. The result indicates that the concentrations of main ions in the mixed water all showed an decrease tendency with continuously extend of ordovician limestone water. The variation of Na\(^{+}\), SO\(_4\)\(^{2-}\), HCO\(_3\)\(^{-}\) is smoother, K\(^{+}\)+Na\(^{+}\) decreased from 19.5 mg/L to 12.5mg/L, SO\(_4\)\(^{2-}\) is reduced from 35.8 mg/L to 17.9 mg/L, and HCO\(_3\)\(^{-}\) shifted from 207.2 mg/L to 159.3 mg/L. In addition, Total Dissolved Solids (TDS) and the mineralization is also gradually decreasing with a large percentage of ordovician limestone water, whereas the total hardness and PH getting bigger. By discriminant analysis of the 4 unknown water points, the recognition precision of the model is up to more than 90% based on the Bayes model, it is expected to provide a scientific basis for the rapid identification of mine water inrush sources.

Keywords: mine; mixed mine groundwater; water inrush sources; water mixed reaction model

Introduction

Coal mine water inrush restricts the safe and efficient production of coal mines, and the economic losses caused by coal mines are also in the first place. It is urgent to find high-precision methods and techniques for identifying the source of water inrush. Scholars have done a lot of research on the identification and prediction of water inrush from different aspects: some studies were performed on identifying the source of water inrush from the perspective of water inrush mechanism. Considering rock mass structure, rock mass strength and mining fragmentation, the study mostly proceeds from the dynamic balance of coal seam roof and floor. The critical equilibrium state of rock mass is taken as the control condition of water inrush from floor of coal seam. This method is used to prevent and identify the source of water inrush by calculating the stress of rock mass before and after mining and some tectonic stresses such as faults. In this respect, the Slesalev formula, the vulnerability index method (Zhang 2008, Wu 2007, Wu 2008, Wu 2009) and the "lower
three zones” theory (Ling 2003, Shi 2007), the geomechanical method (Jin 2000, Zhang 2005, Kong 2008), the key strata theory (Du 2008, Wang 2002) have been formed.

There were other studies focusing on identifying water sources by analyzing background values of aquifers. By analyzing the data characteristics of groundwater chemistry, water level and water temperature in different aquifers, the source of water inrush can be distinguished from the hydrochemical and physical information of water inrush (Yang 2003, Chen 2005, Du 2006, Liu 1999, Liu 2001, Li 2008). The most important method is the hydrochemical analysis method, that is, the analysis of water quality types, physical and chemical characteristics of water samples, combined with the hydrogeochemical distribution, migration and transformation of water quality to analyze the source of water inrush. The object of study is divided into conventional hydrochemical characteristics, isotopes and trace elements. Hydrogeochemical exploration technology is fast, timely and economical in recognizing the source of mine water inrush. Therefore, the method of recognizing the source of mine water inrush by conventional hydrochemical information has been widely studied and applied.

In recent decades, with the extensive development of computer application in coal mine water inrush, such as probability index method (Wu 2007), multivariate statistical method (Liu 2001), analytic hierarchy process (Dong 2014, Liu 2000), fuzzy mathematics method (Yu 2007, Sun 2007), grey relational degree evaluation method (Li 2008, Zhang 2007, Gao 2007), neural network method (Wei 2004), extension identification method (Zhang 2009), etc. The common characteristic of these methods is that by comparing and sorting the similarity degree of chemical data between inrush water samples and possible water sources, or sorting according to the probability of occurrence, the largest result is the inrush water source.

In terms of multivariate statistics, Li Zhifeng (2008) used Fisher model to discriminate the source of water inrush, Guihe Rong and Chen Luwang (2008) used Bayesian discriminant model to discriminate the source of water inrush. Dong Donglin (2012) used a GIS-based Bayesian network (BN) to assess water-inrush situation. As for the method of fuzzy mathematics, Liu Wentao (2000) and others used the analytic hierarchy Process-Fuzzy evaluation to evaluate the safety of floor water inrush. Sun Yajun et al. (2007) got the background value of aquifer based on GIS, and used clustering analysis and fuzzy comprehensive evaluation to identify the source of water inrush, and achieved good results. In the grey relational degree evaluation method, Li Qikang (2008) and Zhang Honggang (2007) used the grey situation decision-making method to distinguish the source of water inrush. In the aspect of neural network method, Wei Yongqiang (2004) expressed and quantified the factors causing water inrush by using GIS technology, obtained training data by using evidence weight method and analytic hierarchy process, and then predicted floor water inrush by using neural network. They all have been achieved good results.

At present, there are few studies on the hydrochemical characteristics of the mixed water from multi-aquifers, but are relatively rare on the aquifers in North China of Jinggezhuang Mine. Therefore, considering the actual water inrush situation, taking Jinggezhuang Mine as an example, this paper was undertaken to explore hydrochemical characteristics of the mixed water basen on the numerical model in PHREEQC and establish a water mixing reaction model suitable for Jinggezhuang mining area by the Bayes discriminant method. It is expected to provide a reference for the recognition of Water Inrush Source in this mining area in the future.

**Methodology**

**Data acquisition**

The hydrochemical characteristics data of aquifers are obtained in Jinggezhuang Mine, including the aquifer where the water samples are located, the pH value and the concentration of cations and anions (Na+, Ca++, Mg++, Fe++, Fe++, Al³⁺, NH₄⁺, Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻, NO₃⁻, NO₂⁻) in the water. The aquifers in Jinggezhuang Mine are Ordovician limestone aquifer, K6-coal 12 aquifer, coal 9-coal 7 aquifer, coal 5 roof sandstone aquifer and Quaternary loose alluvium. The
Bayes Multi-class Linear Discrimination Principle

Bayesian discriminant analysis uses Bayesian probability rule to discriminate. Its theoretical basis is more supported by statistical theory than Fisher’s typical discriminant analysis. Beginning with the multivariate distribution of samples, Bayes makes full use of the information provided by the probability density of multivariate normal distribution to calculate the posterior probability (Wu Guanmao 2008).

For n samples taken from G matrices and each sample contains P variables, each sample can be regarded as a point in P-dimensional space. For an unknown sample, the probability of falling into which subspace is high, that is to say, it belongs to this parent. At the same time, there must be a phenomenon of misclassification, which will cause losses. When the losses of any research individual X=(x1, x2,… xn) caused by other parent is greater than that caused by Ag parent, it is classified as Ag parent. Therefore, Bayes criterion is to minimize the loss of misclassification \( R \) when the prior probability \( Q_G \) of the parent is given.

If the probability of misclassification of samples originally belonging to parent Ag into Ah is recorded as \( P(h/g) \), when the probability distribution \( f_G(x) \) of G parent Ag is known, there are:

\[
P(h,g) = \int f_G(x) dx
\]

The average loss caused by misclassifying a sample originally belonging to the parent Ag to the parent Ah is:

\[
W_h = \sum_{x=1}^{G} \frac{L[b/A]W[b/A]}{b/A} = \sum_{x=1}^{G} L[b/A]f_{b/A}(x|x)dx
\]
The average loss of the G-type parent when the prior probability $q_h$ of each parent is known is:

$$W_k = \sum_{g=1}^{G} u_k \cdot W_h = \sum_{g=1}^{G} u_h \sum_{g=1}^{G} L[h/\mu]P[h/q]$$

If the sample originally belonging to the Ah parent is misclassified into the Ag matrix, the resulting loss is recorded as: $L[g/h]$, for the same reason:

$$P(g/h) = \int_{R_k} f_h(x)dx$$

$$W_g = \sum_{h=1}^{G} L[g/h]P[g/h] = \sum_{g=1}^{G} L[g/h]\int_{R_k} f_h(x)dx$$

$$W_k = \sum_{g=1}^{G} u_k - \sum_{h=1}^{G} L[g/h]\int_{R_k} f_h(x)dx.$$  

$$\{R_k\}: \sum_{g=1}^{G} L[h/g]q_{g}f_{g}(x) > \sum_{g=1}^{G} L[h/g]q_{h}f_{h}(x)$$

Bayes proved that to minimize the total error of the total error, the method of dividing the space $\{R\}$ should satisfy the following inequalities:

$$\{R_k\}: \sum_{g=1}^{G} L[h/g]q_{g}f_{g}(x) > \sum_{g=1}^{G} L[h/g]q_{h}f_{h}(x)$$

That is to say, the individual with the highest posterior probability of the Ag parent is assigned to the Ag parent. The maximum posterior probability is equivalent to the maximum $q_{g}f_{g}(x)$, so the discriminant function of any individual X for discriminant attribution can be derived. The available G discriminant functions are:

$$q_{g}f_{g}(x) = u_{g}^T(2\pi)^{-\frac{G}{2}}|\Sigma|^{-rac{1}{2}}\exp\left[-\frac{1}{2}(x-u_{g})^T\Sigma^{-1}(x-u_{g})\right]$$

Where $X=(x_1, x_2, ..., x_n)$, the parameters $\Sigma$ and $\Sigma$ are the mean vector and covariance matrix of the parent, respectively, $g=1, 2, ..., G$. After derivation and sorting, the normal matrix multi-class linear discriminant function under Bayes criterion can be obtained as:

$$Z(x) = b_{0g} + b_{1g}Y_1 + ... + b_{pg}Y_p$$

Finally, compare $Z_1(x)$, $Z_2(x)$, $Z_3(x)$, and $Z_4(x)$, and select the maximum value to determine the precursor from which sample X is derived (Zhang Dandan 2017).

**Results and Discussions**

**Hydrochemical Characteristics of Mixed Water**

Taking Ordovician limestone and k6-coal 12 aquifer as an example, the simulation results are shown in Table 2.

The result indicates that the concentrations of main ions in the mixed water all showed an decrease tendency with continuously extend of ordovician limestone water. The variation of Na+, SO$_4^{2-}$, HCO$_3^-$ decreased from 19.5 mg/L to 12.5mg/L, SO$_4^{2-}$ is reduced from 35.8 mg/L to 17.9 mg/L, and HCO$_3^-$ shifted from 207.2 mg/L to 159.3 mg/L. At the same time, Ca$^{2+}$ is changed from 58.2 mg/L to 47.6 mg/L, and Mg$^{2+}$ is narrowed from 22.7mg/L to 13.7 mg/L. While Cl$^-$ is increased from 11.1 mg/L to 18.1 mg/L, and NO$_3^-$ is extended from 3.1 mg/L to 27.3 mg/L. In addition, Total Dissolved Solids (TDS) and the mineralization is also gradually decreasing with a large percentage of ordovician limestone water, whereas the total hardness and PH getting bigger.

**Analysis of the Bayes discriminant model**

Bayes discriminant analysis was performed on 36 water samples of four aquifers infiltrated into the gray water using SPSS statistical analysis software. Five principal component variables($Na^+$, $Ca^+$, $Mg^+$, $SO_4^{2-}$, $CO_3^{2-}$) were selected as indicators of the Bayes discriminant analysis model. The coefficient matrix of the Bayes discriminant model is shown in Table 3.

By Bayes discriminant function coefficient matrix, the function expression of Bayes discriminant model can be obtained as follows:

For convenience of writing, replace variables $Na^+$, $Ca^+$, $Mg^+$, $SO_4^{2-}$ and $CO_3^{2-}$ with $Y_1$, $Y_2$, $Y_3$, $Y_4$. $Y_5$ in the function expression.

**Model’s back substitution test, pending test and error analysis**

According to the discriminant function of Bayes, the sample data is substituted into the above discriminant function for calculation. The data of $Z_1$, $Z_2$, $Z_3$, and $Z_4$ can be calculated, corresponding to the water source type: k6–coal 12 water, coal 9–coal 7 water, coal
Table 2 Primary Hydrochemical Data of Water Samples in Jinggezhuang Aquifers

<table>
<thead>
<tr>
<th>Mixing ratio</th>
<th>1:9</th>
<th>2:8</th>
<th>3:7</th>
<th>4:6</th>
<th>5:5</th>
<th>6:4</th>
<th>7:3</th>
<th>8:2</th>
<th>9:1</th>
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<tbody>
<tr>
<td>pH</td>
<td>7.68</td>
<td>7.69</td>
<td>7.71</td>
<td>7.72</td>
<td>7.74</td>
<td>7.75</td>
<td>7.77</td>
<td>7.79</td>
<td>7.82</td>
</tr>
<tr>
<td>Na⁺ (mg/L)</td>
<td>19.52</td>
<td>18.64</td>
<td>17.77</td>
<td>16.89</td>
<td>16.02</td>
<td>15.14</td>
<td>14.26</td>
<td>13.39</td>
<td>12.51</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>58.16</td>
<td>56.84</td>
<td>55.52</td>
<td>54.20</td>
<td>52.88</td>
<td>51.56</td>
<td>50.23</td>
<td>48.91</td>
<td>47.59</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>22.71</td>
<td>21.58</td>
<td>20.45</td>
<td>19.32</td>
<td>18.19</td>
<td>17.06</td>
<td>15.93</td>
<td>14.80</td>
<td>13.67</td>
</tr>
<tr>
<td>Fe²⁺ (mg/L)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe³⁺ (mg/L)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Al³⁺ (mg/L)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>NH₄⁺ (mg/L)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>11.09</td>
<td>11.97</td>
<td>12.85</td>
<td>13.73</td>
<td>14.60</td>
<td>15.48</td>
<td>16.36</td>
<td>17.24</td>
<td>18.11</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>35.76</td>
<td>33.53</td>
<td>31.30</td>
<td>29.08</td>
<td>26.85</td>
<td>24.62</td>
<td>22.39</td>
<td>20.16</td>
<td>17.94</td>
</tr>
<tr>
<td>CO₃²⁻ (mg/L)</td>
<td>207.22</td>
<td>201.23</td>
<td>195.25</td>
<td>189.26</td>
<td>183.27</td>
<td>177.28</td>
<td>171.30</td>
<td>165.32</td>
<td>159.33</td>
</tr>
</tbody>
</table>

Table 3 Bayes discriminant coefficient matrix

<table>
<thead>
<tr>
<th>Variables</th>
<th>K6-coal 12</th>
<th>Coal 9-coal 7</th>
<th>Coal 5 roof sandstone</th>
<th>Quaternary loose alluvium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>475.196</td>
<td>473.305</td>
<td>470.708</td>
<td>489.111</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1276.769</td>
<td>1272.494</td>
<td>1263.714</td>
<td>1313.858</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>990.498</td>
<td>987.113</td>
<td>979.490</td>
<td>1019.370</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>-1128.524</td>
<td>-1126.333</td>
<td>-1117.639</td>
<td>-1162.471</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>-69.493</td>
<td>-69.041</td>
<td>-68.865</td>
<td>-71.599</td>
</tr>
<tr>
<td>(constant)</td>
<td>-23134.172</td>
<td>-22983.290</td>
<td>-22634.467</td>
<td>-24467.549</td>
</tr>
</tbody>
</table>

Table 4 Bayes discriminant model backdating test

<table>
<thead>
<tr>
<th>K6–coal 12 w</th>
<th>Coal 9–coal 7</th>
<th>Coal 5 sandstone</th>
<th>Alluvial aquifer</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>amount</td>
<td>proportion</td>
<td>amount</td>
<td>proportion</td>
<td>amount</td>
</tr>
<tr>
<td>9</td>
<td>100%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>9</td>
<td>100%</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>100%</td>
</tr>
<tr>
<td>1</td>
<td>11.1%</td>
<td>0</td>
<td>0</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 5 Bayes discriminant model pending test

<table>
<thead>
<tr>
<th>K6–coal 12</th>
<th>Coal 9–coal 7</th>
<th>Coal 5 sandstone</th>
<th>Alluvial aquifer</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>amount</td>
<td>proportion</td>
<td>amount</td>
<td>proportion</td>
<td>amount</td>
</tr>
<tr>
<td>3</td>
<td>100%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
<td>100%</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
<td>100%</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>33.3%</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>
sandstone water, alluvial layer water. The maximum value is the type of judged water source. The results of the back-test are shown in Table 4.

The backdating overall correct rate of Bayes discriminant model is 97.2%. The recognition accuracy of k6-coal 12 water, coal 9-coal 7 water and coal 5 water is relatively high, all of which are 100%. One of the water samples is misjudged, accounting for 11.1% of the water samples.

The complex source of alluvial water leads to the unclear hydrochemical characteristics of the aquifer, which results in unsatisfactory linear discriminant effects such as Bayes discriminant analysis.

Conclusions

(1) The concentrations of main ions in the mixed water all showed an decrease tendency with continuously extend of ordovician limestone water. The variation of Na+, SO$_4^{2-}$, HCO$_3^-$ is smoother, K$^+$+Na$^+$ decreased from 19.5 mg/L to 12.5mg/L, SO$_4^{2-}$ is reduced from 35.8 mg/L to 17.9 mg/L, and HCO$_3^-$ shifted from 207.2 mg/L to 159.3 mg/L. In addition, Total Dissolved Solids (TDS) and the mineralization is also gradually decreasing with a large percentage of ordovician limestone water, whereas the total hardness and PH getting bigger.

(2) Bayes discriminant analysis was carried out by SPSS statistical analysis software, and the discriminant model was obtained. The overall accuracy of Bayes discriminant model is 91.7%. It is expected to provide a scientific basis for rapid identification of mine water inrush sources.

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Conflicts of Interest:
The authors declare no conflict of interest.

References
Abstract
The hydrological and hydrochemical characteristics of Tugnui river basin, affected by coal mining activity were obtained. Water turbidity, concentrations of major ions, nutrients and trace elements have changed dramatically. During low water period the effect of mining has been traced over 24 km downstream, increased concentrations of toxic substances were found mainly in dissolved forms. The concentrations decreased in the lower part of the basin owing to dilution and complexation with organic matter, since the hydrochemical transformation was insignificant.

Keywords: coal mining, Baikal, water chemistry, trace elements, pollution, sediments

Introduction
Coal mining leads to a substantial change in water quality of rivers and lakes. Sewage and drainage water coming from the mining area contains high concentrations of toxic substances, which at low water period can lead to degradation of aquatic ecosystems for many kilometres downstream. The flow transports dissolved forms, and pollutants in suspended sediments and bedload. Suspended particles could accumulate in geochemical barrier zones, creating sources of contamination. These accumulative formations could be mobilized during substantial changes in hydrochemical regime or could preserve the contaminants for many years (Thorslund et al., 2016).

Tailing dumps and sedimentation ponds, where suspended particles enriched with toxic substances are concentrated in large amounts, pose a substantial danger. After the end of exploitation and dewatering, the bottom sediments of such water bodies are eroded, resulting in catastrophic discharges of toxic substances (Chalov et al., 2015).

The assessment of spatial scale of mining impact and the intensity of chemical transformation of river waters is often difficult due to insufficient monitoring data and a limited number of monitoring stations. The solution to this problem requires complex hydrological and hydrochemical studies.

This paper shows the results of research in the Tugnui river basin in the southeastern part of the Republic of Buryatia in August 2018. The environment in the upper part of the basin territory is strongly affected because of the Tugnui coal mine – one of the largest in Baikal region. The aims of the study are: (i) to characterize pollutant fluxes formation and transport from the mine into surface waters; (ii) to evaluate major physicochemical mechanisms, governing the attenuation and fate of pollutants downstream the mine.

The study of Tugnui water quality was carried out during summer low-water period. During this period all streams of the area are characterized by a small variability of hydrochemical characteristics. Wastewater discharges from the mining areas could be easily detected in such conditions, as their chemical composition is very different from that of river waters. The results of geochemical survey showed, that the main sources of pollution in Tugnui basin are: atmospheric dispersion of pollutants from thermal power plant, input of pollutants with wastewater, their leaching from waste rocks and mine tailings and sewage of local miner’s village.
Study area
The basin is located in the southeastern part of Buryatia and is a part of the Selenga River basin (fig. 1). This territory is of great importance in Republic economy owing to substantial contribution in industrial and agricultural production. In the upper reaches, between the Tugnui River and its right tributary, the Kusota River, the largest in the Baikal region Tugnui coal deposit is situated. Its capacity is about 12.5 million tons of coal per year. The mine has been functioning since 1981. The mining complex also includes the Nikolsky open pit mine, which began to be developed in 2015. A coal processing plant is located in the northern part of Tugnui coal mine. Both excavation areas are equipped with a system of water-lowering wells and sump for accumulation of drainage water, which are then discharged into the Tugnui River. The volume of drainage water discharge from the Tugnui mine is 11,860 thousand m$^3$/year. Municipal sewage (516 thousand m$^3$/year) from the coal processing plant and the nearby Sagan-Nur village enter the treatment plant, and then discharged into the sewage pond. At the same time, part of the sewage falls into the Olon-Sibir salt lake, which is located 4 km below the treatment plant. Downstream the Nikolsky mine industrial activities are absent. The rest of the valley territory is a valuable agricultural land, where the waters of the Tugnui River and the lakes are used for irrigation and as a source of water for livestock. Banks of the sedimentation pound on the Tugnui River (at station C16, fig.1) and the Olon-Sibir Lake (C24) are used as recreation centers and for fishery. These lakes, middle and lower courses of the Tugnui River belong to the 2nd category of water bodies, intended for fisheries.

Materials and methods
Field studies in the basin took place during the summer low water period in 2018. A network of 29 representative stations including gauging station on the upper reaches of the Tugnui river (point C12) was created. The main water chemical characteristics, such as pH, conductivity (EC), alkalinity

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Figure 1 Map of the studied part of Tugnui River basin
Hydrology

During the survey period, the predominant source of feeding the rivers was groundwater, no precipitation was observed, which determines the hydrochemical conditions as stationary. Many watercourses of Tugnui basin flowing through Nikolsky pit were dried up because of the lack of precipitation. The maximum water discharge in Tugnui river was observed downstream the effluent of wastewater from the pit area (at station C8 – 0.18 m$^3$/s) and at the station in Tugnui village (C18 – 0.12 m$^3$/s). In August the erosion processes of Tugnui river banks are not pronounced. The main sediment flow is associated with channel erosion and the input of fine particles during coal mining. The obtained information on turbidity allows us to divide the Tugnui river basin into 4 areas: background (C1-C5); river water downstream coal mining (C6-C15); river water downstream treatment facility (C16-C19) and sewage (C20-C24). Results of grain-size analysis are represented on a figure 2.

Upper reaches of the Tougneui River are characterized by weak turbidity. The low transport capacity of the stream leads to the mobilization of only the smallest particles (d 0.0005-0.05 mm) with turbidity values of 5–20 mg/L. The river bed experiences vertical deformations, and the channel processes are

![Figure 2 Grain-size distribution and turbidity values in Tugnui river basin](image-url)
poorly developed. Downstream, within the coal pit, the river flows through the system of river-taps and sumps. The appearance of particles is connected both with the transfer of material from the mining area and with the vertical and horizontal channel deformations. Sediment composition in mine watercourses is mainly affected by flushing of waste rock dumps and by wastewater discharges. The last forms more than 80% of river flow (0.1 m³/s at C12 station). Turbidity increases to 120 mg/L. During wastewater discharge it reaches 300 mg/L at sampling station C12 which substantially exceed the MPC of turbidity equal 35 mg/L. From 75 to 100% of suspended particles belongs to silt and clay particles (<0.05 mm). The effect of the small fraction is expressed in clogging of river channels and prevention of benthic organism’s growth. Contaminated water comes to sedimentation pound between Tugnui and Nikolsky mines. Substantial volumes of sediments accumulate in it, but the finest particles are transported downstream. The rate of fine particles (d < 0.05 mm) downstream is quite high (70-75%) which provides turbidity 15-20 mg/L. According to Malinovsky et al. (2001), this fraction mostly determines pollutant’s migration. TEa are concentrated predominantly in particles 0.001-0.05 mm and Zn and Cr migrate mainly in fractions of 0.0005-0.001 mm.

### Table 1 General hydrochemical characteristics and TE concentrations in Tugnui river basin

<table>
<thead>
<tr>
<th>Parameters and their units</th>
<th>MPC (Prikaz … 2018)</th>
<th>Background water (n=5)</th>
<th>Water downstream coal mining (n=10)</th>
<th>Water downstream treatment plant (n=6)</th>
<th>Sewage of coal mine (n=S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>7.8-8.2</td>
<td>8.5-9.3</td>
<td>8.1-8.3</td>
<td>8.3-8.5</td>
</tr>
<tr>
<td>EC** µS/cm</td>
<td>-</td>
<td>175±25</td>
<td>910±140</td>
<td>860±410</td>
<td>570±40</td>
</tr>
<tr>
<td>Cl- mg/L</td>
<td>-</td>
<td>1±0.4</td>
<td>4.4±1.9</td>
<td>22±20</td>
<td>40±10</td>
</tr>
<tr>
<td>SO₄²⁻ mg/L</td>
<td>-</td>
<td>22±6.5</td>
<td>230±90</td>
<td>90±65</td>
<td>56±30</td>
</tr>
<tr>
<td>Alk mg/L</td>
<td>-</td>
<td>120±7.5</td>
<td>280±30</td>
<td>530±280</td>
<td>277±4</td>
</tr>
<tr>
<td>Ca²⁺ mg/L</td>
<td>-</td>
<td>25±1.5</td>
<td>65±32</td>
<td>60±20</td>
<td>85±4</td>
</tr>
<tr>
<td>Mg²⁺ mg/L</td>
<td>-</td>
<td>6.1±0.5</td>
<td>23±3.5</td>
<td>41±25</td>
<td>23±1.5</td>
</tr>
<tr>
<td>Na⁺ mg/L</td>
<td>-</td>
<td>7.7±2.6</td>
<td>100±9.8</td>
<td>110±74</td>
<td>85±6.8</td>
</tr>
<tr>
<td>K⁺ mg/L</td>
<td>-</td>
<td>0.5±0.1</td>
<td>5±2.7</td>
<td>3.1±1.5</td>
<td>2.6±1.8</td>
</tr>
<tr>
<td>TOC mgC/L</td>
<td>-</td>
<td>8.2±0.5</td>
<td>6.3±2.5</td>
<td>11.7±1.4</td>
<td>17.3±2.9</td>
</tr>
<tr>
<td>P₅₀ μg/L</td>
<td>-</td>
<td>18±6</td>
<td>12±2</td>
<td>52±27</td>
<td>300±420</td>
</tr>
<tr>
<td>P-PO₄³⁻ μg/L</td>
<td>-</td>
<td>16±8</td>
<td>8±3</td>
<td>37±25</td>
<td>270±260</td>
</tr>
<tr>
<td>Si mg/L</td>
<td>-</td>
<td>8±0.5</td>
<td>4±2</td>
<td>7±3.5</td>
<td>310±500</td>
</tr>
<tr>
<td>Al (iv) μg/L</td>
<td>40</td>
<td>24±2.5</td>
<td>26.2±8.3</td>
<td>62±30</td>
<td>51.1***</td>
</tr>
<tr>
<td>As (iv) μg/L</td>
<td>50</td>
<td>0.05***</td>
<td>0.05*</td>
<td>0.05***</td>
<td>20.8***</td>
</tr>
<tr>
<td>Fe (iv) μg/L</td>
<td>100</td>
<td>35±10</td>
<td>48±40</td>
<td>80±65</td>
<td>41±30</td>
</tr>
<tr>
<td>Ba (iv) μg/L</td>
<td>740</td>
<td>15.5±2.7</td>
<td>53±15</td>
<td>35±12</td>
<td>51±17</td>
</tr>
<tr>
<td>Zn (iv) μg/L</td>
<td>10</td>
<td>5±0.5</td>
<td>10.3±7</td>
<td>39±70</td>
<td>8.3±2.3</td>
</tr>
<tr>
<td>Sr (iv) μg/L</td>
<td>400</td>
<td>236±80</td>
<td>3195±1520</td>
<td>1377±517</td>
<td>2904±1515</td>
</tr>
<tr>
<td>Mo (ii) μg/L</td>
<td>1</td>
<td>9.3±4.3</td>
<td>58±28</td>
<td>9.1±9</td>
<td>63±21</td>
</tr>
<tr>
<td>U (iii) μg/L</td>
<td>-</td>
<td>4.2±2.2</td>
<td>9.8±3</td>
<td>9.1±23</td>
<td>16±3.3</td>
</tr>
<tr>
<td>V (iii) μg/L</td>
<td>1</td>
<td>0.15*</td>
<td>0.15***</td>
<td>1.6*</td>
<td>6.4***</td>
</tr>
<tr>
<td>Mn (iv) μg/L</td>
<td>10</td>
<td>4±3.3</td>
<td>18.3±15</td>
<td>15.6*</td>
<td>3.1±2.6</td>
</tr>
<tr>
<td>Co (ii) μg/L</td>
<td>10</td>
<td>0.08±0.07</td>
<td>1±0.7</td>
<td>0.27±0.09</td>
<td>0.3±0.07</td>
</tr>
<tr>
<td>Ni (iv) μg/L</td>
<td>10</td>
<td>0.25***</td>
<td>6.4±4.3</td>
<td>1.2***</td>
<td>35***</td>
</tr>
<tr>
<td>Cu (ii) μg/L</td>
<td>1</td>
<td>1.1±1</td>
<td>0.7±0.8</td>
<td>2.4***</td>
<td>2.9±1.1</td>
</tr>
<tr>
<td>Cd (ii) μg/L</td>
<td>5</td>
<td>0.01***</td>
<td>0.08±0.07</td>
<td>0.01***</td>
<td>0.1±0.07</td>
</tr>
<tr>
<td>W (ii) μg/L</td>
<td>0.8</td>
<td>0.01***</td>
<td>0.03±0.03</td>
<td>0.041***</td>
<td>1.5±0.5</td>
</tr>
<tr>
<td>Pb (ii) μg/L</td>
<td>6</td>
<td>0.46±0.06</td>
<td>0.5±0.4</td>
<td>1.1±0.8</td>
<td>0.5±0.2</td>
</tr>
<tr>
<td>Sb (iii) μg/L</td>
<td>-</td>
<td>0.01***</td>
<td>0.4±0.5</td>
<td>0.12±0.08</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>Cr (iii) μg/L</td>
<td>70</td>
<td>1.1±1</td>
<td>1.9±2</td>
<td>2.5±1.4</td>
<td>4.3±1.5</td>
</tr>
</tbody>
</table>

Note. MPCs are given for dissolved form of TEa; *n – number of sampling stations; **EC – electrical conductivity, ***only single measurement; (iii) –hazard class of a TE.
General water chemistry

The study of chemical characteristics of surface waters in the Tugnui river basin is important as they allow understanding migration processes of such contaminating components as TEs (Table 1). Water of background areas is of hydrocarbonate-calcium type with mineralization 150–200 mg/L; pH 8–8.5. The differences in mineralization and content of the main water ions in background areas are small and related to the composition of the rocks prevailing in river basins and the relief features. High content of organic matter is caused by swamps that are situated on riversides. Increased Si concentrations are caused mainly by underground sources of water during low water period.

The water chemistry of inner mining water bodies and watercourses downstream the mine is similar. It belongs to hydrocarbonate type with alkaline pH values 8.5–9.3 and high mineralization (up to 1000 mg/L). Increased concentrations of \( \text{SO}_4^{2-} \) (up to 340 mg/L) and Na+ (up to 100 mg/L), which are 50-100 times higher than background, were found. These ions are leached from the coal, and due to explosion operations (\( \text{NO}_3^- >50 \) mg/L). The lower part of Tugnui River basin (stations C16-C19) has hydrocarbonate–sodium waters due to mining influence and evaporation of river waters. Mineralization decreases because of dilution of contaminated waters. Total phosphorous concentration \( P_{\text{tot}} \) inside mining area is low. More than 80% of P is in mineral form. After water treatment facilities the content of phosphorous increases up to 37 μg/L. Organic forms of phosphorous dominate in these conditions due to wash out of organic matter from farms and fields.

Sewage water in the basin of Lake Oلون-Sibir contain high concentrations of nutrients. Total phosphorous concentration reaches 300 μg/L, \( P_{\text{PO}_4} \) share is 50%. The lake water is characterized by sodium type with increased content of Cl- that possibly comes from sewage water and underground sources. Lake Oлон-Sibir has high content of \( P_{\text{PO}_4} - 780 \) μg/L(90% of \( P_{\text{tot}} \)). Sewage pound, which stores contaminated water from Sagan-Nur has total phosphorous concentration up to 480 μg/L with very low content of \( P_{\text{PO}_4} \) (<20%). High water temperature, nutrient supply and high content of organic matter (>19 mg/L) can cause an eutrophication of this water body.

The background concentrations of the main ions and TEs in the undisturbed parts of the basin do not exceed sanitary - hygienic and fishery MPCs (GN 2.1.5.2280-07; Prikaz ... 2016), except for Mo and Cu (\( K_0 = 9; 1.1 \)). In the confluence of wastewater from the coal mine, the sanitary and hygienic MPCs are exceeded for Mo (\( K_0 = 1.2 \)) and fishery MPCs – for Zn, Sr, Mn (\( K_0 = 1.1-8 \)) and Mo (\( K_0 = 58 \)). The waters downstream the mining area are also characterized by exceeding the fishery MPCs for Al, Zn, Sr, Mo, V, Mn, Cu (\( K_0 = 1.6-9.1 \)). The fishery MPCs for Mo (\( K_0 = 60 \)), Al, Sr, V, Cu, W (\( K_0 = 1.3-7.3 \)) are also strongly exceeded in sewage. During the expedition near the treatment facilities and downstream dead fish was observed. In the closing section (station C19), values of hazard coefficient \( K_0 \) decrease to 1.5-2 as a result of dilution.

Forms of trace elements

The basin of the Tugnui River is distinguished by increased background concentrations of TEs in water (TDS) and in suspension (TSS) due to its complex geological structure. In comparison with the average TDS concentrations of TEs in world rivers (Gaillardet et al., 2003), the background content of Zn, Sr, Mo, U is increased. In the upper part of Tugnui basin TEs concentrations are determined by groundwater flow through fractures in the rocks, leaching of dumps, and also with atmospheric aerosols that come from settlement and coal producing plant.

To study the variability of TEs in dissolved phase, a correlation matrix (n=21, r>0.55) was calculated and two groups of elements were distinguished: Sr, Ba, U, Mo, Co, Ni and Fe, Al, Zn, V, Cr, Mn, Pb, Cu, Sb displayed a weak correlation with other metals (fig. 3). All groups of elements have low concentrations in upper reach of the Tugnui River, which slowly increase downstream due to TEs washout from mining dumps and infrastructure operations in mining area. High enrichment factor was estimated for Co (\( EF_{\text{water}} : 500 \)) and for Sb, Cd, Ni, Mo, Mn, Cu (\( EF_{\text{water}} : 8-1,5 \)). The intensity of sorption processes could also increase inside mining zone due to inflow of clay fraction and...
dust, washed out from roads. Downstream, sedimentation ponds decrease the sediments concentration, dilution changes pH conditions (from 9 to 8), and decreases the TSS migration. Downstream the treatment plant a large part of other TEs tied with organic matter (TOC >11 mg C/l). This also causes the decrease of TE concentrations.

Second group of elements has an upraise of concentrations close to Tugnui village in river lower reach. This is governed mainly by sewage inflow and pollution with TEs, washed out from the road.

The solid–solution partitioning of major and trace elements was quantified using the distribution coefficient $Kd$ (fig. 3). $Kd$ depends upon the abundance and speciation of elements in materials. Increased $Kd$ values reveal that elements have high affinity for solid phases, while elements with low $Kd$ values are more easily weathered, removed in soil solution and/or groundwater and transported in dissolved phases in the river (Ollivier et al., 2011). For the study area, the variability of $Kd$ for elements in background, waste and transformed waters is rather large, but the main part of TEs is transported in dissolved form because of weak sediment flow. This situation can threat the ecosystems below mining area because the dissolved forms of TEs are the most bioavailable. Local concentrations of TEs exceed the average global TEs values in TSS, with the exception of Ni and Cr. The multi-elemental pollution for contaminated waters is moderately dangerous (Zc 21-19). Concentrations of suspended V, Mn, Co, Ni, Cu, Zn, Mo, Cd, W, Pb exceed background concentrations ($EF_{susp}$: 6.37-1.09).

Analysis of TE migration in Tugnui river showed the predominance of suspended form in upper reach and in mining area for Al (>60%), V (>50%), Fe (40-50%). From 10 to 30% of Cr, Co, Cu, As, W, Pb is also in suspended form, but only upstream the treatment facilities. Sr, Mo, U migrate only in dissolved form. Using the data on the water consumption and concentrations of TEs, the share between the dissolved and suspended forms of element’s flow was obtained. TEs are predominantly transported in dissolved form. The maximum intensity of transport in the solution was observed for Sr (42 mg/day), Mo (700 μg/day), Fe (600 μg/day), Mn (500 μg/day), Ba (400 μg/day). Aluminium (4 mg/day) and iron (2 mg/day) dominate in the suspended form.

Analysis of TEs in dissolved and suspended forms showed the exceptional role of mining water for the area. The influence of this factor can be traced for more than 24 km downstream and leads to the accumulation of toxic substances in bottom sediments mainly in artificial channel below mining and in sedimentation pound. The thickness of bottom sediments there exceeds 1.2 m.
Environmental impact

Coal mining has a strong effect on the Tugnui river basin, but it is relatively small throughout the Selenga River Basin. The average annual water discharge at the mouth of the Tugnui River is about 20 m³/s. Pollutants are diluted by 2 times at the confluence of Tugnui into the Sukhara River, and even more substantially at the confluence of the Sukhara and Khilok River (its average water discharge is 120 m³/s).

In the period of increased water flow in the upper reaches of the Tugnui River, intensive discharge of drainage waters from the quarry area and activation of the migration of TEs downstream were observed and in the lower reaches of the river, increased concentrations of Fe, Pb, Zn, Co, V, Ni, Cr, Mo in water and suspended sediments were determined (Environmental … 2019). During the low water period the effect was traced in 20-30 km downstream. This time, most of the suspended pollutants accumulated in the upper and middle reaches of the Tugui River.

The negative effect of coal development on the Tugnui River can be reduced by upgrading the mine wastewater drainage system and by construction of another sedimentation pond downstream the treatment plant of the Nikolsky pit. This will provide additional purification of waters discharged from both quarries, especially when the development of the Nikolsky mine reaches its full capacity. Another effective measure would be the construction of a dam between the Olon-Shibir lake and the ditch into which the sewage of the Sagan-Nur village and the mining and enrichment plant is discharged. This dam will substantially reduce the flow of sewage into the lake. It is also important to create an effective system of hydrochemical monitoring in the section below the confluence of the Tugnui River with wastewater from the Nikolsky field.

Conclusions

Anthropogenic (industrial and agricultural) activities exert a strong effect on water quality in Tugnui River basin. Tugnui mining complex influence could be found in more than 24 km downstream. Water quality of the Olon-Sibir lake worsens due to sewage flow from non-effective water treatment systems.

Trace elements Ba, Cr, Pb, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, W in waters of the Tugnui River have increased concentrations in comparison with other rivers of the Selenga basin.

Our study showed that the main source of TEs in the basin is mining activities and the concentration of elements decreases substantially in the sedimentation pond owing to sorption and organic complexation processes.

During low water period main part (45-50% in upper reach and 70-100% in lower reach) of TEs migrates in dissolved form. The rates of migration are high for Sr, Mo, Fe, Mn, Ba in TDS and for Al, Fe in TSS form. Sediments downstream mining area are largely represented by silt and clay fractions (<0.05 mm), which are the most chemically active. During high water period this particles could significantly increase migration of TEs in solid phase.

The major agent of water pollution in the area is sewage discharge from local settlements and coal production plant. They cause upraise in organic (in 2-5 times) and nutrient (in 100 times) flows. These conditions promote eutrophication of local freshwater lakes and sewage reservoirs.

Acknowledgements

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GN 2.1.5.2280-07 Predelno dopустимые концентрации (PDK) химических веществ в водных объектах хозяйственно-питьевого и культурно-бытового водопользования Дополнения и изменения № 1 к GN 2.1.5.1315-03 [GN 2.1.5.2280-07 Maximum Permissible Concentrations (MPC) of Chemicals in the water of water bodies of household, cultural and domestic water use. additions and amendments №. 1 to GN 2.1.5.1315-03] URL: http://pravo.gov.ru/. 17.05.2019 (in Russian)


Water abundance prediction method of weathered bedrock based on improved AHP and the entropy weight method

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Abstract
The Jurassic weathered bedrock aquifer in Northwest China is the main aquifer for filling water in coal mines. Many water inrush disasters in the coal mine are related to the aquifer. The south wing of Ningtiaota coalfield was taken as an example to analyze the water abundance of weathered bedrock and its controlling factors. The water-rich zoning of weathered bedrock aquifer is carried out by using AHP and entropy weight method to calculate the weights separately and coupled with each other. The results indicated that coupled of improved AHP and the entropy weight method can be used to predict the water-richness of weathered bedrock accurately.

Keywords: AHP, the entropy weight method, weathered bedrock, water abundance, Ningtiaota coalfield

Introduction
Northwest China is rich in coal resources and is the main coal production area in China at present and in the future (Chen and Jiang 2007). In recent years, many water inrush disasters of Jurassic weathered bedrock occurred in the mining of Jurassic coal resources in Northwest China, which made people gradually realize the importance of mastering the water richness of Jurassic weathered bedrock in mine water prevention. However, the water abundance of Jurassic weathered bedrock is very uneven in space. How to evaluate and predict the water-rich of it has become an urgent problem to be solved. The evaluation and prediction of aquifer’s water-enrichment is an important basic work in mine water disaster prevention and control (Xi et al. 2015). Many scholars have studied it and put forward a multi-factor comprehensive analysis method (Dai et al. 2016; Wu et al. 2011; Hou et al. 2016; Wang et al. 2014), which is on the basis of analyzing the influencing factors of aquifer’s water-enrichment, the quantitative evaluation and prediction model of aquifer’s water-enrichment is established.

It is very important to determine the weight of each factor when a model of aquifer water-rich evaluation and prediction is established. Because different weights have different prediction results for water abundance, and it is often determined by Analytic Hierarchy Process (AHP). However, most of the weights of water-rich influencing factors in AHP are determined by experts according to the 1-9 scale method created by T.L.SAATY, and the weights of each factor are not make full use of the measured data and the calculated weights are subjective (Guo et al. 2008). Zhang et al. (2006) proposed an improved method for determining the weight of AHP indicators. In addition to considering the scoring of experts, the method also considers the standard deviation of the measured data of each index, which improves the application effect to a certain extent. In order to overcome the subjectivity of AHP computing weights and predicted the heterogeneity of the aquifer, the entropy weight method was adopted by Ma et al. (2011). The advantage of this method is an objective evaluation method for determining the weight based on the measured data of
each index, but the disadvantage is that the expert’s experience is not considered when determining the weight of each index. Therefore, there are certain limitations to using either method alone. The south wing of Ningtiaota coalfield in North Shaanxi is used as example, discussing the prediction method of weathered bedrock water abundance by coupling the improved AHP and entropy weight method to determine the index weight. The coupling is through reasonable mathematical methods, which considering both expert experience and measured data characteristics, so that the prediction results of water richness evaluation are more accurately.

**General Situation of the Study Area**

The Jurassic coalfield is one of the main coal producing areas between Shanxi, Shannxi and Inner Mongolia of north China, which coal resources account for about 14% of the national total. The study area is located in south wing of Ningtiaota coalfield in Shenmu City, Shannxi Province. The overlying aquifer is porous phreatic water of Quaternary, fissure confined water in weathered bedrock of Zhiluo Formation and fissure confined water in Yan’an Formation. The fissure confined water in weathered bedrock of Zhiluo Formation is widely distributed in the study area, with an average thickness of 26.62 m. The unit inflow of borehole is 0.1183 L/s.m, which is the main water-filling aquifer and poses more threat to mine safety production.

**Controlling factors of weathered bedrock water abundance**

In order to evaluate water enrichment more effectively, author analyzed 41 pumping tests data of weathered bedrock aquifer in the study area. It was found that the water enrichment of weathered bedrock was mainly controlled by 4 factors:

1. **Top-level index**

According to the analysis of pumping tests data, there is a certain correlation between the water abundance of weathered bedrock and its top-level. For example, the unit inflow of boreholes BK42 and K3-1 are 0.1051 L/s.m and 0.1220 L/s.m. The corresponding top-level are 1180.40 m and 1218.32 m. In order to clearly express this correlation, the elevation of weathered bedrock is graded according to the height of 15 m. The larger the value, the stronger the water richness.

2. **Lithologic association index**

According to the data of pumping boreholes, use the contribution of the lithology combination to the water-richness, it is quantified (Table 2). The larger the value, the stronger the water-richness.

3. **Weathered index**

The stronger the weathering degree is, the better the water-rich is. Quantify rock weathering by category (Table 3). The weathering influence index $W$ is constructed to describe the influence of weathering degree.

---

**Table 1 Assignment to weathered bedrock top elevation level**

<table>
<thead>
<tr>
<th>Elevation m</th>
<th>&gt;1240</th>
<th>1225–1240</th>
<th>1210–1225</th>
<th>1195–1210</th>
<th>&lt;1195</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantized value</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 2 Lithologic grade assignment of weathered bedrock**

<table>
<thead>
<tr>
<th>Lithology category</th>
<th>Mudstone</th>
<th>Sandy mudstone</th>
<th>Siltstone</th>
<th>Fine sandstone</th>
<th>Medium sand</th>
<th>Coarse sandstone</th>
<th>Conglomerate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantized value</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

**Table 3 Assignment to weathering degree of bedrock**

<table>
<thead>
<tr>
<th>Weathering degree</th>
<th>Weak</th>
<th>Medium</th>
<th>Strong</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantized value</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>
and thickness on water abundance. The larger the value, the stronger the water-rich.

\[ w = \frac{\sum w_i h_i}{\sum h_i} \]  

(2)

In this formula, \( w_i \) is weathered degree of different lithologic rocks, \( h_i \) is thickness of weathered bedrock with different lithology.

### 4 Core rate index

The lower the value and the better water richness. The core rate of weathered bedrock in each borehole is calculated by constructing core recovery index \( c \), which reflects the water-rich of weathered bedrock from the side. The smaller the value, the stronger the water richness.

\[ c = \frac{\sum c_i h_i}{\sum h_i} \]  

(3)

Where \( c_i \) is rock formation rate; \( h_i \) is strata thickness.

In conclusion, water abundance of weathered bedrock can be predicted by four indexes: top-level index, lithologic association index, weathered index and core rate index. The hierarchical structure model is shown in Figure 1.

**Method**

**Improved AHP indicator weight determination method**

The specific content of the improved analytic hierarchy process is as follows: for each of \( n \) index, the standard deviation of samples is calculated separately, then the standard deviation of samples is compared with each other, and the values of other elements of the judgment matrix can be obtained in turn (Huang and Zheng 2003).

The sample standard deviation \( S(i) \) of each evaluation index can be used to reflect the influence degree of each evaluation index on aquifer water-rich, and to construct a judgment matrix \( B_{max} \). The calculation formula of its internal value \( b_{ij} \) is as follows:

\[
b_{ij} = \begin{cases} 
\frac{S(i)}{S_{max}} - \frac{S(j)}{S_{min}} (b_{ij} - 1) + 1, & S(i) \geq S(j) \\
\frac{1}{S_{max} - S_{min}} (b_{ij} - 1) + 1, & S(i) < S(j)
\end{cases}
\]

\[
b_{ij} = \min \left[ 9, \inf \left[ \frac{S_{max}}{S_{min}} + 0.5 \right] \right]
\]

In this formula, \( S_{max} \) and \( S_{min} \) are the maximum and minimum values of \( S(i) \) respectively; Relative importance parameter \( b_{ij} \), \( \min \) and \( \inf \) are the smallest and integral functions respectively. Finding the eigenvector \( \mathbf{u} \) corresponding to the maximum eigenvalue \( \lambda_{max} \) according to the matrix.

\[
M_i = \prod_{j=1}^{n} b_{ij} \quad (i = 1, 2, 3, \ldots, n)
\]

\[
u_j = \frac{u_j}{\sum_{i=1}^{n} u_i}
\]

Because of the complexity of multi-order judgment matrix and some values in the judgment matrix may be inconsistent. It is necessary to check the consistency of
In the evaluation questions of n evaluation targets and m evaluation indicators, the entropy of the j index is defined as:

\[ H_j = -k \sum_{i=1}^{n} f_i \ln f_i, \quad (j = 1, 2, 3, \ldots, m) \]  
(13)

In this formula, \( f_i \) is the weight calculated by the entropy weight method.

### 3. Evaluation index entropy weight

The entropy weight of the j index is defined as:

\[ v_j = \frac{y_j}{\sum_{j=1}^{m} y_j}, \quad k = \frac{1}{\ln n}, \]  
(14)

In this formula, \( v_j \) is the weight calculated by the entropy weight method.

### Method for determining index weights for coupling method

In this paper, the least square method of optimization method is used to couple improved AHP and the entropy weight to form a subjective and objective weighting method.

The constraint condition is as follows:

\[ \sum_{j=1}^{m} w_j = 1, \quad w_j \geq 0 \quad (j = 1, 2, \ldots, m) \]

Represented by a matrix:

\[ \begin{bmatrix} A & e \end{bmatrix} \begin{bmatrix} w_j \end{bmatrix} = \begin{bmatrix} B \end{bmatrix} \]  
(16)
In this formula, $A$ is a diagonal array. $e$, $W$ and $B$ are $m$ rows and one column vector.

$$A = \text{diag} \left[ \sum_{i=1}^{n} z_{i1}^2, \ldots, \sum_{i=1}^{n} z_{i2}^2, \ldots, \sum_{i=1}^{n} z_{im}^2 \right] \quad (17)$$

$$e = [1, 1, \ldots, 1] \quad w_j = [w_1, w_2, \ldots, w_m]^T$$

$$L = \sum_{i=1}^{n} \frac{1}{2} \left[ (u_i + v_j) z_{i1}^2 + \sum_{i=1}^{m} \frac{1}{2} \left( u_i + v_j \right) z_{im}^2 \right] \quad (18)$$

Solve the matrix equation above and get $w_j$:

$$w_j = A^{-1} \times \left[ B + \frac{1-e^T A^{-1} B}{e^T A^{-1} e} \times e \right] \quad (19)$$

Where $w_j$ is the weight of the improved AHP and entropy weight method coupling calculation, $Z_{ij}$ is a standardized data matrix with $m$ evaluation indicators and $n$ evaluation objects.

**Prediction of weathered bedrock water abundance in study area**

*Water richness index weight calculation*

According to the data of 172 boreholes in the study area, the weight of water-rich prediction indicators are calculated by improved AHP, entropy weight method and the coupling method.

1. **Index Weight Calculation Based on Improved AHP**

The judgment matrix $B_{4x4}$ calculated according to the formula 4 is as follows:

$$B_{4x4} = \begin{bmatrix} 1 & 4.41 & 5.23 & 9 \\ 0.23 & 1 & 1.81 & 5.58 \\ 0.19 & 0.55 & 1 & 4.77 \\ 0.11 & 0.18 & 0.21 & 1 \end{bmatrix}$$

The judgment matrix is a $4 \times 4$ matrix, which is calculated by formulas (7) and (8). The maximum eigenvalue of the judgment matrix is $\lambda_{\text{max}} = 4.1513$, $CR = 0.0348 < 0.1$. Therefore, the judgment matrix satisfies the consistency test.

The weight of the index layer $u_j$ is obtained by calculation: The weight $u_1$ of top-level index is 0.6197, the weight of lithologic association index $u_2$ is 0.2016, the weight of weathered index $u_3$ is 0.1372, and core rate index $u_4$ is 0.0415 (Table 4).

2. **Index Weight Calculation Based on Entropy Weight**

The matrix normalized by Equation 10 as follows:

$$Y = \begin{bmatrix} 0.2500 & 0.2950 & 0.4850 & 0.8939 \\ 0.0000 & 0.5000 & 0.6787 & 0.2641 \\ 0.2500 & 0.5000 & 0.5826 & 0.2643 \end{bmatrix}$$

The normalized matrix is calculated by using formulas (13) and (14) in Matlab, and the weight $v_j$ of each index is obtained: The weight $v_1$ of top-level index is 0.4136, the weight of lithologic association index $v_2$ is 0.1779, the weight of weathered index $v_3$ is 0.2614, and core rate index $v_4$ is 0.1471 (Table 4).

3. **Index Weight Calculation Based on the Coupling Method**

The improved AHP and the entropy weight method are coupled by the least squares method. From equation (17), $A$ is a $4 \times 4$ diagonal matrix, as follows:

$$A = \begin{bmatrix} 51.6875 & 0 & 0 & 0 \\ 0 & 74.5079 & 0 & 0 \\ 0 & 0 & 49.5930 & 0 \\ 0 & 0 & 0 & 51.0274 \end{bmatrix}$$

In Matlab, formulas (18) and (19) are used to calculate the optimal weight $w_j$ of the index layer: The weight $w_1$ of top-level index is 0.5166, the weight of lithologic association index $w_2$ is 0.1898, the weight of weathered index $w_3$ is 0.1993, and core rate index $w_4$ is 0.0943 (Table 4).
Evaluation and Verification of Water Abundance

According to the standardized data rasterized in Surfer, the grid maps of each index are imported into ArcGIS, then the raster calculator is used. Combined with the improved AHP, the entropy weight method and the weight calculated by coupling, the overlay analysis is carried out respectively. Finally, the zonal prediction maps of weathered bedrock water abundance in the southern wing of Ningtiaota coalfield under different weighting conditions are obtained (Fig 3, Fig 4 and Fig 5). According to the natural discontinuity method, the water abundance is divided into four grades: extremely weak (I), weak (II), medium (III) and strong (IV).

According to the characteristics of unit inflow of 41 pumping holes in this area, the unit inflow of borehole is divided into four categories, namely less than 0.01L/s·m, 0.01–0.1L/s·m, 0.1–1L/s·m and 1–5L/ s·m corresponds to the extremely weak (I), weak (II), medium (III) and strong (IV) in Figures 3, 4 and 5 respectively (Table 5).

In order to compare the advantages and disadvantages of three water abundance partition prediction methods based on improved AHP, entropy weight method and the coupling method, the water abundance level of the weathered bedrock pumping

<table>
<thead>
<tr>
<th>indicators</th>
<th>top-level index of the weathered bedrock</th>
<th>lithologic association index</th>
<th>weathered index</th>
<th>core rate index</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHP weight ( (u_j) )</td>
<td>0.6197</td>
<td>0.2016</td>
<td>0.1372</td>
<td>0.0415</td>
</tr>
<tr>
<td>The entropy weight ( (v_j) )</td>
<td>0.4136</td>
<td>0.1779</td>
<td>0.2614</td>
<td>0.1471</td>
</tr>
<tr>
<td>Coupling weight ( (w_j) )</td>
<td>0.5166</td>
<td>0.1898</td>
<td>0.1993</td>
<td>0.0943</td>
</tr>
</tbody>
</table>

*Fig.3 Water abundance prediction zoning map based on AHP*

*Fig.4 Water abundance partition prediction map based on the entropy weight method*
borehole in the area is compared with forecast categories in Figures 3, 4 and 5. If they are consistent, they are considered to be the same, indicating that the prediction results are correct. By comparison, it is found that the water abundance classification predicted by the improved AHP method, the entropy method and the coupling method are 68.29%, 70.73% and 92.68% respectively. So the least squares method is the best method for water abundance zoning prediction.

Conclusion

The fissure aquifer of weathered bedrock in Jurassic coalfield in northern Shaanxi is the main water-filling aquifer in the mine. Its water abundance varies greatly in space. Four indexes can be used to predict the water richness of weathered bedrock aquifer, top-level index, lithologic association index, weathered index and core rate index.

The water abundance prediction method based on coupling of improved AHP and entropy weight method is a accurate method. It is more effective than the improved AHP and entropy weight method when used alone.

Acknowledgements

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References


Abstract
International guidelines exist for reporting of mineral resources (SAMREC, JORC), (engineering and hydro-) geological investigations (ASTM, British Standard) and environmental geochemical characterisation (GARD). Yet, mining hydrogeological investigations have been neglected in this regard, relying on varying district governmental guidelines. This study reviews and analyses existing guidelines to produce standardised guidelines similar to ASTM or JORC. However, this is the first step to conflating international practices to compile an internationally accepted reporting benchmark. This research explores fundamental principles of groundwater movement and hydrogeological influences on a mining site, identifying appropriate characterisation methods and data resolutions required for various levels of characterisation.

Keywords: reporting standard, quantified benchmark, mine water, hydrogeological investigation

Introduction
Reporting guidelines for mining related hydrogeological studies vary widely based on geographical setting (Barnett et al. 2012; EBRD 2014; EPA 1994; ICMM 2017; IFC 2007; IFC 2007; JORC 2012; NI43-101; Stephenson 2000). Often these guidelines are based on a national or international understanding and approach to investigation. However, the requirements are often subjective and unquantifiable. This results in a variable benchmark in justification of the use of specific methods to perform investigations. Further to this is the absence of technical guides providing methods to quantify e.g. representative sample numbers and test numbers per investigation. Therefore, subjective judgement of the validity of mining hydrogeological studies is possible if a universal quantitative guideline does not apply. An example of the elimination of this bias is the JORC standard of mineral resource reporting where quantified approaches are followed to determine a resource/reserve estimation with various levels of certainty which are internationally accepted. The development of quantified benchmarks for reporting is imperative if mine water challenges are to be addressed effectively and co-operatively.

Methods
Comparisons of various guidelines for the reporting of hydrogeological parameters and investigations was performed to identify any possible quantitative guides (Barnett et al. 2012; EBRD 2014; EPA 1994; ICMM 2017; IFC 2007; IFC 2007). However, none of these documents provide a quantifiable level for data compliance and rely on expert judgement. In contrast, the methods articulated in JORC contain clear definitions on the quantification of resources/reserves. Since its implementation, substantially improved standards of public reporting have prevailed in mining throughout Australasia (Stephenson 2000). This can largely be attributed to consensus on standards between mining companies, quantitative standards and the code being a requirement for listing on the Australian Stock Exchange. Therefore, the identification of a method to quantify a reporting standard for data as well as interpretation confidence in mining-related hydrogeology was deemed necessary. Mining assets (resources/reserves) can only be quantified realistically by also accounting for quantified liabilities with water management and control being a critical expenditure during operations. However, the complexity of hydrogeological systems must be realistically
represented spatially and temporally to define reliable water management goals.

Spatial parameter variability and the quantification of its effect on natural systems is the focus of many natural scientific studies. However, without fixed, measured parameters this can seem like an impossible task. Furthermore, the representation of a natural system by a subset of samples is generally a limiting factor in the accuracy of calculations with regards to that system. However, by applying a “theory of constraints” (Goldratt 2016) combined with statistical analysis of available data the quantification of a hydrogeological system’s behaviour becomes increasingly reliable. The application of the theory of constraints and the associated statistical analyses are discussed in the sections below.

Results and Discussion

Delineating the Area of Influence/Main Constraint

Delineation of this main constraint is no stranger to numerical flow modellers of both surface- and groundwater. However, topography, surface drainage and mining depths provide some clues to the delineation of the aquifers influenced by mine depressurisation. In a fractured rock aquifer, groundwater levels often emulate topography. Therefore, a conceptual understanding of the three-dimensional distribution of groundwater heads and transfer of groundwater between aquifers can be developed. To simplify, the main constraint on the quantification of the hydrogeological system is the identification of a system domain (Diersch 2013). This boundary must follow zero-flow and constant head boundaries which are as near as possible to the maximum extent of potential steady-state mine depressurisation without influencing calculation results and including all potentially affected water sources (Barnett et al. 2012).

Sub-Constraints within the Main Constraint

Selecting the hydrogeological domain fixes the spatial variability of hydraulic parameters to a certain degree in terms of sources, sinks and fluxes. Although temporal variability is not fixed within the main constraint, temporal variables can be measured much more accurately and representatively e.g. rainfall, streamflow, groundwater abstraction etc. These variables act as sub-constraints of mathematically describing the hydrogeological system. Similarly, aquifer hydraulic properties e.g. transmissivity, porosity, specific storage etc. (another sub-constraint) may remain fixed but are spatially variable. The quantification of this variability is considerably more challenging with limited resources and the identification of boundaries to a representative elemental volume may become impossible. However, defining a sub-constraint requires multiple properties for its delineation. In a hydrogeological system, the main focus of a spatial sub-constraint definition is geometry of physical attributes. An example would be the delineation of the geometric extent of a specific lithology with a specific hydraulic conductivity, porosity and storativity. This approach also applies to structural discontinuities and would include spatial orientation.

Selection of Sample Size to Represent Sub-Constraint Properties

A sub-constraint therefore represents a population with a specific set of attributes. Several testing methods are used to determine e.g. the hydraulic properties of an aquifer. However, the spatial extent of these tests are only representative of a portion of the sub-constraint population i.e. the aquifer. Unfortunately, no guideline currently addresses how representative a dataset should be in a quantitative manner. Therefore, sample numbers are left to the subjective discretion of the scientist. To eliminate bias from this method statistical methods of sample size selection are proposed e.g. Cochran’s formula. This provides a quantitative confidence level to the selection of statistical sample numbers to describe a population in a representative way (Field 2013). An example of sub-constraint sample size determination would be a specific lithology on-site with specific hydraulic parameters unique to that lithology. Therefore, a number of hydraulic tests may need to be performed on that
lithological unit to representatively quantify its hydraulic parameters.

**Extrapolation of Sub-Constraint Properties**

Once the sub-constraints of the hydrogeological system have been identified and representatively quantified in a statistically sound dataset, extrapolation of these properties throughout the main constraint domain is possible, per sub-constraint. Because a representative dataset of each sub-constraint population exists, various interpolation methods can be tested against the dataset to best represent the sub-constraint spatial variability (Reilly and Harbaugh 2004). This eliminates subjective selection of interpolation methods to represent sub-constraint populations.

**Quantification of the Hydrogeological System**

A representative set of fixed spatial sub-constraints and potentially variable temporal sub-constraints can now be incorporated into the calculation of a hydrogeological system’s behaviour with an associated confidence level. A subsequent result of applying this method is the reduction in potential stochastic realisations which could describe a calibrated system and a more realistic representation of system dynamics. Numerical flow modelling is currently the best available tool for the calculation of groundwater flow in various scenarios. However, a model is only accurate and representative to the level of confidence of its input data (Diersch 2013). Statistically representative sampling of sub-constraints in a hydrogeological system provides a quantitative method of demonstrating model reliability.

**Changes in Sub-Constraints – System Behaviour Re-Quantification**

As mentioned, the spatial variables in a hydrogeological system are often fixed and challenging to quantify on a large scale while temporal variables are often easily measured and quantified. However, some of these variables e.g. hydraulic conductivity, can change from a spatial variable to a temporal variable. This applies especially in mining environments where excavation and dewatering of a mine substantially changes the localised hydraulic properties of an aquifer, turning a lithological mass into a free draining void. The implication of this increase in reliability of calculation as a statistically represented value turns into a certain and measured value. Introduction of this additional constraint therefore has a positive effect on quantification as subjectiveness and data uncertainty are reduced. This implies that confidence in the calculation of system behaviour can now further be quantified rather than judged subjectively.

**Conclusions**

Although various guidelines and standards exist for the approach to performing a hydrogeological investigation at a mining site none provide a fixed reference point. Variation in methodologies between countries, jurisdictions and scientific communities have left this task subjective and its approaches qualitative based on circumstantial evidence. A unified, measurable standard is needed for evaluation even if a degree of freedom in terms of methods is retained. Therefore, a quantifiable benchmark in terms of characterisation would serve to eliminate bias and provide an invariable standard of evaluation, regardless of geographical location or approach. Identifying the constraining factors for the quantification of natural systems with regards to spatial and temporal variables and quantifying the confidence of representations will not only improve scientific understanding but the international standard of reporting quality. Integration of system constraints, statistics and science is fundamental to representativeness and transparency in mine water hydrogeological investigations and imperative for advancement as a unified scientific community.

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Hydro-Geochemical Properties of Class F Fly Ash When Leached with Acid Mine Drainage

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Abstract
The aim of this study is to assess the hydraulic and geochemical properties of fly ash with reference to acid mine drainage (AMD). In the laboratory, ash was leached with natural AMD to assess the changes in hydraulic conductivity and chemical leachate over time. Influent and effluent was monitored for pH, EC and metal concentrations, while monitoring discharge volumes as well. Hydraulic conductivity exhibited overall decreasing trends over time, reducing from $10^{-1}$ m/d to $10^{-3}$ m/d. Calcium was the dominant cation that leached out, with sulphate being the dominant anion. Ash backfill will improve current discharging AMD water quality.

Keywords: Hydraulic conductivity, opencast coalmine, Backfill

Introduction
There are various historic coalmine sites in the Mpumalanga Province of South Africa. According to McCarthy (2011), some of these mines have collapsed over time and many of them are discharging acid mine drainage (AMD) into the environment, thus having negative effects on the water quality of downstream rivers, streams and dams. Additionally, vast amounts of fly ash are produced at coal-fired power stations and are disposed onto landfills, with limited space. Therefore, a need arises to mitigate or prevent AMD generation from pre-existing mines and to find alternative ash disposal methods.

Ash backfill as a monolith into pre-existing and future coalmines might potentially mitigate the generation and effects of AMD. However, there is limited knowledge on how South African fly ash would behave under opencast backfilled conditions and its effect on the immediate environment of the proposed opencast mine sites. Thus, the aim of this study is to assess the hydraulic and geochemical properties of fly ash with reference to AMD that leaches from the mines and comprehend how ash backfill would affect the natural water environment (groundwater and surface water).

Materials
Ash: Ash from two coal-fired power stations were used in this study and were collected directly off the conveyor belts. Ash 1 that was collected from the first power station is named K-ash, whereas, ash 2 from another power station are named T-ash. Ash from both power stations show characteristics of Class F ash, making it a natural pozzolanic material. Both K-Ash and T-Ash have a SiO₂ + Al₂O₃ + Fe₂O₃ weight above 70%, with a low CaO (CaO < 10 wt. %) content which is common for South African fly ash. Additionally, K-ash has a slightly higher CaO (6.9 %) and MgO (1.28 %) weight percentage compared to the CaO (5.3 %) and MgO (1.14 %) weight percentage in the T-ash.

AMD: Natural AMD water with a pH = 2.5, was collected from Driefontein, a pit lake at an old opencast coalmine site in the Witbank area in Mpumalanga. According to Bell et al. (2001) the pit lake is a product of a historical shallow underground coal mine that collapsed due to multiple pillar failures. As a result, the mine voids filled up with water and discharged to form the pit lake. The water in the pit lake is of an acidic nature resulting from the reaction with oxygen and pyrite minerals in unmined coal and host rocks.
AMD had Iron (Fe) content > 130 mg/L and Sulphate (SO₄) content > 2000 mg/L.

Methods

The hydro-geochemical properties of ash were determined in the laboratory by leaching ash with AMD through the use of a constant head permeameter test (Darcy constant head column test) in accordance with a modified version of method 1314 from the LEAF methodology and ASTM D 4874 leaching standard (Ecology 2003; USEPA 2014). Testing lasted approximately 6 months where fly ash was leached continuously with natural AMD. Method 1314 from the LEAF methodology was modified with the aim of achieving the closest field conditions. Thus, instead of distilled water, natural AMD water was used as the leaching liquid (influent) due to the high probability of fly ash being backfilled into AMD generating environments. Furthermore, ash was not packed into the columns as according to the ASTM D 4874 leaching standard but, rather mixed to a slurry at 40%, 50% and 60% moisture respectively before it was poured into the columns. All the columns were cured for 28 days before hydraulic conductivity testing. Columns named K40, K50, K60, T40, T50 and T60 were 0.2 m in length, whereas, columns named K60b and T60b were 0.5 m in length, indicating that the 0.5 m columns consisted of substantially larger volumes of fly ash.

A total of 8 columns filled with ash were connected to a headwater reservoir through a piping system (Figure 1). The hydraulic test was performed by introducing AMD water to the ash columns under constant hydraulic gradient (ΔH) conditions. AMD moved from head 1 (H₁) down the piping and upwards through the ash sample in the column until it eventually discharges at head 2 (H₂). The upward flow of AMD through the ash sample ensured fully saturated conditions as the distribution of AMD spreads evenly through the cross-sectional area (A) of the column. At outflow, the discharge (Q) was measured as length cubed per unit time. Initially, discharge (effluent) was measured 4 - 8 times a day during the first two weeks of testing. Thereafter, discharge was measured twice a day as the flow rates decreased until week 5 of testing. Final flow measurements were measured once every 3 days. The hydraulic conductivity (K) is then calculated through applying the measured parameters into Darcy’s equation:

\[ Q = KIA \]

Where:
- Q = Discharge in units of length cubed per unit time (m³/d)
- K = Hydraulic conductivity in units of length per unit time (m/d)
- I = Hydraulic gradient (ΔH) measured as the difference in head (H₁ - H₂) in meters over the length (L) of the sample in meters (m/m).

Figure 1. A schematic depiction of a constant-head permeameter (after Fetter, 2001).
A = Cross sectional area in units of length squared (m²)

Influent and the effluent from 4 columns (K50, T50, K60b and T60b) were routinely collected throughout the testing period. Samples were sent to the laboratory for chemical metal analysis, to evaluate the influence of ash on AMD water quality. The target elements in the evaluation were the concentrations of Fe, Ca and S as SO₄. Additionally, pH and EC was monitored throughout the testing period.

Results and Discussion

Hydraulic conductivity results are depicted in Figure 2, whereas the pH is presented in Figure 3. Moisture in the ash during mixing and curing, allows for pozzolanic reactions to occur, solidifying the ash and resulting in the initial low K of 10⁻¹ m/d. During leaching, calcium oxide in the ash dissolves at the bottom of the columns and causes gypsum precipitation towards the middle and top of the columns. Gypsum precipitation towards the middle and top of the columns causes void spaces to decrease, thereby lowering the hydraulic conductivity to 10⁻² m/d. Variations in hydraulic conductivity of ash are also highly influenced by the high mineral content in the AMD, such as high iron and sulphate concentrations. Also, Fe(OH)₃ in the ash dissolves at low pH at the reaction front between ash and AMD, jarosite minerals form which is stable Fe-sulphate in acidic conditions and clogs up pore spaces. This results in the lowering of the K at the reaction front by an order of magnitude compared to deeper in the ash, reducing the K to 10⁻³ m/d. One of the columns (K40) completely clogged up and flow through stopped (Figure 2).

The alkaline nature of the ash initially neutralizes the acidic levels of AMD from inflow pH = 2.5 to an outflow pH = 11. Acidification of the outflow from pH = 11 towards a pH = 4 is observed during testing (Figure 3). According to Nhan et al. (1996), the initial pH of the effluent is controlled by the dissolution of Ca(OH)₂ and Mg(OH)₂ in the ash. Moreover, K-Ash columns exhibited a stronger buffering behaviour compared to the buffering behaviour of the T-Ash columns. K-Ash also consists of slightly higher concentrations of CaO and MgO compared to the T-Ash, hence the stronger buffering behaviour. Overall, the K decreased by 2 orders of magnitude from an initial K of 10⁻¹ m/d to 10⁻³ m/d, with the AMD iron concentration of above 130 mg/L playing the dominating role in reducing the hydraulic conductivity under the lower pH conditions at the reaction face between AMD and ash.

The temporal trend in electrical conductivity (EC) of influent compared to effluent are shown in Figure 4 and Figure 5. It was observed that the EC concentrations of the effluent remained lower than the EC of the influent AMD. The overall EC peak of the effluent measured during the testing period, was 490 mS/m for most of the columns. General EC concentrations in the effluent ranged between 350 mS/m and 490 mS/m. In contrast, effluent of T40 exhibited higher EC values, with a peak of 525 mS/m. T40 also exhibited the highest initial hydraulic conductivity peaking at 0.6 m/d, suggesting that the ash had partial effect on the AMD quality due to the higher flow rates during the initial stages of testing. Overall, the effluent
EC concentrations from all the columns were lower than the EC of influent AMD.

Iron concentrations in the AMD ranged between 138 mg/L and 190 mg/L throughout the leaching period. The early time Fe concentrations in the effluent of all the columns were measured at $10^{-2}$ mg/L. Effluent Fe concentrations from the K60b and T60b columns persisted at $10^{-2}$ mg/L (mostly below detection limit of 0.06 mg/L) throughout the entire testing period. However, due to lesser volumes of fly ash in the shorter K50 and T50 columns, the Fe concentrations in the effluent increased after 22 days of leaching, with the K50 effluent concentrations increasing to $10^1$ mg/L and the T50 effluent concentration to $10^0$ mg/L until the testing was concluded. Overall, the Fe concentrations in the effluent from all the columns remained lower than the Fe concentrations in the influent AMD water, suggesting that ash retains Fe concentrations (Figure 6).

Calcium was the dominant cation that leached out, with sulphate being the dominant anion. Sulphate concentrations was high in the leachate due to the high sulphate content in the AMD (Figure 7). Ca originates from both the lime in the ash (that neutralise the acid) and the influent AMD (Figure 8). S concentrations in the AMD and the effluent of the K50 and T50 columns, showed very similar results throughout the duration of the leaching period. Effluent concentrations from the K60b and T60b columns showed S concentrations of about 1000 mg/L lower than the AMD S concentrations. The S concentrations in the K60b and T60b increased at day 22 of leaching, however, it remained below the AMD S concentration for the remainder of the leaching period (Figure 7).

It is expected that an ash monolith deposited at the discharging position of the backfill pit as shown in Figure 9, would hydraulically and geochemically behave similar to the laboratory column testing. As a result, the water table in the backfill will be substantially influenced by the monolith. Initially, the water table is expected to be at the lowest discharge elevation in the backfill area, however, with the decreasing hydraulic properties of fly ash over time, it is expected that flow through will be limited resulting in the rise of the water table. If the water table rises over time, it limits the pyrite minerals in the backfill spoils to oxygen exposure. Ultimately, resulting in reduced discharge volumes from the backfill as well as limiting AMD generation due to reduced oxygen exposure to spoils (Figure 9).

**Conclusions**

The hydraulic conductivity testing of ash showed decreasing trends of K over time. Overall, the hydraulic conductivity decreased from initial K values of $10^{-2}$ m/d to $10^{-3}$ m/d. These changes in hydraulic conductivity over time, are initially subjected to the pozzolanic bindings that formed during the curing phase of the experiment. During the experiment, secondary mineralization occurs induced by calcium rich minerals which are deposited in the flow paths, causing a decrease in K to $10^{-2}$ m/d. Lastly, the Fe (>130 mg/L) and SO$_4$ (>2000 mg/L) concentrations in the AMD together with the low pH =
Figure 6. Influent Fe concentrations vs effluent Fe concentrations.

Figure 7. Influent S concentrations vs effluent S concentrations.

Figure 8. Influent Ca concentrations vs effluent Ca concentrations.

Figure 9. A conceptual depiction of ash backfilled in an opencast mine.

LEGEND
- Fly Ash Monolith
- Backfill Spoils (Unmined Coal and Host rocks containing Pyrite minerals)
- Unmined Host Rock
- FlowDir
- Initial Waterlevel
- Final Waterlevel
- Groundwater Flow Direction
- Recharge
- AMD Flow Direction
- Surface water body

*Not to scale
2.5 causes a clogging effect at the front face of the fly ash, which ultimately causes the hydraulic conductivity to decrease towards $10^{-3}$ m/d. Within 8 columns being tested, one column experienced a complete clog up which indicates that fly ash may become impermeable over time if exposed to AMD with low pH and high concentrations of iron and sulphate.

From the geochemical leach test results, it was observed that most of the leachate water was of a better quality than the influent AMD water quality. The effluent pH (from pH = 11 towards pH = 4) was higher than the pH of the influent AMD (pH = 2.5). Overall EC reduced in discharge compared to inflow AMD ($EC_{inflow}$: 535 – 545 mS/m versus $EC_{outflow}$: 350 – 490 mS/m). Although sulphate was the dominant anion that leached out, Fe ($10^{-2}$ – $10^{+1}$ mg/L) and SO$_4$ ($10^{+2}$ – $10^{+3}$ mg/L) in the effluent showed lower concentrations when compared to the inflow Fe ($10^{+2}$ mg/L) and SO$_4$ ($10^{+3}$ mg/L) concentrations.

Based on this research, an ash monolith backfilled into an opencast coal mine would improve the discharging AMD water quality. An ash monolith deposited at the discharging position within the backfill, may have positive influences, including:

1. Increases pH of the water that do flow through the ash monolith, and the associated reduction in concentrations of Fe and SO$_4$ of the AMD water, thus retaining some contaminants.
2. Due to decreasing hydraulic conductivity of the ash, the water table in the backfill is expected to rise to the top of the monolith over time, thereby reducing oxygen exposure of the waste rocks in the backfill, ultimately reducing AMD generation.

The topography, hydraulic conductivity and the water table within the backfill may be altered to manage the discharge position, elevation and improve water quality from the ash monolith backfilled coal mines.

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**References**


Pump Tests in Deep Ore Mine Shafts for the Evaluation of a Possible Geothermal Use

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Abstract

Mine water of deep abandoned and flooded ore mine shafts are suitable for geothermal use. In the presented case (Germany, Rhineland-Palatinate), geothermal water is pumped from a shaft of the San Fernando mine into a shaft of the Friedrich-Wilhelm mine. Further use is planned in the outlet of the Wolf mine. For this purpose both a sufficient water inflow and outflow must be guaranteed. In the years 2018 to 2019 the suitability of the shafts were tested by a long-term pumping test. The water level in San Fernando shaft reacts only marginally to water withdrawal, while the water level in Friedrich-Wilhelm shaft and in the outflow Wolf fluctuates considerably.

Introduction

The Rhenish Massif was an important ore mining district with shafts reaching local depths of more than 1,000 m. The ore deposits of the Siegerland are spread over hundreds of individual veins. An economic extraction was only possible for individual mines that had sufficiently large deposits (Gleichmann 1990). In the middle of the last century individual mines were combined to form large composite mines. The individual mines were connected to each other in depth by adits several kilometres in length. So the mining could be continued in some compound mines until 1965 (Fenchel et al. 1985). After closure the underground workings were flooded and groundwater filled the mine shafts. This created large water reservoirs in the underground which can be used for geothermal heat extraction or heat storage. There are more than 500 abandoned mines in the Siegerland-Wied district, and they have considerably altered the large-scale hydrogeological properties of the subsurface in this area (Fenchel et al. 1985). The widespread Devonian silt and sandstones in the area unaffected by mining typically have low permeability (Wieber et al. 2011). In contrast, the backfilled mine workings have increased hydraulic conductivities. Mine water in neighbouring shafts is often connected by laterally extended underground developments (Wieber et al. 2019). The tunnels and shafts, together with the mining areas, have created permeable areas in which mine water can flow with high velocity. Heat circulation is likely in these mines, and heat conduction across the large rock–water interfaces in the mine workings is expected to replenish heat rapidly after exploitation.

In Herdorf (Fig. 1) two geothermal uses are planned or in operation. In the Sotterbach valley, a geothermal plant is operated with mine water. Water is pumped from shaft 2 San Fernando and infiltrated into shaft 2 Friedrich Wilhelm. Further geothermal utilisation is planned at the outflow of the Wolf mine. Against this background, different quantities of water have been pumped and infiltrated from the above-mentioned shafts in recent months.

The composite mine originally consisted of five initially separate iron ore mines, namely Wolf, San Fernando, Friedrich Wilhelm, Füsseberg, and Glaskopf. The mines were later connected by deep drifts or crosscuts (Fig. 2).

The Wolf Mine comprises the main shaft, a blind shaft, an old shaft (not shown in Fig. 2), and 16 further levels below the lowest mine adit, the “Tiefer Stollen” (Fig. 2). The San Fernando Mine has two main shafts to depths of 675 and 1002 m, and a 340 m deep blind shaft connecting the five lower mine shafts.
levels. Both mines are connected between the 560 m and the 770 m level. The 240 m level of the San Fernando Mine is connected by a decline with the 300 m level workings of the Wolf Mine. Another connection exists between the 450 m level of the Wolf Mine and the 400 m level of the San Fernando mine. Other connections between the two mines are through galleries below 550 m, from which there is a hydraulic gradient towards the Wolf Mine shaft. The mine shafts #1 and #2 of the San Fernando Mine (Fig. 2) are filled with backfill material from the surface to the “Tiefer Stollen”. Between the mines San Fernando and Friedrich-Wilhelm there is only one connecting adit between the 830 m level (San Fernando) and the 17th level (Friedrich-Wilhelm). Connections between the Friedrich-Wilhelm mine and the Füsseberg mine exist between the 486 m level and the 18th level. The connections of the entire system are verified by tracer tests.
Streb (2012) estimated the water volume of the Wolf Mine shaft at 6,700 m³, while the total volume of the San Fernando Mine shafts is approximately 26,500 m³. The shaft volumes of the Friedrich Wilhelm, Einigkeit, Füsseberg, and Glaskopf mines account for about 70,000 m³ in total (Wieber et al. 2019).

**Methods**

For the operation of the geothermal plants, mine water is pumped from the San Fernando shaft into the Friedrich-Wilhelm shaft after heat extraction or heat supply. Effects such as the water levels in the shafts and the water quantities in the Wolf outlet must also be determined because there is another geothermal plant planned. A still running long-term pump test started in April 2018 was carried out for this purpose. Information are collected by using data loggers which are installed in San Fernando Shaft 2, Friedrich-Wilhelm shaft 2 and in the outflow Wolf. In addition, manual measurements were done weekly by means of electric contact gauge. The pumping test was carried out with a water withdrawal of 8 L/s at the beginning over 12 L/s to 16 L/s at present.

**Results**

Even before the start of the pumping test, a comparison of the water leakage of the Wolf mine and the water levels in the Friedrich-Wilhelm shaft shows that these are 2 sensitive systems that respond in a similar way. When the pump power is switched on or changed, both systems react abruptly. There is a slight lowering of up to 0.2 m of the water level in the pump shaft and a simultaneous increase of up to 1.9 m in the injection shaft Friedrich-Wilhelm (Fig. 3). After switching off the pump, the water levels react vice versa.

The Wolf outflow also reacts directly to the switching on or off of the pump. When the pump is started, the flow rate drops sharply and then rises again while pumping stops. As the duration of the pump test progresses, however, the flow rate recovers somewhat. With a pumping capacity of 8 L/s (April to July 2018) no stationary state occurs at the Wolf outflow. With the increase of the pumping capacity to 12 L/s (July to August 2018) and 16 L/s (September to October and November to December 2018) a stationary state seems to be reached in each case by a flow rate of approximately 3.5 L/s respectively 1.5 L/s and 2.5 L/s.

However, it should be noted that 2018 was an unusually hot and dry year in Germany. The mean precipitation (2000 to 2015) in the Siegerland-Wied district is 1,056 mm/a, and the annual average temperature is 8.0 °C (Deutscher Wetterdienst climate station Bad Marienberg). The mean precipitation in 2018 was 787 l/m², the annual average temperature 9.4 °C.

**Conclusions**

As the pumping capacity from the San Fernando shaft increases, the amount of water at the outflow of the Wolf mine decreases,
while the water level in Friedrich-Wilhelm shaft rises. It is therefore necessary to carry out additional evaluations of the hydraulic connection between the San Fernando - Wolf and Friedrich Wilhelm - Füsseberg - Glaskopf composite pits. The two composite mines (Fig. 2) are connected only by the 830 m underground level (San Fernando) and the 17th level (Friedrich-Wilhelm). The connecting adit traverses the “Mahlscheid” fault, which was already identified at the beginning of the investigations as a possible weak zone. It can be assumed that the entire system drains water via the Wolf outflow, since no drainage takes place in the outlet of the Glaskopf mine. Another outflow in the area of the Glaskopf mine could not be detected despite intensive search. It is possible that the outflow via the Devonian mountains into the Heller will take place.

All in all, this is a mine water system that reacts sensitively to changes. A hydraulic connection between the two composite mine via the 830 m level (or 17th level) appears to be limited. Further investigations to optimise the system by increasing the pumping capacity and later by reversing the pump and injection shaft are planned.

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References


The advance detection and treatment of karst collapse columns –
A case study of the Renlou Coal Mine in Anhui Province, China

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Abstract
Karst collapse columns are widely developed in Renlou Coalmine, Anhui Province, China. More than 10 collapse columns are detected so far in this mining area. In 1996, the first testing Panel 7222 encountered water inrush disaster because of the karst collapse column. The maximum volume of the water inrush quantity came up to 34570 m$^3$/h, which caused mine flooding and enormous economic loss. In this paper, a potential karst collapse column found during the excavation of No. II5,1 tunnel in 2010 is selected as a case study to establish the advanced detection and treatment approaches for karst columns. The approaches proposed by this paper include three strategies: the first is the preliminary monitoring and anomaly analysis of water quantity, quality, temperature and pressure. Secondly, based on the monitoring work, geophysical prospecting is applied to determine the abnormal position of the collapse column. Thirdly, the accurate position and the range of column are confirmed by ground or underground drilling to the geophysical anomaly areas. Finally, the advanced detection approach in the way of grouting is applied, which blocks the hydraulic connection with the high pressure bottom Ordovician aquifer and plugs the collapse column. The approach eliminates the potential risk of water inrush during the roadway excavation.

Keywords: coal mining; tunnel excavation; karst collapse column; combined detection and investigation; grouting treatment

Among the water inrush disasters that occur in coal mines, those that do so through karst collapse columns in Ordovician limestone aquifers are some of the most influential and serious types, as they have caused several of the largest water inrush accidents in history (Yin et al. 2004). Buried collapse columns are usually found at depth and are therefore difficult to detect. However, research on the prevention of water inrush incidents and the control of collapse columns has focused on post disaster governance, while few studies have investigated the advance exploration and treatment of collapse columns. In recent years, coal mining problems have been encountered continuously in high and superhigh-pressure confined aquifers, and the influences of Ordovician limestone aquifers have become increasingly serious. Hence, the effective advance detection and preventative treatment of collapse columns have become some of the most important fields of research in controlling water inrush events.

During the construction of the Renlou Coal Mine, two hidden water-conducting karst collapse columns were discovered and harnessed (Duan et al.2005; Kong et al. 2012), which indicates that there are geological conditions for the formation of collapse columns in the mine (Fang et al. 2008).

In 2010, during the construction of the II5, track, water was discharged through the upper anchor bolt eye, and various forms of exploration, such as underground and surface geophysical exploration, geochemical exploration and drilling, were carried out. A comprehensive analysis confirmed the existence of a water-conducting collapse column. To quickly and efficiently prevent a disaster associated with the collapse column, the advanced detection and comprehensive identification of the ultrahigh-pressure
water-conducting collapse columns concealed at depth were carried out: through comprehensive exploration and control technology with advance geological prediction, water quality warning systems, geophysical exploration and drilling verification. Predisaster detection and control of superhigh-pressure water-conducting collapse columns concealed at depth provide an important geological basis for grouting and preventing the future occurrence of serious disasters.

**Background conditions**

**Mine traffic location**

The Renlou Coal Mine is located in the Linhuan Coal Mine area in northern Anhui Province. The extent of the mine area is as follows. The northern boundary is bounded by the SunTuan Mine area, the F7 fault is adjacent to the XuTuan Mine area in the south, and the F23 fault bounds the area to the southeast, while the plane projection of the -800 m contour line of coal seam 31 bounds the area to the east, and the outcrop of coal seam 11 bounds the area in the west. The Renlou Coal Mine is 4–7 km wide from east to west and 8–11 km long from north to south with a defined area of 42.0705 km², the mining depth ranges from -315 – -720 m.

**Hydrogeological background**

The coal field within which the coal mine is located is completely concealed by a loose aquifer of Quaternary age. The coal-bearing strata belong to the Carboniferous Permian system. The coal-bearing basement is Ordovician karst limestone. The top of the direct water-filled aquifer of the mine is a coal-bearing stratum, while the bottom is a fractured sandstone. The indirect water-filled aquifer is composed of the Quaternary aquifer at the bottom of the Quaternary system, a coal-bearing fissured sandstone, the Taiyuan group limestone and the Ordovician limestone aquifer (290 m from the 7, mined coal seams). If no large vertical water structure is present, it is extremely unlikely that water from the Ordovician limestone will be directly exposed.

**Water outflow along the II 5, track roadway**

On June 8, 2010, when the roadway was constructed to 28 m before G33, the upper shoulder bolt eyelet produced water at a rate of approximately 1 m³/h with a total hardness of 8.34°dH and no permanent hardness. When the excavation reached 31.5 m before G33 on June 9, the water volume increased, and the total water inrush rate through the upper three water exploration bolt eyelets reached nearly 30 m³/h. The permanent hardness of the effluent began to appear on June 10. By November 7, 2011, the total hardness of the water was 60.5°dH, the permanent hardness was 48.8°dH, the water temperature was 41°C, and the water inrush

![Fig.1 Location map of the Renlou Coal Mine area](image-url)
rate was 8 m³/h. The permanent hardness of the water from the upper side of the roadway rose from zero, and the total hardness and permanent hardness of the water increased.

**Geological prediction analysis**

The main roadway is located in the Gongguang coal protection pillar. The minimum vertical distance between the bottom boundary of the new overlying strata “fourth aquifer” and the roadway roof is approximately 440 m, and the minimum vertical distance between the underlying Taiyuan Formation limestone and the roadway floor is approximately 210 m.

The strata of the II₅₁ mining area compose a nearly monoclinic structure with a yield of 90°<16° ±. The exposed lithology of the roadway is mainly fine sandstone and mudstone. The DF8 normal fault is exposed at 3 m (lower) and 12 m (top) before G33; its occurrence is 295°<60°–69°, and its fault throw is 10 m. The fault fracture zone is 1 m with no water seepage through it (Fig. 2). The lithology in the middle and lower parts of the head section is characterized by several small faults in the fine sandstone, and there is no deep fault structure in the area.

In summary, there are material bases and hydrodynamic conditions for karst development in the coal field. At the same time, through a comprehensive analysis, we can exclude water-conducting faults as the cause of the abnormal water inrush along the II₅₁ track roadway. Therefore, through the abovementioned geological prediction and comprehensive analysis of the fractures and faults in the vicinity of the mining area, the inrush of water along the II₅₁ track roadway eliminates the possibility of water being conducted through a fault, and a collapse column is suspected to connect a deep water source with the II₅₁ track roadway.

**Water quality warning identification**

**Analysis of the inrush water value**

When the construction of the II₅₁ track roadway reached approximately 28 m before G33, water began to rush out of the upper shoulder anchor hole, and the initial water volume was approximately 1 m³/h. When the
excavation reached approximately 31.5 m in front of G33, the amount of water increased. The total water volume rushing out of the three anchors in the upper construction area was nearly 30 m$^3$/h, and the single-hole (aperture of 32 mm) maximum water output was 16 m$^3$/h. After performing the initial grouting to plug the water, the water volume was stable at 8 m$^3$/h, and there was no decrease in the inrush rate (Figure 3). According to the increase in the amount of effluent water and the stability of the water volume after plugging, the comprehensive analysis suggests a relatively stable supply from the water source.

**Analysis of the water temperature change**

On June 8, 2010, the water temperature was 33°C, after which the effluent water temperature gradually increased to 41°C on November 29, 2011 (Figure 4). According to the normal geothermal gradient of 3°C/hm at the Renlou Coal Mine, the normal ground temperature is 34–36°C; hence, there is an abnormality in the head-on effluent temperature along the II5$_1$ track roadway. Based on a comprehensive analysis of the abnormal increase in the water temperature, which is higher than the normal ground temperature, the water is preliminarily determined to be sourced from a deep, high-temperature water supply.

**Water quality warning**

On June 8, 2010, water emerged from the anchor hole of the upper shoulder at 28.5 m before G33 in the main roadway with a total hardness of 8.34°dH and no permanent hardness. The water began to show permanent hardness on June 10. By November 7, 2011, the water had a total hardness of 60.58°dH and a permanent hardness of 48.81°dH. From

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**Fig. 4** Curve of the change in the head-on water bursting point temperature along the II5$_1$ track roadway

**Fig. 5** Curve of the change in the water quality at the water inrush point along the II5$_1$ track roadway
June 8, 2010, to November 2011, the total hardness increased from 8.34 to 60.58°dH, and the permanent hardness increased from 0 to 48.81°dH. The full hardness and permanent hardness of the water displayed an increasing trend (Figure 5).

An analysis of the main hardness of the effluent water quality along the II51 track roadway conducted from scratch shows that the water hardness and permanent hardness were generally increasing. This implies that there may be a deep water supply with a high hardness (Ge et al. 2007). Comprehensively, according to the increase in the effluent water volume, the rise in the water temperature and the abnormal water hardness and water pressure along the II51 track roadway, it is concluded that the water outlet point may be connected to a deep water reservoir with a high temperature, a high hardness and a stable source of replenishment (Gui 2005). Combined with the abovementioned geological prediction results, hidden karst collapse columns are suspected at the point of water inrush along the II51 track roadway, seriously threatening the safety of further mine production.

**Integrated geophysical exploration**

A comprehensive surface downhole geophysical exploration method was designed in which the ground was probed by three-dimensional seismic and transient electromagnetic instruments. Five kinds of geophysical methods, namely, the transient electromagnetic method, high-resolution electric method, parallel electric method, seismic survey method and ground-penetrating radar method, were used to perform advance exploration of the subsurface along the II51 track roadway, including the front and the sides of the II51 track roadway (Liu et al. 2008). The exploration encircled the abnormal target area, providing the basis for drilling verification.

**Surface geophysical exploration**

Three-dimensional seismic exploration and transient electromagnetic detection were carried out at ground level along the main road, and the detection results revealed the following:

1. On the west side of the water inrush point, the reflected waves at the top interface of the Ordovician limestone are disorganized and broken, indicating a fissure development zone.
2. There is a suspected collapse column approximately 350 m ahead of the main roadway.
3. There are water-rich areas in different layers to the southeast of the main roadway, and there are abnormal superpositions. To the southwest, there are water-rich areas distributed at the 51 coal roof and the 72 coal floor.

**Subsurface geophysical exploration**

1. Transient electromagnetic method. There is an abundant water body at distances in

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Fig. 6 Surface three-dimensional seismic results

Fig. 7 Comprehensive results of the surface transient electromagnetic survey revealing water-rich anomalous areas
front of the main road ranging from 60 to 110 m, at horizontal distances ranging from 20 to 65 m, and below the floor of the roadway below 30 m.

2. Transient electromagnetic and parallel electrical methods. There is an abundant water body at distances in front of the main road ranging from 0 to 50 m and at horizontal distances ranging from 70 to 110 m, 65 to 110 m and 30 to 80 m. There are 2 water-rich areas.

3. Seismic surveying and high-density resistivity methods. Fissures are developed at 160 m behind the roadway and within 50–80 m from the roof of the roadway. Approximately 130–20 m in front of the roadway, fissures are developed, and the presence of water is strong with a hydraulic connection to a deep aquifer.

4. High-resolution method. There are 3 low-resistance anomalous areas in the range from 10 to 90 m in front of the G34 wire point.

5. Transient electromagnetic method. There is a substantial low-resistance anomaly.

6. Ground-penetrating radar method. There are 3 anomalous areas in the apical plate, 1 anomalous area in the bottom plate, and 1 anomalous area in front of the tunneling direction.

Comprehensive analysis of the above various geophysical exploration results and other data: the conductor of the II5_1 track roadway is a water-conducting collapse column, and preliminary analysis shows that this column is located 65–115 m behind the roadway at horizontal distances of 38–65 m.

**Drilling control**

On the basis of the preliminary analysis of the concealed collapse column in combination with the comprehensive geophysical exploration results, the key target areas for drilling verification were delineated. Drilling verification methods were employed to determine the spatial position and development of the collapse column. Ground drilling verification holes, downhole roadway drilling holes, ground-oriented exploration holes (Ge et al. 2007; Zhou et al. 1996), etc., were implemented. Drilling verification was performed in anomalous areas defined by the integrated geophysical exploration results to identify the spatial patterns and boundaries of the water inrush and the concealed water-conducting column.

1. Underground drilling exploration. A total of 19 boreholes in 3 groups were used for the up roadway, and 6 boreholes were drilled for the haulage roadway.

2. Surface-guided directional drilling. Four column exploration holes (the first hole revealed the collapse column) and 1 underground branch hole based on the abnormal area delineated by geophysical exploration were drilled. The four column exploration holes all exposed the collapse column.

Combined with the drilling verification described above, the collapse column was accurately mapped, and the spatial position, boundary and height of the collapse column were controlled. At the same time, the drilling verification also showed that the identification and comprehensive detection results of a

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Fig. 8 Comprehensive results of subsurface geophysical exploration
concealed collapse column are reliable and effective, providing an important reference for the spatial location and determination of concealed collapse columns.

**Conclusions**

1. Through an analysis of the development of a collapse column in the mining area and the water inrush conditions of past collapse columns in combination with the water inrush conditions, the hazard of the concealed collapse column was determined, thereby providing a theoretical basis for early treatment.

2. Aiming at the preventative exploration and treatment of the collapse column, geological prediction, water quality warning systems, geophysical exploration and drilling verification were conducted. Through systematic exploration, the spatial position and development pattern of the collapse column were accurately detected.

3. To investigate the collapse column through drilling, high-precision directional drilling technology and the porous joint exploration method were adopted to effectively and accurately control the boundary of the collapse column, thereby providing a basis for subsequent treatment.

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*Fig. 9 Drilling plan for the II5, up roadway*

*Fig. 10 Drilling plan for the II5, track roadway*

*Fig. 12 The collapse column boundary*
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Abstract

Resolving the potential groundwater yield zonation of sandstone aquifers is an important task for prevention of flood hazards from coal roof in coal mines. Based on the accessible geological exploration data, we present a method of predicting the potential groundwater yield zone in sandstone aquifers based on entropy weight method (EWM) and the technique for order performance by similarity to ideal solution (TOPSIS). The relationships between the factors and groundwater yield in sandstone aquifers were discussed and determined by EWM. And finally, a potential groundwater yield contour map was constructed by PGYI values using TOPSIS method. And the field data were used to test the accuracy of the prediction model.

Keywords: potential groundwater yield zonation, sandstone aquifers, coalmine, China

Introduction

Coal mining activities will inevitably damage or disturb the roof aquifers (Wu et al. 2017). It is more possible to cause serious water inrush in the rich water abundance zone during mining. So it is one of the most important tasks to explore the potential sandstone aquifers situated in the proximity of active mine sectors, which could contribute to the prevention of flood hazards in coal mines. Predicting the potential groundwater yield zonation of sandstone aquifers has been an important and challenging objective of the hydrogeological research focused on the prevention of the flood hazards (Yin et al. 2018). And several methods have also been used to estimate the groundwater potential zonation in sandstone aquifers, such as analytic hierarchy process (AHP) method (Wu et al. 2017), fuzzy analytic hierarchy process index (Han et al. 2012), and trapezoidal fuzzy number (TFN) method (Yin et al. 2018). These methods provide a powerful tool for estimating the groundwater potential zonation in sandstone aquifers, but the weights of the factors are obtained based on expert analysis in these methods which are of relatively subjective. In addition, it is relatively rare that hydrogeological studies exceed the geological exploration during mining activities especially in new coal mines. So it is important to accurately estimate the potential groundwater yield zone of the sandstone aquifers by using data acquired during geological exploration.

Accordingly, a method was proposed for predicting the groundwater potential zone in sandstone aquifers based on the entropy weight method (EWM) and the technique for order performance by similarity to ideal solution (TOPSIS) by using data collected from coal mine. EWM was applied to discuss and determine the relationship between the factors and the groundwater yield zone in sandstone aquifers, decreasing the subjectivity of traditional expert analysis. And finally, a potential groundwater yield contour map was constructed based on data of conditioning factors by using the TOPSIS method. The field data were used to test the accuracy of the prediction model.

Study area and data

Study area

The No. 1 mine field of Changcheng coalmine belongs to the Otog Front Banner, Erdos City, Inner Mongolia, China, which covers an area of 6.65 km$^2$, extending between 106°32′40″-106°37′04″E and 38°14′26″-38°17′16″N. It has a typical characteristic of desert steppe and the surface is almost covered by wind-deposited sands of quaternary with sparse vegetation. The mean annual rainfall of the area is about 270.4 mm, and the mean annual
temperature is 7.3°C. Generally, the area is a monocline with a south-north strike and dipping east, where faults and anticlines are well developed (Fig. 1).

The No. 1 mine field of Changcheng coalmine is a North China coalfield of Permo-Carboniferous age. The main coal-bearing strata are Taiyuan Formation (F) and Shanxi F of the Permo-Carboniferous system, including seven minable seams, i.e. No. 1, 31, 32, 5, 8, 91, 92. One of the mining activities is No. 3 coal seam, which is 0.63-5.72 m thick, extensive and of high quality. The lithology of the main aquifers overlying the No. 3 coal seam are mainly sand and gravel at the Quaternary and Neogene, and sandstone within the Permo-Carboniferous deposits. The main aquifers include clay beds in Quaternary and Neogene, and mudstone and siltstone in Permo-Carboniferous, which cut off the hydraulic connecting between groundwater in sandstone aquifers and surface water and rainfall. When mining the No. 3 coal seam, water flows into the work-face are from the roof sandstone in the Shanxi F. The study focuses on the sandstone occurring on the roof of the No. 3 coal seam, which is the fractured confined aquifer with a thickness and depth ranging between 0 m and 74.1 m, and 214.79 m and 1046.3 m below the surface, respectively. In this study, only two well pumping tests on the roof sandstone aquifers of the No. 3 coal seam were carried out in the No. S01 and No. XJ3, and the results showed that the aquifer had a low

<table>
<thead>
<tr>
<th>Hydrologic well</th>
<th>Water level (m)</th>
<th>Water yield per unit of drawdown (L/s.m)</th>
<th>Permeability coefficient (m/d)</th>
<th>Actual yield description</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. S01</td>
<td>+1192.5</td>
<td>0.0339</td>
<td>0.10477</td>
<td>low</td>
</tr>
<tr>
<td>No. XJ3</td>
<td>+1203.82</td>
<td>0.032277</td>
<td>0.297847</td>
<td>low</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Work-face</th>
<th>Actual yield(m³/h)</th>
<th>Work-face</th>
<th>Actual yield(m³/h)</th>
<th>Work-face</th>
<th>Actual yield(m³/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1301N</td>
<td>30</td>
<td>1302S</td>
<td>24</td>
<td>1304N</td>
<td>126</td>
</tr>
<tr>
<td>1301S</td>
<td>25</td>
<td>1303N1</td>
<td>160</td>
<td>1304S</td>
<td>33</td>
</tr>
<tr>
<td>1302N</td>
<td>126</td>
<td>1303N2</td>
<td>160</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
However, eight water inrushes occurred from the roof sandstone aquifers during mining the No. 3 coal seam, and the maximum water yield ranges from 24 to 160 m$^3$/h (Table 2).

The existence and abundance of groundwater in a given aquifer is controlled by many factors. Six main potential groundwater yield conditioning factors selected in this study are thickness of sandstone, lithological composition index, depth of sandstone, fault intensity index, density of fault intersections and endpoints, and fold axis length density, which were collected mainly from boreholes and 3D-seismic exploration throughout the mine field.

- **Thickness of sandstone (TS)**
  The thickness of sandstone is the basis of determining the potential groundwater yield, which was acquired from the geo-exploration data. The thicker the sandstone layer, the greater the yield in a aquifer when all the other factors are the same (Yin et al. 2018). The sandstone overlying the No. 3 coal seam in the study area varies from 0 m to 74.1 m, shown in Fig. 2 a.

- **Lithological composition index (LCI)**
  Different types of lithology affect groundwater storage. The layers overlying the No. 3 coal seam are sandstone of all grain sizes, siltstone, and mudstone. The coarser the sandstone, the greater is the water storage capacity (Zhang 2008). Due to brittle and susceptible to fracturing, sandstone thus increases porosity and permeability. The sandstone with bigger grain size would have greater influence on the groundwater storage capacity than the soft rock with small grain size. The lithological composition index is calculated by the following Equation:

\[
\text{LCI} = (a \times 1 + b \times 0.8 + c \times 0.6 + d \times 0.4 + e \times 0.2 + f \times 1) \times g 
\]

Where LCI is the lithological composition index; $a$, $b$, $c$, $d$, $e$, $f$ are the thickness of the conglomerate, coarse sandstone, medium-grained sandstone, fine-grained sandstone, siltstone, and limestone, respectively; $g$ is the structure coefficient, and 0.2, 0.4, 0.6, 0.8, and 1 are the equivalent coefficient for different rock types. when the sandstone thickness represents more than 80% of the total thickness, $g$ is 1; when the proportion is between 60% and 80%, $g$ is 0.8; when the proportion is between 40% and 60%, $g$ is 0.6; when the proportion is between 20% and 40%, $g$ is 0.4; when the proportion is less than 20%, $g$ is 0.2. Lithological composition index was shown in Fig. 2 b.

- **Depth of sandstone (DS)**
  With the increase of depth, the lithostatic pressure increases, which decreases secondary porosity slightly by possibly closing the fractures present. The depth of sandstone is one of the factors affecting the groundwater storage. The depth of sandstone was acquired from 3D-seismic exploration, geoexploration, and roadway and roadway constructions, ranging from 124.79 m to 1046.3 m below the ground surface, as shown in Fig. 2 c.

- **Fault intensity index (FII)**
  Faults have a great influence on groundwater potential and especially on groundwater storage and migration, which have usually been used as an indicative tool for locating potential groundwater yield zones (Dar et al. 2010; Sander et al. 1997). The fault intensity index is the sum of the fault throws multiplied by their corresponding fault length divided by the grid cell area:

\[
FII = \frac{\sum_{i} n_{i} h_{i}}{S} 
\]

Where $H$ is the fault throw and $L$ is the corresponding strike length; $S$ is the area of the grid cell; and $n$ is the number of faults in the grid cell. In general, FII is directly correlated with the groundwater potential, as shown in Fig. 2 d.

- **Density of fault intersections and endpoints (DFIE)**
  More fault intersections and endpoints will weaken the integrity of the rock and increase sandstone permeability and water storing capacity. The density of fault intersections and endpoints is expressed by Eq. (3) and shown in Fig. 2 e.

\[
\text{DFIE} = \frac{n}{S} 
\]

Where $n$ is the total number of fault intersections and endpoints of all faults in
each grid unit, and $S$ is the area of the grid unit.

- **Fold axis length density (FALD)**
  For folds, the fold axis is the main factor describing the fold distribution, along which fractures are well developed which are destructive to the integrity and continuity of the strata, thus increasing sandstone permeability and water storing capacity. The fold axis length density is expressed by Eq. (4) and shown in Fig. 2 (f).

$$FALD = \frac{\sum_{t} L_{t}}{S}$$  \hspace{1cm} (4)

where $FALD$ is the fold axis density; $L_{t}$ is the $t$th fold’s axis length; $S$ is the area of the grid unit; and $t = 1, 2, …, r$, where $r$ is the total number of folds in each grid unit.

**Methodology**

**Determination of the factors weights**

Entropy weight method is a measure of the degree of uncertainty represented by a discrete probability distribution, which can objectively weights factors as a feasible scientific method. Three steps were followed to calculate the weights of the six assessment factors (Wang et al. 2018):

(a) Constructing the decision matrix as follows (Wang et al. 2018):

$$R = \begin{pmatrix} x_{11} & \cdots & x_{1n} \\ \vdots & \ddots & \vdots \\ x_{m1} & \cdots & x_{mn} \end{pmatrix}$$  \hspace{1cm} (5)

where $x_{ij}$ is the value of the $i$th sample $j$th factor; $i = 1, 2, …, 76; j = 1, 2, …, 6$; and $m$ and $n$ are the total number of the samples and factors respectively.

**Figure 2** Assessment factors of the potential groundwater yield

(a) Thickness of sandstone aquifers  (b) Lithological composition index  (c) Depth of sandstone

(d) Fault intensity index  (e) Density of fault intersections and endpoints  (f) Fold axis length density
Calculating the entropy of the jth factor (Wu et al. 2015):

\[ E_j = - \frac{1}{\ln m} \sum_{i=1}^{m} \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \ln \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \]  

(6)

(c) Establishing the entropy weight of the jth factor (Huang et al. 2017):

\[ \omega_j = \frac{1-E_j}{\sum_{j=1}^{n}(1-E_j)} \]  

(7)

Following the above steps, a 76×6 decision matrix was established, and the entropy E and entropy weights of the factors were calculated as shown in Table 3. The weights of TS, LCI, DS, FII, DFIE, and FALD were 0.043, 0.059, 0.242, 0.192, 0.220, and 0.244, respectively.

The TOPSIS method is a multiple-attribute decision making techniques applied to a wide variety of decision problems (Ataei et al. 2012; Baykasoğlu and Gölcük 2017; Sepehr and Zucca 2012). In this paper, the TOPSIS method was used to determine the final ranking of the potential groundwater yield, and three steps were followed.

1. Constructing the weighted standardized matrix based on the original data and the weights calculated by EWM by using the following Eq. (7):

\[ V = (v_{pi})_{nx} = \begin{bmatrix} W_{c_{i1}} & W_{c_{i2}} & \cdots & W_{c_{ina}} \\ W_{c_{i2}} & W_{c_{i2}} & \cdots & W_{c_{ina}} \\ \vdots & \vdots & \ddots & \vdots \\ W_{c_{ina}} & W_{c_{i2}} & \cdots & W_{c_{ina}} \end{bmatrix} \]  

(7)

Where V is the weighted standardized matrix; \( v_{pi} \) is the weighted standardized value of the pth sample’s ith factor; \( W_{c_{ia}} \) is the weight of the ith factor derived by EWM, \( i \in [1, n] \); \( c_{ia} \) is the standardized value of the pth sample’s ith factor, which is normalized by the following Equation:

\[ c_{pi} = b_{pi}/\sqrt{\sum_{p=1}^{n} b_{pi}^2} \]

\[ i = 1, 2, \cdots, n \]  

where \( b_{pi} \) is the observed value of the pth sample’s ith factor.

2. Determining the ideal solutions.

During determination of the ideal solutions, the potential negative and positive related factors of the potential groundwater yield had to be considered separately. If \( J_1 \) and \( J_2 \) indicate the set of negative factors and positive factors, respectively, the negative ideal solution and the positive ideal solution are determined by Equations 8 and 9:

\[ V^- = \{ (\max_{1 \leq p \leq n} v_{pi}) | i \in J_1 \}, \{ (\min_{1 \leq p \leq n} v_{pi}) | i \in J_2 \} \]  

(8)

\[ V^+ = \{ (\min_{1 \leq p \leq n} v_{pi}) | i \in J_1 \}, \{ (\max_{1 \leq p \leq n} v_{pi}) | i \in J_2 \} \]  

(9)

Where \( V^- \) and \( V^+ \) are the negative ideal solution and positive ideal solution, respectively.

3. Determining the final ranking of the potential groundwater yield for each sample, which is expressed by a potential groundwater yield index (PGYI) calculated using Equation 10:

\[ \text{PGYI} = \frac{D_p^-}{D_p^- + D_p^+}, \quad (p = 1, 2, \cdots, l) \]  

(10)

Where \( D_p^- \) and \( D_p^+ \) indicate the distance between the pth sample and the negative ideal solution, and the positive ideal solution respectively, which were calculated by Equations 11 and 12, respectively:

\[ D_p^- = \sqrt{\sum_{i=1}^{n} (v_{pi} - v_i^-)^2} \]  

(11)

\[ D_p^+ = \sqrt{\sum_{i=1}^{n} (v_{pi} - v_i^+)^2} \]  

(12)

The larger the PGYI value, the greater the potential groundwater yield is. The ranking of the potential groundwater yield can be determined by arranging the PGYI value in descending order.

**Results**

The PGYI value was calculated for each 500 m × 500 m grid unit, and all grid data was then processed by using Surfer and MapGis software and interpolated with the Kriging function interpolation technique to create the PGYI contour model map as shown in Fig. 3. According to the contour map, the potential groundwater yield which is expressed by PGYI value ranges in the study area from 0.032 to

<table>
<thead>
<tr>
<th>Factor</th>
<th>TS</th>
<th>LCI</th>
<th>DS</th>
<th>FII</th>
<th>DFIE</th>
<th>FALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>entropy E</td>
<td>0.984</td>
<td>0.978</td>
<td>0.911</td>
<td>0.930</td>
<td>0.920</td>
<td>0.911</td>
</tr>
<tr>
<td>entropy weight ( \omega )</td>
<td>0.043</td>
<td>0.059</td>
<td>0.242</td>
<td>0.192</td>
<td>0.220</td>
<td>0.244</td>
</tr>
</tbody>
</table>

Table 3: Values of entropy E and entropy weights of the assessment factors of the potential groundwater yield

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
0.497. Thus, the area was divided into three water abundance zones: low (<0.07), medium (0.07-0.12), and high (≥0.12). The prediction result shows that the details of the distribution of the potential groundwater yield: the areas with the highest groundwater potential are mainly located in the central and northwest parts of the mine field whereas the low and medium potential areas are mainly located in the southwest and northeast parts of the mine field. The results of the study can be applied to guiding dewatering the sandstone aquifers during the mining of No. 3 coal seam using boreholes, which also can be used to provide water for mining activities for other mines with sandstone aquifers.

Conclusions

To prevent coal mine flooding from coal seam floor, it is essential to determine the distribution of groundwater in sandstone aquifers. In this study, a PGYI model was successfully applied to predict the potential groundwater yield zonation in the sandstone aquifers overlying No. 3 coal seam in the No. 1 mine field of Changcheng coalmine, China. The PGYI model integrated six factors consisting of thickness of sandstone, lithological composition index, depth of sandstone, fault intensity index, density of fault intersections and endpoints, and fold axis length density. The weights of the six factors were determined by EWM, which were 0.043, 0.059, 0.242, 0.192, 0.220, and 0.244, respectively. And potential groundwater yield contour map was built by the PGYI values using the Kriging function interpolation technique. The area was divided into three water abundance zones: low (<0.07), medium (0.07-0.12), and high (≥0.12).

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References


Influence of Karst Collapse Column on Coal Mine Safety Mining - A Case Study of the Yangjian Mine in Shuozhou Mining Area, Shanxi Province, China

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Abstract
Karst collapse columns are a special geological body, commonly found in the Carboniferous-Permian coalfields in northern China and posing a major hazard to mine safety. Mining activity near the collapse columns, especially ones that conduct water, can cause serious water inrush accidents, causing heavy casualties and property losses. To assess the influence of karst collapse columns on coal mining safety, the case of the Yangjian Coalmine in Shuozhou, Northern Shanxi Province, China is investigated. Five collapse columns were detected in Panel 90102 during tunnel excavation and advanced exploration. The extent of karst development, the water-bearing conditions and the conductive state of the columns, as well as the composition and physical properties of the rocks, were explored. Then the hydrogeological characteristics of the five collapse columns were summarized. Based on analysis of the water pressure of the Ordovician limestone aquifer and the thickness of the aquiclude, the influence of each collapse column on the safe mining of Panel 90102 was evaluated. To mitigate the water inrush threat from the collapse columns, a drilling and grouting reinforcement treatment for two water-conducting columns were implemented to block the Ordovician aquifer water from flowing onto the mine floor. This approach improved the safety of the mining operation in Panel 90102.

Keywords: karst collapse column; coal mining; floor water inrush; comprehensive prospecting; grouting

Introduction
Coal is a commonly used energy source in China and the country's coal deposits are extensively mined. Mining operation safety is an important issue, one of the hazards being water inrush in the coal panel floor. In the coal mines of northern China, the Ordovician limestone aquifer is the main aquifer affecting the coal seams; this aquifer has a high artesian head and the water flow is controlled by faults and karst collapse columns. Mining activities can transform the aquifer into an underground watercourse for the water-bearing rock of the base plate, endangering mine safety. (Wu et al. 2016) Statistical data shows that karst collapse columns exist in 45 coal mines in more than 20 large coal fields in China. The disaster in the Fangezhuang Coalmine in Kailuan is an example of the dangers of karst collapse columns. Due to the exposure of the collapse column, the most serious water inrush accident in the history of the world's coalmining occurred in panel 2171 of the mine in 1984. The maximum water inflow into the mine was 123,180 m$^3$/h, and three nearby coalmines were flooded. This resulted in direct economic losses of more than 1 billion yuan, and the loss of coal production of nearly 8.5 Mt. (Zhong. 2001) Another water inrush accident occurred on March 1, 2010 in the Luotuoshan coalmine, located in Wuhai, Neimenggu Province. This was a result of the exposure of a hidden subsided column during the excavation of coal roadway #16. Seventy minutes after the water inrush, the volume of the submerged roadway was 67,000 m$^3$, and the peak rate of the water burst was 60,036 m$^3$/h, which caused 31 deaths. (Zhang. 2015)

Karst collapse columns are commonly
found in the northern China coalfield and pose a serious threat to mining activity. Therefore, since the 1960s, hydrogeologists in China have been studying the causes, form, distribution and detection means of karst columns. Detection and prediction of collapse columns involve mainly two aspects: (Cao et al. 2012; Fengtian et al. 2016; Jiang et al. 2015) (1) geophysical exploration, for example, the use of radio-wave detection, surveying potential collapse areas using the direct-current method and transient electromagnetic method. Hydrogeological anomalies can be examined using advanced geophysical methods after a preliminary exploration. These methods can be combined with on-site drilling to verify the geological anomalies, enabling accurate control of the mine area surrounding collapse column. (2) Basic research is carried out to investigate the development of collapse columns, their mechanism of formation, the water inrush and the structure of the rock and the surrounding rock. To study the water inrush affected by the karst collapse column, laboratory simulation tests and numerical simulations are performed to explain the structural characteristics and the development of the collapse column. Based on the geophysical data and study results, damage control methods such as injected grouting transformation and leaving water pillars (Liang, 2015) have been used to prevent and mitigate karst collapse column water damage.

This paper focuses on the influence of karst collapse columns on the mining safety in the Yangjian coalmine, which is located in the Shuozhou mining area of northern Shanxi province. We use various exploration methods to identify the collapse columns, evaluate the risk of water inrush, and treat the rock surrounding the columns to prevent water inrush and tunnel collapse.

Hydrogeological conditions of the study area

The Yangjian coalmine is located in Shuocheng District, Shuozhou City, north of Shanxi Province, China (Fig.1). The Danshui ditch fault is the main geological feature in the region, while secondary faults are also common. Generally, the geological and hydrogeological conditions in the area are complex, leading to the development of collapse columns. The coal-bearing strata in the area are Carboniferous Permian strata, deposited directly above the Middle Ordovician. The Middle Ordovician consists of thick limestone, located more than 50 m below the upper main mining seam. The location of the fault and high pressure in the aquifer are the main threat to the mining operations. The stratigraphic column (Fig.2)
shows that the main water-filled aquifer is the Ordovician limestone karst aquifer which is more than 800 m thick. The water abundance in the aquifer is not uniform, an aquifer pumping test showed units-inflow range of 0.12–93.36 L/s·m, indicating an extremely uneven flow. The Ordovician limestone water pressure in the mine floor reached a maximum value of 2.265 MPa, posing a serious threat to mine safety.

Materials and Methods

Considering the geological conditions in the Yangjian coalmine, a thorough investigation of the effect of the mining operations on geological anomalies, such as potential collapse columns, should be carried out. In this study, we evaluate the risk of water inrush in the Yangjian coalmine to facilitate disaster prevention and control and ensure safe mining operations.

Panel exploration methods

In recent years, geophysical techniques have become more common in studies of collapse columns. In this paper, the electromagnetic wave perspective method (Dong et al. 2003; Jiao et al. 2014) is used for surveying the study area. The principle is the use of electromagnetic waves to detect anomalies in the underground rock formation. Rocks will exhibit different electrical properties (resistivity and dielectric constant) depending on their ore content. The level of absorbed electromagnetic energy will change, with low-resistance rock layers having higher absorbance of electromagnetic waves than high-resistance rocks. When the wave encounters the interface of a fault structure, the electromagnetic wave will be reflected or refracted at the interface, resulting in energy loss. In mine geology, if the electromagnetic waves emitted by the transmitting source encounter a fault, collapse column, water-bearing fracture, coal seam thinning area or any other structure as they propagate through the coal seam, the wave energy is absorbed or completely shielded. The monitoring receiver will receive a weak signal or no signal, which is interpreted as an anomaly, indicating the possible location and range of an abnormal body.

Exploration drilling is the most direct method of mine water-hazard exploration; it can also reveal water-rich anomalies. Core data analysis can determine the composition and physical properties of the strata, including water conductivity, thus leading to early detection of a developing collapse column and enabling a comprehensive risk assessment of the column. At the same time, core drilling can reveal other hydrogeological conditions and water sources, providing useful information for mitigating water-triggered threats to the safety of the coal mining area (Li et al. 2011b).

Risk assessment of floor water inrush

The risk assessment of floor water inrush is a quantitative assessment of the risk of water outburst in each point (or each panel) using a mathematical model that reflects the influencing factors and mechanisms of action of each water inrush case in a specific mining area. (Zhu et al. 2013) In China, combined with existing experience in groundwater hazard control technology, the most commonly used and applicable method for assessing the risk of floor water inrush is to calculate the water-inrush coefficient.

\[
T = \frac{P}{M}
\]

where T is the water-inrush coefficient for aquifers below the coal layer floor, in MPa/m; P is the aquifer pressure, in MPa; and M is the floor aquiclude thickness, in m.

The Chinese Mining Bureau of Science and Technology provided guidelines for critical values based on data from coal mines in northern China. Based on Table 1, the critical water-inrush coefficient can be determined as

<table>
<thead>
<tr>
<th>The integrity of the floor</th>
<th>Safety</th>
<th>Danger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete backplane (normal block)</td>
<td>≤0.1 MPa/m</td>
<td>&gt;0.1 MPa/m</td>
</tr>
<tr>
<td>Incomplete floor belt (construction block)</td>
<td>≤0.06 MPa/m</td>
<td>&gt;0.06 MPa/m</td>
</tr>
</tbody>
</table>
0.1 MPa/m in a normal geological block and 0.06 MPa/m in a tectonic failure block.

The floor water inrush is usually the result of the combined effect of many influencing factors, resulting in complex geological conditions which vary between the different mining areas. In addition to determining the water-inrush coefficient, the assessment of water inrush risk involves considerations of the tectonic setting of the mine, collapse columns and other structures that may affect the water inrush.

**Controlling floor water inrush**

In this paper, the karst collapse column is treated by grouting technology. (Li et al. 2011a; Oda M. 1986; Yang et al. 2002; Zhang et al. 2012) The basic principle of the grouting transformation is that concrete slurry is injected into the water-occupied layer, The basic principle of grouting transformation is that the slurry is injected into the fault fissures or channels in the rock under high pressure, so that they become the whole of water blocking, in order to improve the geological conditions and the ability of anti-destructive of the aquifers. This method is widely used in China to control groundwater inflow into mines. The pulp used for grouting can be divided into ground pulp and underground slurry, both types of pulp being very efficient grouting slurries.

**Results and discussion**

**Results of collapse column survey**

For the electromagnetic wave investigation, the fixed-point method was used in this study. With the wave transmitter fixed at a certain point of the roadway, the receivers record the magnetic field intensity point by point within a certain range along another roadway. To determine the position and distribution range of the anomaly area, the position of the transmitter and receiver were swapped and the process repeated. Thirty-eight transmission points were set along Panel 90102 at 50 m intervals, with the receiving points being 10 m apart. Each transmission point is recorded by eleven receiving points, totaling 418 data points.

The tomographic image (Figure 3) shows a higher intensity in the soft layer. Combined with hydrological and ground pressure data, two abnormal areas were identified, which included five collapse columns (XL₁–XL₅), see Figure 4.

According to the geophysical exploration results, 53 drilling sites were set in the transport roadway of Panel 9012 to verify the geological conditions surrounding the five collapse columns identified in the electromagnetic survey. The engineering parameters are shown in Table 2. Of the 53 boreholes, 43 revealed abnormalities.
in the rock and coal seams, indicating the development of the collapse columns. However, the collapse columns were found to consist of dense material due to reduced water flow, indicating the low water content and weak conductivity of the collapse column.

The core data showed five collapse columns (Fig. 5) comprising mainly sandstone, mudstone and coal rock debris. No water flow was observed during more than three months of monitoring. During the excavation of the tunnel along the transport roadway of Panel 90102, XL₁ was exposed and water gushed through the floor of the tunnel. The exploration results are shown in Table 3.

**Safety evaluation of floor water inrush**

Panel 90102 has a bottom water barrier thickness of 50 m and bottom plate pressure of 1.3 MPa; considering only the water pressure and the thickness of the aquifer, the water inrush value is about 0.026 MPa/m, which is less than 0.06 MPa/m; therefore, the panel is considered safe. However, the theory of water-inrush coefficient method does not take into account the effects of the geological formations, groundwater conditions and other environmental factors. For example, if the Ordovician limestone aquifer has a high water content, even if the water-inrush coefficient is less than 0.06 MPa/m, water inrush events may occur in this area. Five collapse columns were exposed in Panel 90102. Geophysical prospecting data, drilling results and mining data from the top of the face #4 of the coal mine found five subsidence columns consisting of dense rock of low water content. However, collapse columns XL₁, XL₄ and XL₅ are connected to the aquifer through the floor of the working face, which makes the panel prone to water inrush. While the threat of the XL₅ collapse column has been ruled out, it is necessary to control the XL₁ and XL₄ collapse columns.

**Treatment Scheme of Karst Collapse Column**

Considering the special structure of Panel 90102, near water-rich anomalies and other characteristics, floor grouting reinforcement can be used to enhance the mechanical strength of the floor and increase the thickness

<table>
<thead>
<tr>
<th>Table 2 Drilling conditions in Panel 90102</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drilling location (track alignment)</td>
</tr>
<tr>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>Number of boreholes (unit)</td>
</tr>
<tr>
<td>Amount of work (m)</td>
</tr>
</tbody>
</table>

**Fig 5. Boreholes in Panel 90102**

<table>
<thead>
<tr>
<th>Table 3 Condition of Collapse column in Panel 90102</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name of subsided column</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>XL₁</td>
</tr>
<tr>
<td>XL₂</td>
</tr>
<tr>
<td>XL₃</td>
</tr>
<tr>
<td>XL₄</td>
</tr>
<tr>
<td>XL₅</td>
</tr>
</tbody>
</table>
After the grouting operation, the scope of the collapse column in Panel 90102 is calculated (green line, Figure 6). The boundary contour of XL\(_1\) is reduced by 16 m along the longitudinal axis. The water are not effluent from the drilling and the void has been filled in XL\(_1\) collapse column. In addition, several water inrush points disappear in Panel 90102, which indicates that the effect of XL\(_1\) collapse column treatment engineering is good.

**Conclusions**

1. Karst collapse columns pose a serious safety threat on the coal fields of northern China. Hence, it is very important to examine the hydrogeological characteristics of karst collapse columns and implement effective means of controlling mine safety.

2. In this paper, the range, composition and physical properties, including water content and water conductivity, of karst collapse columns in northern China coal mine were identified by geophysical and drilling methods, and the water inrush safety was evaluated.

3. Based on this evaluation, the grouting reinforcement method was used to control the karst collapse column, which can effectively control water inrush and water damage in the floor.

**Acknowledgements**

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**References**


MINE WATER GEOCHEMISTRY
**Heat and Mineral Mining by adding CO$_2$ to Deep Groundwater**

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**Abstract**

CO$_2$ can be added to groundwater as an innovative approach to extract valuable elements where in most cases the dissolved mineral concentration would be too low to be considered for economic recovery. Water-rock-CO$_2$-interactions were investigated under simulated reservoir conditions using carbonate rock from the molasse basin and carbonatite rock from Delitzsch, Germany. This approach can be also joined with geothermal energy production, which – in addition to enhanced in-situ leaching of minerals – would improve permeability in low permeable formations and maintain fluid pathways. Co-recovery of minerals with geothermal energy production can improve the overall economic attractiveness of geothermal energy.

**Keywords:** Geothermal, carbon utilization, metal recovery, permeability, REE, solution mining

**Introduction**

In conventional mining, large quantities of rock must be mined and deposited in the form of heaps and dumps. Then, the ore is milled and the metal is extracted from the rock. In case of low grade ores in particular, large amounts of tailings are produced. These tailings are an environmental hazard as well as creating massive pile-ups. Another form of mining is in situ leaching. Currently, chemicals such as sulfuric acid or lye (sodium hydroxide or ammonia) are injected into the ground which brings a great risk potential for the groundwater and the environment. As a consequence, there are high remediation costs for in situ leaching mining. Minimizing the interference of mining activities with the integrity of nature is a necessity which is still very far from ideal.

Two vital aspects in geothermal energy production, especially in deep carbonate aquifers such as the Southern German Molasse Basin (SGMB), are adequate permeability and favorable fluid pathways. But very often both criteria cannot be assumed as given. Besides, due to scaling and precipitation, the worsening of permeability in different locations poses a great challenge to maintain constant production. Therefore, preserving and improving these pathways during long-term operation is a key task in deep geothermal energy production. With these in mind, this research aims to implement using carbon dioxide as an innovative method in the geothermal, mining and ore processing technology portfolio.

Deep groundwater has lengthy interactions with the layers of the earth’s crust, resulting in the dissolution of minerals and metals from the aquifer rocks into the geothermal hot water until becoming close to or exactly at equilibrium with respect to certain minerals. These aqueous solutions, especially geothermal waters, can be processed to recover the dissolved valuable elements (e.g. Maimoni 1982, Bakane 2013, Harrison 2014). But often, the concentration of these dissolved elements is too low to be considered for economical extraction. Merkel et al. (2012) suggested a patented method for leaching valuable elements from ore bodies that are not economically feasible using conventional techniques. When CO$_2$ is added to water, the following steps occur:

\[
\begin{align*}
\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(aq) \\
\text{CO}_2(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{H}_2\text{CO}_3(aq) \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

According to the mechanistic rate law of Chou et al. (1989) for various carbonates, the elementary steps during the dissolution reactions of carbonates are expressed by:

---

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MeCO₃ + H⁺ ⇌ Me²⁺ + HCO₃⁻,
MeCO₃ + H₂CO₃ ⇌ Me²⁺ + HCO₃⁻,
MeCO₃ ⇌ Me²⁺ + 2HCO₃⁻,

where Me represents metal ion e.g. Ca²⁺ or Mg²⁺.

At pH above 3.5, carbonate dissolution becomes interface-controlled as opposed to diffusion-dominated (Buhmann and Dreybrodt 1985) as well as being dependent on the partial pressure of CO₂. It is worth mentioning that this dissolution happens kinetically which is mainly reliant on: i) specific surface area of calcite, ii) dislodgement from equilibrium, iii) the purity of the rock, and iv) presence of inhibitors.

When used in geothermal energy production, by increasing the partial pressure of CO₂ in water, the water becomes undersaturated in minerals such as carbonate. This process does not only inhibit unwanted precipitation, but also triggers favorable dissolution and an enrichment of dissolved elements. This dissolution will continue until the formation water is once again in equilibrium with the aquifer rock. Accordingly, even a small increase in porosity has a substantial effect on enhancement of permeability.

**Methods**

Three experiments were performed using three types of high pressure-temperature (H-P-T) autoclaves, which are named Autoclave 1, 2, and 3 (Table 1 and Table 2) and three rock specimens. Two of the sample rocks were from Kirchweidach, a geothermal field designed for both electricity production and thermal use located in the Malm aquifer system of the Southern German Molasse basin. Kirchweidach is one of the most important reservoirs for geothermal energy production in the south of Germany due to its extensive fault system, water-bearing nature at depth coupled with high permeability from partially karstified limestones and fractured dolomite at favorable temperatures (Seithel et al. 2015). This progressive increment in temperature in the aquifer system, especially towards the Alps, makes areas on this part of the Malm strata potential sites for electricity generation (Ganz et al. 2013). Chemical analysis of the geothermal water from the production borehole in Kirchweidach was done (Table 3) which showed that it has a total mineral concentration of about 696 mg/L.

X-ray powder diffraction (XRD) based on qualitative and semi-quantitative analysis with the Rietveld method was performed on all the rock samples to obtain mineral compositions. GT1 rock cuttings contained 68 wt % dolomite, 26 wt % calcite and 4 wt % ankerite, while GT2 rock cuttings were composed of 75 wt % dolomite, 14 wt % calcite, 4 wt % ankerite, and 2 wt% quartz. Microscopic examination of samples was carried out before and after the experiments using scanning electron microscope (SEM) for possible changes to the surface of the specimens.

The carbonatite specimen used in this study was sampled before 1989 between 200 m to 550 m below the earth’s surface from Storkwitz, Delitzsch in Saxony, which is one of the two most important carbonatite complexes in Germany (Goodenough et al. 2016) and assumed to be the biggest REE reservoir in Europe. According to these authors, carbonatite dykes found in Delitzsch go as far as 1100 m below the surface and rock samples analyzed by earlier investigators have identified some important rare earth minerals such as pyrochlore, bastnäsite, and apatite. The specimen is described as an intrusive breccia which, fits into the geological description of earlier investigators. XRD analyses revealed that the sample consists of 34 wt. % ankerite [Ca(Fe, Mg, Mn)(CO₃)₂], 17 wt. % dolomite (CaMg(CO₃)₂), 14 wt. % calcite (CaCO₃), 13 wt. % anorthite (CaAl₂Si₂O₆), 11 wt. % germanium-phlogopite [K,Mg,(AlSi₄O₁₀)F₆], 6 wt. % fluorapatite [Ca₅(PO₄)₃F], and 5 wt. % albite (NaAlSi₃O₈). Also, SEM-EDS analysis showed that the rock contained elements such as Na, Mg, Al, Si, S, Ca, Mn, Fe, Sr, F, P, K, La, Ce, Nb, Sn, and Ti. The sample was crushed and the particles with 1 to 2 mm diameter were used.

To determine the change of dissolved elements concentrations over time, sampling was done at predetermined periods during the experiments. For each sampling run, the first 3 mL taken were discarded to account for the water, which was left inside the autoclave tubing from the previous run. Then, the sampled solution was acidified with supra-pure nitric acid so that no precipitation would
Table 1 Specifications of the 3 autoclaves used in the 3 experiments.

<table>
<thead>
<tr>
<th>Autoclave</th>
<th>Volume (mL)</th>
<th>Type and location</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>Rocking with flexible titanium grade 2 cell, water as pressure medium, gfz Potsdam</td>
<td>40</td>
<td>105</td>
</tr>
<tr>
<td>2</td>
<td>1500</td>
<td>Top opening, Static, CO2 as pressure medium, TU Bergakademie Freiberg</td>
<td>40</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>170</td>
<td>Top opening, Static, CO2 as pressure medium, TU Bergakademie Freiberg</td>
<td>15</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2 Details of experiments GE1, GE2 and GE3

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>Duration</th>
<th>Type</th>
<th>Autoclave</th>
<th>W.R ratio</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>GE1</td>
<td>GT1</td>
<td>21 days</td>
<td>kinetic</td>
<td>1</td>
<td>20:1</td>
<td>ICP-MS, SEM-EDS</td>
</tr>
<tr>
<td>GE2</td>
<td>GT2a</td>
<td>14 days</td>
<td>kinetic</td>
<td>2</td>
<td>13:1</td>
<td>ICP-MS, SEM-EDS</td>
</tr>
<tr>
<td>GE3</td>
<td>Carbonatite</td>
<td>28 days</td>
<td>kinetic</td>
<td>3</td>
<td>21:1</td>
<td>ICP-MS, SEM-EDS</td>
</tr>
</tbody>
</table>

Table 3 Chemical composition of groundwater from Kirchweidach, Germany (±5% relative error).

<table>
<thead>
<tr>
<th></th>
<th>Conc. (mg/L)</th>
<th>Conc. (mg/L)</th>
<th>Conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>109.08</td>
<td>Br</td>
<td>0.397</td>
</tr>
<tr>
<td>K</td>
<td>18.82</td>
<td>F</td>
<td>3.802</td>
</tr>
<tr>
<td>Ca</td>
<td>30.49</td>
<td>I</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>4.19</td>
<td>Li</td>
<td>0.1242</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.498</td>
<td>PO₄⁻</td>
<td>0.0899</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>276.0</td>
<td>Se</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>Cl</td>
<td>82.52</td>
<td>Si</td>
<td>58.80</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>7.7</td>
<td>Sr</td>
<td>0.8447</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>&lt; 0.2</td>
<td>Si</td>
<td>58.80</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>&lt; 0.01</td>
<td>Sr</td>
<td>0.8447</td>
</tr>
<tr>
<td>Ba</td>
<td>0.1649</td>
<td>Mo</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B</td>
<td>0.6775</td>
<td>Ce</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>

Figure 1 Autoclave systems used in the experiments. Top pictures show autoclave 1, Bottom left and center show autoclave 2 and bottom right shows autoclave 3.
occur in the sampling vials as a result of changes in boundary conditions or degassing. The samples were analyzed by ICP-MS to obtain cation concentrations. Along with measuring the pH and electrical conductivity (EC) during each sampling run, the exact time of sampling was documented on a permanent basis. Due to page restrictions, only element concentrations for the last sampling run are given in this paper and special kinetic aspects accompanied by results from further experiments will be presented in a future publication.

Results and discussion

Electrical conductivity increased rapidly in the first hours for all 3 experiments (Figure 2). In the GE1 experiment, EC decreased to 1500 μS/cm during the second and third day of the experiments and then rose steadily afterwards. Similar to EC, the pH also rose very rapidly to values around pH 6, which then continued in the further courses to about 6.5 (Figure 2). A methodological problem that exists in such experiments is the measurement of pH, since there are no sensors which provide reliable in-situ values under such P-T conditions. Measurements of the pH after sampling are always associated with some spontaneous degassing and could differ from in-situ pH.

When taken out of the reactor, some of the particles showed a distinct change in color to brick red. Some fine particles and grains were also present, which were smaller than the initial sample particle size. These fine fragments are assumed to be liberated due to the dissolution of the cementing minerals around them. SEM comparison of particles before and after the experiments showed noticeable changes to the surface, widening of pores and rounding of edges, which in most cases indicate dissolution and weathering of the minerals (Figure 3). Secondary precipitation can also be seen on some of the mineral surfaces, which occurred during the experiments or after the pressure inside the autoclave was relieved.

In all three experiments, elements such as calcium, magnesium, zinc, potassium, sodium, manganese, aluminum, and barium reached (quasi)-equilibrium before the end of the experiments. On the other hand, elements such as sulfur, nickel, silicon, strontium, molybdenum, uranium, and lithium did not reach equilibrium. Extracted mass of elements including REE in experiments GE1, GE2 and GE3 are presented as mg/kg and µg/kg in order to quantify how much of each element from the rock sample was released into the solution (Table 4). Compared to the initial aquifer water, a noteworthy enrichment of dissolved elements had occurred.

With this method, element separation takes place in situ and thus transport of process volumes and waste is minimized. Several technologies to extract minerals from geothermal waters have been developed over the years (e.g. Brown 1986, Gallup and Ririe 1994, Bourcier 2009). Nevertheless, other methods of element extraction including methods for rare earth elements (REE), e.g. molecular recognition technology, solvent extraction, adsorption, ion exchange, magnetic segregation, microbe technology could also be employed in the geothermal plant or as standalone to process the dissolved elements in the groundwater that has been enriched and brought to the surface. Assuming that a circulation of 10 L/s would be achieved.

Figure 2 Measured EC (left) and pH (right) during the experiments

Figure 2 Measured EC (left) and pH (right) during the experiments
and the solution contains 5 valuable metals at concentrations of 1 mg/L, this sums up to 50 g/m³ and thus 4.32 kg per day. Estimating an average price of 3000 to 8000 € per kg this would result in 13,000 € to 35,000 € value add per day (and 4.7 to 12.6 million € per year, respectively). Therefore, it is rather likely to produce well beyond the costs of conventional mining plus aboveground processing because costs for labor work are substantially lower.

The continuous leaching of minerals will improve permeability and increase the production performance without having to use conventional hazardous and costly reservoir stimulations (such as acidizing, mechanical precipitation removal, pressure increase and hydraulic fracturing). Co-recovery of minerals with geothermal energy production can improve the overall economic attractiveness of geothermal energy production.

Interestingly, limited geological utilization and storage of CO₂ is another positive by-effect of the approach used in this research. Geological CO₂ sequestration refers to the storage of CO₂ underground in depleted oil and gas reservoirs, saline formations, or deep, un-mineable coal beds (carbon capture and

Table 4 Extracted mass of elements in GE1, GE2 and GE3 [mg/kg and µg/kg] (±5% relative error).

<table>
<thead>
<tr>
<th>Unit</th>
<th>GE1</th>
<th>GE2</th>
<th>GE3</th>
<th>Unit</th>
<th>GE1</th>
<th>GE2</th>
<th>GE3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>mg/kg</td>
<td>36</td>
<td>14</td>
<td>351</td>
<td>Mn</td>
<td>mg/kg</td>
<td>10.97</td>
</tr>
<tr>
<td>K</td>
<td>mg/kg</td>
<td>138.6</td>
<td>17.5</td>
<td>1323</td>
<td>As</td>
<td>mg/kg</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg</td>
<td>11934</td>
<td>7703</td>
<td>11553</td>
<td>Pb</td>
<td>mg/kg</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg</td>
<td>477.7</td>
<td>1008.2</td>
<td>979.8</td>
<td>U</td>
<td>mg/kg</td>
<td>0.01</td>
</tr>
<tr>
<td>Rb</td>
<td>mg/kg</td>
<td>0.61</td>
<td>0.088</td>
<td>3.51</td>
<td>La</td>
<td>mg/kg</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Mo</td>
<td>mg/kg</td>
<td>0.10</td>
<td>0.006</td>
<td>15.79</td>
<td>Ce</td>
<td>mg/kg</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Ba</td>
<td>mg/kg</td>
<td>54.39</td>
<td>1.38</td>
<td>9.27</td>
<td>Pr</td>
<td>µg/kg</td>
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</tr>
<tr>
<td>B</td>
<td>mg/kg</td>
<td>1.34</td>
<td>0.277</td>
<td>0.7</td>
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<tr>
<td>Zn</td>
<td>mg/kg</td>
<td>6.55</td>
<td>0.524</td>
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<td>Sm</td>
<td>µg/kg</td>
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</tr>
<tr>
<td>Br</td>
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<td>0.8</td>
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<td>0.7</td>
<td>Eu</td>
<td>µg/kg</td>
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<tr>
<td>Ni</td>
<td>mg/kg</td>
<td>2.7</td>
<td>0.627</td>
<td>183.69</td>
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<td>µg/kg</td>
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</tr>
<tr>
<td>Li</td>
<td>mg/kg</td>
<td>0.23</td>
<td>0.034</td>
<td>0.44</td>
<td>Tb</td>
<td>µg/kg</td>
<td>&lt; 1</td>
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<tr>
<td>P</td>
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<td>1.3</td>
<td>1.174</td>
<td>801.8</td>
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<td>µg/kg</td>
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<tr>
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<td>312.34</td>
<td>Ho</td>
<td>µg/kg</td>
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<tr>
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<td>-</td>
<td>23.57</td>
<td>1291</td>
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<tr>
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<td>0.44</td>
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<tr>
<td>Sr</td>
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<td>18.9</td>
<td>298.8</td>
<td>312.34</td>
<td>Yb</td>
<td>µg/kg</td>
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<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>123.4</td>
<td>6.43</td>
<td>3.98</td>
<td>Lu</td>
<td>µg/kg</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Figure 3 SEM images before (left) and after (right) the experiment shows distinct pits and holes have formed on the surface of the particle as a result of dissolution.
storage, CCS). The aim of storage of carbon dioxide or other forms of carbon is to mitigate CO₂ emissions caused by fossil fuel usage. CO₂ via dissolution in formation water is one of the approaches, which are used for solubility trapping of CO₂. If during actual geothermal energy production, as low as 0.1 moles of CO₂ is added to one liter of the water that is being re-injected back into the aquifer at a rate of 100 kg/s, around 14,000 metric tons of CO₂ will be used per year per plant. This CO₂ is dissolved in the geothermal water and there is no risk of the gas escaping to the surface. For scenarios of direct introduction of CO₂ inside of the aquifer, much higher amounts than the mentioned weight is used. Such a CO₂ storage by-effect (Carbon Capture, Utilization and Storage, CCUS) requires no additional energy or equipment which adds economic and environmental benefits. However, possible problems related to impurities of the CO₂ used must be considered as well.

Acknowledgments

The authors thank the Irish Authorities (DCENR, EPA, KCC, LCC), Vesi Environmental (Wetland Design), Golder Associates (TMF engineering), TMB Construction, Aberystwyth University, and support from Tara Mines and Lisheen Mines, in addition to all the Galmoy staff who worked on the progressive remediation.

Conclusions

H-P-T autoclave tests showed that adding CO₂ to groundwater leads to economically noteworthy enrichment of dissolved elements in the groundwater, which could then be processed after it has been brought to the surface.

Similarly, by adding CO₂ to the geothermal water, co-recovery of valuable minerals from geothermal water during geothermal energy production can increase the economic attractiveness without the negative effects of conventional mining, e.g. tailings, deforestation, water pollution.

The continuous leaching of minerals will improve aquifer permeability and increase the production performance in low permeable formations.

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Metal partitioning and pH-buffering during mixing processes in an estuary strongly affected by acid mine drainage – The Ria de Huelva estuary (SW Spain)

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Abstract
The acidic and metal rich waters of the Odiel and Tinto rivers flow into the Huelva Estuary (SW Spain), where mixing with seawater take place. During these mixing processes intense precipitation of Fe and Al in the fluvial domain of the estuary is observed. Hence, a buffer at pH ranges between 3 and 5.5 is observed, although the spatial location of these buffers is determined by river water/seawater ratio and tides. The information provided by this study is essential to trace the metal fate from rivers affected by AMD to the ocean, particularly to the Gulf of Cádiz and the Mediterranean Sea, which are enriched in metals compared to other seawaters worldwide.

Keywords: Iberian Pyrite Belt, acid rivers, Huelva Estuary, mixing zone, buffer pH

Introduction
Exposure of sulfides to atmospheric conditions leads to contamination of receiving waters by acid mine drainage (AMD), one of the main environmental problems associated with mining of sulfide-bearing ore deposits (Nordstrom and Alpers, 1999). These acid waters are characterized for having a wide range of dissolved constituents and low pH values (Nordstrom 2011). The Iberian Pyrite Belt (IPB, SW Iberian Peninsula) is one the oldest and largest metal-mining district in the world as well as one of the most AMD-affected area (Olias et al., 2006; Nordstrom 2011). Due to its mineral richness, mining activity dates back to Romans and Phoenicians times, but it was especially intense in the last 150 years. Such intense mining activity has left an environmentally impacted area of more than 4800 ha, with around 90 mines (most of them abandoned) and 200 million m3 of mining wastes as a legacy (Grande et al., 2014; Sainz et al., 2004; Cánovas et al., 2010). As a consequence, the Odiel and Tinto rivers, which drain the IPB, are strongly AMD-polluted and present extremely low pH values and high concentrations of metal(oid)s and sulfate (Nieto et al., 2013). Although AMD is usually neutralized by freshwaters downstream of mine sites, there are extreme cases where AMD can cause a direct effect on estuarine systems and coastal areas (Achterberg et al., 2003). An example of this is the Ria of Huelva estuary (SW Spain), which receives the inputs of the acidic (pH 2-4) and metal-rich waters from the Odiel and Tinto rivers. Thus, the estuary is affected by chronic metal pollution and both rivers have been considered to be an important metal contributor to the Gulf of Cádiz (Olias et al., 2006; Nieto et al., 2013). For this reason, this estuary has been focus of much research (e.g. Davis et al. 2000; Elbaz-Poulouchet, 2001). However, a detailed characterization of metal behavior and metal fluxes along the estuary upon different hydrological regimes (i.e. dry season, flood events and accidental mine spills) has not been properly addressed. In order to address this issue, systematic field water samplings upon different climate conditions were carried out comprising the sharp pH gradient (3-8) observed along the Ria de Huelva estuary.
Methods

Two field water sampling campaigns upon different climate conditions (i.e. high and low river discharges) were carried out along the estuary (fig. 1) at similar tide conditions. To determine dissolved element concentrations, water samples were collected from a ship, using a Van Dorn bottle (fig. 1a and b). The samples, collected in HDPE bottles previously washed with a 10 % HNO₃ solution, were filtered (0.45 µm), acidified with 1 % ultrapure Nitric Acid and refrigerated until their analysis by iCAP TQ ICP-MS at the HydroSciences laboratory of the University of Montpellier. Estuarine water reference material for trace metals (SLEW-3) and nearshore seawater certified reference material for trace metals (CASS-6) were also analyzed to check the analytical accuracy. In addition, filtered aliquots were used to analyze chloride and sulfate by ion chromatography (Dionex DX-120) at the R+D laboratories of the University of Huelva. Aluminum was determined using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using a specific protocol for estuarine and seawaters at the R+D laboratories of the University of Huelva. Temperature, pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) were measured in situ using HANNA HI 98190 and 98192 portable meters. A three-point calibration was performed for both EC (147 µS/cm, 1,413 µS/cm, and 12.88 mS/cm) and pH (4.01, 7.00, and 9.21), while ORP was controlled using two points (240 and 470 mV).

Results and discussion

Three differentiated areas can be defined in the estuary attending to the physicochemical parameters (tab. 1 and fig. 1); the Tinto domain (T8-T1), directly influenced by the Tinto River input; the Odiel domain (O14-O1), where Odiel river waters enter the estuary; and the Padre Santo Channel (C8-C1), where the confluence of both river inputs occurs. A progressive pH gradient is observed along the estuary, with pH values between 3-4 at the fluvial domain and 7-8 at the seawater domain. Electrical conductivity (EC) ranges from around 0.5-0.7 at the most fluvial influence zones to >40 mS cm⁻¹ at the

Figure 1 Location map of the Ria of Huelva estuary and sampling points indications (left side). On the right side, photos of the sampling Van Dorn bottle (a, b) and sampling campaign sites, i.e.: Tinto River Domain (c, d), Odiel River Domain (e, f) and Padre Santo Channel (g, h).
channel. Parameter variations can be observed in the estuary associated with the ratio of river water/seawater; for example, lower pH values are observed in the upper zone of the fluvial domain (T8-T5 and O14-12) during low-flow than river high-flow conditions. However, lower pH values are observed in the lower zones of the fluvial domain (T4-T1 and O8-O1) and Padre Santo channel (tab. 1 and fig. 2) during high-flow than during low-flow river conditions.

A similar trend for dissolved Al and Fe concentrations along the estuary can be observed (fig 2). Higher concentrations of both elements were observed at the upper part of the estuary coinciding with the lowest pH values. Higher dissolved Al (27.2±10 mg/L) was observed for low-flow river conditions in both upper estuary zones (fig. 2, left side); while lower Al concentrations (7.2±6 mg/L) were observed during high-flow river conditions. Decreasing concentrations when pH values exceeded 5.5 were observed for the rainy season, being more dramatic in the dry season. At the Padre Santo channel (C8-C1), Al concentrations were close to the detection limit for both low and high-flow river conditions, and only some values (i.e. C7, C4, C5) were reported. Regarding Fe (fig. 2, right side), noticeably higher dissolved concentrations were also observed for low-flow river conditions (May) at the upper part of the Tinto domain (18-49 mg/L; pH <3) than for high-flow conditions (0.8-1.0 mg/L; pH around 4). Concerning the Odiel domain, slightly higher Fe concentrations were observed in the upper part during low-flow river conditions (i.e. 1-1.6 mg/L) than during high-flow (around 1.1 mg/L). The opposite tendency was also observed for Fe in the lower section of the estuary; higher values were observed during the high-flow conditions in both the Tinto (1.8 to 2.9 mg/L, T4-T1) and Odiel (0.6 to 0.01 mg/L, O8-O1) domains than during low-flow conditions. This inverse metal concentration pattern is explained by the hydrology-mediated chemical characteristics of river waters and the topography of the estuary. During low-flow river conditions, Tinto and Odiel river waters show lower flows but higher concentrations than during high-flow conditions. Mixing processes at the upper zone of the estuary are physically controlled by topography, characterized by narrow estuarine channels which limit seawater arrival. Upon these conditions, higher metal concentrations are observed during low-flow river conditions due to the higher concentrations in river water. However, downstream, in the lower section of the estuary, the existence of wide channels allows the contact of large volumes of seawater. Upon these conditions, intense neutralization occurs during low-flow conditions, achieving higher pH values and lower metal concentrations (fig. 2). However, lower pH values and higher metal concentrations are observed during high-flow conditions at the lower section of the estuary (fig 2) by the buffer effect.

Table 1 Dissolved elements concentrations and selected physicochemical parameters for the two sampling campaigns (high river discharge and low river discharge). Cl-, SO₄, Al, Fe, Cu and Zn values are expressed in mg/L whereas As and U are expressed in µg/L. EC means electrical conductivity (mS/cm).

<table>
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<th>Sites</th>
<th>pH</th>
<th>EC</th>
<th>Cl⁻</th>
<th>SO₄</th>
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<th>Fe</th>
<th>Cu</th>
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<td>0.7</td>
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<td>0.80</td>
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<td>1.23</td>
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<td>1.34</td>
<td>1.20</td>
<td>0.8</td>
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Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
This buffering effect exerted by Fe and Al as a result of the mixture of acidic mine waters with more alkaline waters has been previously studied (e.g. Nordstrom 2011; Carrero et al., 2015) and reported to occur at pH ranges between 2-4 for Fe and 4.5-6 for Al. Although less studied, similar processes take place in estuarine systems affected by AMD as the presented case study. Thus, an intense Fe-Al precipitation zone can be identified in the fluvial domain of the estuary (pH 3.5-5). However, this zone may move depending on the hydrological conditions. For example, this buffer zone is observed to reach T2-T1 and O2 sampling points (fig. 1) during high-flow river conditions, however, both buffer zones are found upstream of these points during low-flow conditions.

The intense precipitation of Fe and Al in the estuarine waters during mixing processes may also affect to other trace metals. As can be seen in figure 3, dissolved Cu and Zn (as well as other elements not shown, e.g. Co, Ni and Cd) decreased their concentrations in the Padre Santo channel (fig. 3). The affinity of both metals to be incorporated in Fe and Al secondary minerals during AMD neutralization has been previously reported (e.g. Carrero et al., 2015). This is evidenced by the high correlations observed in estuarine waters between Fe-Cu, Fe-Zn, Al-Cu and Al-Zn (R2 0.66-0.96) for low and high-flow river conditions. These Fe and Al secondary minerals may also scavenge other elements such as As and U (e.g. Carrero et al., 2015). However, the behavior showed by these elements differs from that of Fe and Al (fig. 3); a progressive increment of concentration for both elements is observed during high-flow conditions, with maximum concentrations observed in the main channel (fig. 3) while a more erratic evolution is observed during low-flow conditions, with maximum concentrations in T5 for the Tinto domain (fig. 3). This evolution can be explained by desorption processes of both elements from Fe minerals, carried by the river as particulate matter, due to increase of salinity during mixing processes, especially important for U, which forms very stable U-carbonate complexes. At T5 and T4 sampling points, the maximum U peak observed during low-flow conditions, with maximum concentrations in T5 for the Tinto domain (fig. 3) is also observed for Fe, Al, Cu and Zn. This peak seems to be displaced during low high-flow conditions due to the higher contribution from river water, which dilute this contribution. A similar incremental behavior was observed in a survey carried out between 1997 and 1998, at the same location (Braungardt et al., 2003), that was also attributed to the phosphogypsum deposit.

The European Water Framework Directive (WFD, EU Commission, 2000) urges the adoption of restoration measures in this area.

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**Figure 2** Dissolved concentration of Al (left) and Fe (right) in the different zones of the estuary (i.e., Tinto (reddish shading), Odiel (greenish shading) and Padre Santo Channel (bluish shading) domains) for high (March; black bars) and low (May; gray bars) river discharges. Triangle green (May) and circle red (March) lines represent pH along the estuary for both periods.
to achieve a good chemical and ecological status of the water bodies. In this sense, several passive treatment plants based on dispersed alkaline substrate (DAS) technology (Ayora et al., 2013) have been successfully working at selected acid discharges in the last years. The implementation of other plants and the adoption of other measures will lead to a noticeable improvement of the river water quality (Macías et al., 2017), limiting thus the pollutant load transported from the mines to the estuary.

Conclusions

The Ria of Huelva estuary is a severely AMD-affected system, which receives the inputs of two strongly polluted rivers, the Odiel and Tinto, which drain the IPB. Consequently, enormous concentrations of dissolved elements are transported to the Ria of Huelva estuary and through it to the Atlantic Ocean. The distribution of the contaminants in the estuary is, therefore, highly controlled by the ratio of river water and seawater in the mixing zones.

A buffering effect exerted by Fe and Al as a result of the mixture of the acidic mine waters with more alkaline waters (i.e. seawater) take places in the estuarine system. Thus, an intense Fe-Al precipitation zone can be identified in the fluvial domain of the estuary (pH 3.5-5), for both Odiel and Tinto systems. However, this zone shifts spatially along the estuary depending on the hydrological conditions. For example, this buffer zone is moved downstream during high-flow river conditions, while both buffer zones are found at the more fluvial-influenced zones of the estuary in low-flow conditions. The intense precipitation of Fe and Al also affects to other trace metals. Hence, decreasing dissolved concentrations of elements such as Cu and Zn are observed in the estuary in line with the higher seawater contribution (i.e. higher salinity and pH values). Conversely, progressive As and U concentration increments observed in the Padre Santo channel suggest desorption.

Figure 3 Dissolved Cu, Zn, As and U concentrations for the Ria of Huelva estuary during March (left side) and May (right side) surveys. Reddish, greenish and bluish shadings indicate the Tinto, Odiel and Padre Santo Channel domains, respectively.

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processes associated with increase of salinity during mixing processes.

Even though intense precipitation processes were observed in the estuary, most conservative elements (e.g. Cd, Co, Ni) may be yet transported in the dissolved form throughout the estuary reaching the littoral waters. On the other hand, the intense precipitation of Fe and Al minerals along the estuary may lead to increasing levels of metal-rich particulate matter which could cross the estuary until final deposition in the littoral, and therefore it should be studied. In this sense, the spatial variation of pollution in the different sedimentary environments of the estuary and littoral zones, determining the link between the metallic content and the sediment grain size and mineralogical properties should be also assessed in future works. In addition, a reduction of the pollutant load is expected due to restoration measures foreseen in the near future at the mining areas within the actions required by the WFD.

Acknowledgements
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References
Transformation of Trace Element Composition of Fresh Natural Waters in the Central Part of Upper Kama Potash Deposit

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Abstract

Potash salts primarily used in the manufacturing of potash fertilizer are an important and highly valuable commodity in our modern economy. This study includes analysis of trace element composition of fresh natural waters (rivers, springs) in the area of the Upper Kama potash deposit. Indicators of the change in the trace element composition of water affected by potash mine effluents were determined. The results of the study will allow a more comprehensive approach to environmental monitoring and to a list of environmental protection measures in such regions.

Keywords: groundwater, surface water, chemical composition, potash deposits, technogenesis, geochemical indicators

Introduction

As with all mining activities, the extraction of potash has the potential to cause a change in the composition of natural water. The influence of potash ore deposits on the chemical composition of fresh water has been identified in the beginning of the XX century. Since the 1860s, the activity of potash mines in Germany has resulted in contamination of drinking water in the Weser River and some other rivers in the Rhine basin (Rauche 2015).

The chemical composition of fresh surface water and groundwater is studied in all regions, manufacturers of potash fertilisers. The goal of these studies is to ensure drinking water safety and quality control. These studies revealed the following changes in the water composition: an increase in TDS, total hardness, and concentrations of major anions and cations (e.g., sodium chloride, potassium chloride). These changes occur naturally when salts and their products are dissolved. However, analysis of the trace element composition of surface water and groundwater often remains beyond the scope of research.

It should be noted that the most substantial change in the composition of fresh water occurs in areas with humid climate conditions. The high humidity and surface disposal of soluble wastes contribute to the transformation of the hydrosphere. At the same time, the largest potash deposits, which are currently being developed, are located in such regions. These are Canada (Saskatchewan), Russia (Perm Region), Belarus, and Western Europe (U.S. Geological Survey 2018).

Let us briefly consider the results of trace element studies of natural waters and wastewater from a variety of potash ore deposits.

Studies on the composition of wastewater from waste storage facilities, as well as their further effect on the composition of groundwater were conducted on the example of Upper Kama potash deposit (Khayrulina & Maksimovich 2012; Khayrulina 2014). They revealed the extremely high concentrations of sodium and potassium chlorides and elevated contents of a wide range of trace elements (Sr, Mn, Pb, Ba, Cr, Zn, Li, and V).

Bachurin (2007) presents the data on potentially toxic metal contents in anthropogenically-generated wastewater at the mining sites of the Urals. He showed that the concentrations of the following elements (Mn, Fe, Pb, Zn, Co, Ni, Cu, and Cr) in wastewaters generated at the Upper Kama potash deposit are much higher than the background.

Similar results were obtained for groundwater in Spain, Germany, France and other countries (Otero & Soler 2002). This study presents the results of wastewater and natural water monitoring in the Llobregat River basin in the north-east of Spain. Among trace elements, strontium is present in high concentrations, while manganese, zinc, copper and lead are present in elevated concentrations. Studies
of the composition of natural waters were carried out in the Upper Rhine region, where the potash mines of Alsace have been operated for a long time (Bauer et al. 2005, Durand et al. 2005, Lucas et al. 2010). Rubidium, strontium and barium are found in the trace element composition of waters from this area. Similar data were obtained for Thuringia, Germany (Siefert et al. 2006).

We investigated the hydrochemical influence of the potash mine at the Upper Kama deposit (Belkin 2018). The work summarizes the data on monitoring of the groundwater chemical composition in the area slated for development, and the data on multi-year monitoring of springs in the vicinity of existing enterprises. Comparison of the average chemical compositions of natural and wastewaters using statistical methods showed substantial changes in the composition of waters. The major ion composition of groundwater is enriched in chlorides, bromides, sodium, potassium, calcium, magnesium and ammonium cations. Hydrochemical indicators of microelemental changes are manganese, cobalt, arsenic, vanadium, nickel, antimony, barium, strontium, and selenium.

The results of this work confirmed the potential effect of potash fertiliser production on the trace element composition of fresh natural waters, which has been identified during monitoring (Belkin 2018) at specific natural sites. A total of 11 groundwater samples from springs were studied. In addition to groundwater sampling, surface water samples were taken from the Usolka River.

**Study area**

The Upper Kama potash deposit, located in the Perm Region, is an important global resource due to its large size. The study area located in the central part of the field, in the vicinity of Solikamsk, in the middle and lower reaches of the Usolka River (fig. 1). Potash mines under operation are located on the left bank of the river, while on the left bank any major production facilities are absent. The main aquifer in this area is the Upper Solikamsk subformation (P1-sl) it is represented by terrigenous-carbonate rocks (limestones, marls) and is extensively used for water supply. The Sheshma aquifer (P1-šš) represented by sandstones, clays, siltstones, and mudstones occurs locally. Groundwater has a salinity of 0.2-0.5 g/L, the predominant ions are bicarbonates and calcium.

![Figure 1](image_url)  
Figure 1 Schematic map of the central part of Upper Kama potash deposit with surface water and groundwater sampling localities.
**Methods**

Surface water and groundwater samples were taken in March 2018. The study of natural waters not affected by potash mining was carried out in springs on the right bank of the Usolka River. Springs B1, B5, B11, B25 are confined to the Upper Solikamsk terrigenous-carbonate aquifer (P₁sl₂), spring B25 is confined to the Shesha aquifer (P₁šš). Groundwater is fresh (0.4-0.5 g/L TDS), of a calcium-bicarbonate type. Surface water samples (ST-1) were collected 9 km upstream of the plant (fig. 1).

Water samples collected from the area affected by potash mining activities were taken in close proximity to waste disposal facilities. Two groundwater discharge zones were studied. The first zone is located 800 m northwest of the potash liquid waste storage dam. The zone comprises a group of five springs (of which four were sampled). Springs discharge on the southeastern side of the man-made lake. The second zone comprises springs discharging on the left bank of the Usolka River, in the town of Solikamsk. Two springs were sampled at a distance of 1000-1200 m from the salt dump. Surface water sampling (ST-2) is carried out 2 km downstream of the plant (fig. 1).

The trace element composition (Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, W, Tl, Pb, Bi) of water samples was analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

The change in the concentration of each trace element in the composition of groundwater is analyzed by comparing the element concentrations with its background value. Due to the similar chemical composition of all sampled springs, the arithmetic mean of the analyzed samples is taken as a reference background. The data were compared with the results of groundwater monitoring (Belkin 2018). Changes in the concentration of each trace element in surface water were quantified by comparing its content in the background sample (ST-1) and that in the sample taken downstream of the mining sites (ST-2).

**Results and Discussion**

The results of comparison between trace element concentrations in surface water and groundwater samples collected in the study area are given in Table 1. We determined the concentrations of trace elements present in concentrations higher than the background value (groups “sharp increase” and “significant increase”) and the concentrations of trace elements not related to the effect of potash mining (groups “slight increase”, “no increase or decline”). The elements shown in bold are those present in elevated concentrations in surface water and groundwater sample, according to the 2018 monitoring and summary of monitoring data.

Analysis of the data revealed the following patterns. A sharp increase in the element concentrations in natural waters is typical of a limited number of elements. Arsenic, barium, rubidium, strontium, and titanium show the most significant increase. This set of elements is typical of both surface water and groundwater. Boron, cobalt, gallium, germanium, lithium, and nickel also show a significant increase in their concentration (from 2 to 8 times). The concentrations of manganese, which increases substantially in groundwaters affected by potash mining, remains almost unchanged in surface waters. This can be explained by the geochemical

<table>
<thead>
<tr>
<th>Table 1 Grouping of trace elements by the degree of change in concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Groundwater (monitoring)</strong></td>
</tr>
<tr>
<td>Sharp increase (&gt; 8 times)</td>
</tr>
<tr>
<td>As, Ba, Mn, Rb, Sr, Ti</td>
</tr>
<tr>
<td>Significant increase (2-8 times)</td>
</tr>
<tr>
<td>B, Co, Ga, Ge, Li, Ni, Sl, Se, V, Zn</td>
</tr>
<tr>
<td>Slight increase (&lt; 2 times)</td>
</tr>
<tr>
<td>Be, Bi, Cd, Cr, Sn, Ti, Zr</td>
</tr>
<tr>
<td>No increase or decline</td>
</tr>
<tr>
<td>Cs, Cu, Mo, Pb, W</td>
</tr>
<tr>
<td><strong>Groundwater (2018)</strong></td>
</tr>
<tr>
<td>As, Ba, Rb, Sr, Ti</td>
</tr>
<tr>
<td>B, Co, Cu, Ge, Li, Ni, Mn, Ni</td>
</tr>
<tr>
<td>Be, Bi, Cd, Cr, Se, Sn, Ti, V, Zr</td>
</tr>
<tr>
<td>Bi, Cs, Mo, Pb, Sn, W</td>
</tr>
<tr>
<td><strong>Surface waters (Usolka River, 2018)</strong></td>
</tr>
<tr>
<td>As, Ba, Rb, Sr, Ti</td>
</tr>
<tr>
<td>B, Co, Ga, Ge, Li, Ni</td>
</tr>
<tr>
<td>Cd, Cr, Cu, Mo, Se, Ti, W</td>
</tr>
<tr>
<td>Be, Bi, Cs, Mn, Pb, Sn, W, Zn</td>
</tr>
</tbody>
</table>
mobility of this element in different environments.

The results of groundwater studies conducted in March 2018 using a single sampling and single laboratory analysis method confirmed the previously identified set of specific trace elements characteristic of natural waters in the potash mining area. In addition, the study of the surface waters of the Usolka River shows that the same set of elements is also present in river waters.

Conclusions
A series of specific components determined in this study is consistent with the elements, indicators of the effect of potash mining activities on the chemical composition of natural waters presented in Belkin & Kataev (2018). Studies showed that the same elements are found both in groundwaters and surface natural waters in the area affected by potash waste storage facilities.

Therefore, the results of the study were used to assess and identify a number of trace elements in natural waters, the concentration of which is influenced by potash mining activities. This indicates the need to add the environmental monitoring programs for these areas with the analysis of trace element composition of water and to take into account the possibility of their high concentrations in implementation of environmental protection measures.

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Physical and chemical conditions for colonization by *Euglena mutabilis*: case studies in two acid mine drainage sites

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Abstract
Acid mine drainage promotes high metals concentrations, low pH and high acidity and sulfate. In this way these waters are characterized by extreme environments with low biodiversity. *Euglena mutabilis* is unicellular alga specie that colonizes AMD sites. In order to understand the abiotic factors, necessary for colonization, two old sulphide mining sites were studied. Valdarcas and São Domingos represent different chemical and physical environmental conditions. Thus, it was concluded that lentic and low depth environments, situated between pH 2.8 and 3.0, and a maximum metals concentration of 20 mg/L, are favorable conditions to the abundant presence of *Euglena mutabilis*.

Keywords: Extreme Environments, Acidophilic Algae, Abiotic factors, *Euglena mutabilis*

Introduction
Sulphides are reactive minerals, which oxidation promotes acid mine drainage (AMD). This process, with strong biogeochemical component is focus of major concern in mining sites (Valente et al. 2012). Typical contamination is characterized by metal mobilization, and acidification of water and soil. The streams are commonly highly stressed ecosystems being described by low biodiversity, promoting in this way, degradation of freshwaters (Hogsden and Harding 2012). Although the stressful circumstances, it is possible to observe colonization by extremophilic organisms that have mechanisms to resist to such a contamination (Valente et al. 2016). In the recent decades, ecology of this type of extreme environments has been studied by several authors (e.g. Gross 2000; Nixdorf et al. 2001; Lottermoser 2003; Valente and Gomes 2007). According to Novis and Harding (2007), acidophilic algae can survive in these waters by developing a diversity of mechanisms to prevent metals entry into cells, namely forming metal complexes. So, these organisms interfere with the mobility of chemical species, both dissolved and particulate, playing an important role within the system (Valente and Gomes, 2007). In literature, Euglena genus has been consistently reported to occur in AMD sites (e.g. Freitas et al. 2011). In general, these studies cover identification and quantification of algae populations. In addition, it is necessary to provide a holistic perspective to understanding, not only the AMD effects, but also other abiotic factors, potentially critical for colonization and global health of the ecosystems. Therefore, the present work aims to assess the specific characteristics that may determine the occurrence and abundance of *Euglena mutabilis*, including ore paragenesis of the exploited mine, which is the first control factor of the system evolution. Then, effect of chemistry, hydrology, climate and physical properties should be analyzed to understand algae distribution, thereby promoting more comprehensive understand of ecology and help environmental monitoring. To evaluate the influence of above factors, the present study was carried out in two former sulphides mines: Valdarcas and São Domingos (NW and SE of Iberian Peninsula), representing different geological and bioclimatic contexts.

Materials and Methods

**Studied sites**
The study was carried out in two abandoned mining sites, with sulphide-rich ore deposits exploited for W (NW Portugal) and Cu, pyrite...
(SE Portugal): Valdarcas and São Domingos, respectively (Figure 1). They are situated in two different metallogenetic provinces. The waste dumps have in common the presence of sulphides, but they have mineralogical differences, due to genetic type of deposits. Valdarcas, in the Northwest Portugal, is a skarn deposit with massive sulphides, mainly pyrrhotite and pyrite. Skarn contributes with neutralizing minerals, like calcite and Ca-silicates. It has a maritime temperate climate with July and August as the hottest (average temperature of 20.5°C) and January the coldest month (9.5°C). The annual precipitation is 1470 mm (Gomes et al. 2014), representing one of the rainiest region of Portugal.

São Domingos was one of the biggest mining complexes in Portugal that is located in the Iberian Pyrite Belt, one of the largest metallogenic provinces in the world, with massive sulphide deposits (pyrite, chalcopyrite, sphalerite; arsenopyrite and galena) with a diverse lithology of host rocks. Here the precipitation occurs mostly in the autumn and winter months, producing drought situations in summer and part of the spring. This is one of the driest regions in southwestern Europe, with typical characteristics of Mediterranean semi-arid climate (Gomes et al. 2018). The precipitation distribution is highly variable, with an average annual value of 595 mm.

Both mines were closed without environmental rehabilitation and show manifestations of AMD (Valente et al. 2007; Gomes et al. 2017). As referred paragenetic and climate as well as physical/hydrological contexts of the receiving water system are different.

Water sampling and analysis
In both sites, there was a monthly sampling during an entire hydrological year. At Valdarcas, water was collected in a small mountain creek comprising 5 sites over a distance of about 900 m. At São Domingos there were 12 sampling sites. These locations are represented in Valente et al. (2007) and Gomes et al. (2017), respectively for Valdarcas and São Domingos. 1 L of surface water was collected in a sterilized polyethylene container at each point, to be used for the laboratory analyses. Other 50 mL was filtered with 0.45 µm membranes and acidified with acid nitric to obtain pH<2, in order to prevent the metals precipitation and bacterial growth. With a portable meter, Thermo Scientific Orion, temperature (°C ), pH, electrical conductivity (EC µS/cm, at 25 °C ), potential redox (Eh) and total dissolved solids (TDS) were recorded in situ.

The turbidimetric method (Standard Methods 4500 E) was used to analyze sulfate. Total acidity and alkalinity were immediately measured by volumetric determination (AWWA 1992). Fe, As, Cu, Zn, Mn, Cd, Pb, Co, and Ni were obtained by inductively coupled plasma-mass spectrometry (ICP/MS). All the reagents were of analytical grade or Suprapur quality (Merck, Darmstadt, Germany). The standard solutions were Merck AA Certificate. Milli-Q water was used in all the experiments. Metals and arsenic analyses were performed at Activation Laboratory, Lda (Actlabs, Canada), including analysis of duplicate samples and blanks to check
According to the Ficklin diagram (Figure 2), most samples from São Domingos are classified as High-acid, High-metal, whereas all the samples from Valdarcas are in the range High-acid, Low-metal and Acid, Low-metal.

At São Domingos Euglena mutabilis (Figure 3) was only observed in two sampling sites with similar hydrochemistry (PAT3 and PAT10 in Table 1). Both sampling sites exhibited identical hydrology, with low water flow conditions, forming shallow lagoons (≈10 cm) with slight current (like puddles). At Valdarcas Euglena was found widely spread throughout the system. The only sampling site without observations of this unicellular alga presents high flow water regime and shadow conditions, thus with lower light incidence, and higher depth comparing to the others points. These observations are in accordance with the work of Smucker and Vis (2011), which refers that differences in water flow regime are decisive in the implementation and stabilization of primary organisms. Other abiotic factors, such as photic zone, photoperiod, and sun exposure may have high importance. Also, Sabater et al. (2003), refers that Euglena genus attaches to substrate, and thus vigorous currents can pose difficulties to fixation. In this way, the lentic features, precision, whereas accuracy was obtained by using certified standards.

**Algae sampling and identification**

Algae sampling was coincident with the water sampling points, in order to contemplate the observations in the field. They were obtained by scraping the substrates and by dredging the water surface through a polyethylene container. The taxonomic identification was achieved by optical microscopy (Leica Microscope CTR5000 with autofluorescence).

All samples were accommodated in a portable refrigerator at 4°C to avoid degradation. Some algae samples were identified immediately when arrived to the laboratory. In other cases preservation with Kew solution was carried out.

**Results and discussion**

**Hydrochemical characterization and Euglena distribution**

Table 1 presents annual average values of water parameters. At Valdarcas pH vary between 2.9 and 3.1. On the other hand, São Domingos shows a wide range, from extreme acid to circumneutral. The same different behavior occurs with other parameters as variation is considerably higher at São Domingos.

Table 1 **Average parameter values from the two systems. Σ metals (Fe, As, Cu, Zn, Mn). Location/distribution of sampling points can be found in Valente et al. (2007) and Gomes et al. (2017).**

<table>
<thead>
<tr>
<th>Mining Sites</th>
<th>Samples</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>T (°C)</th>
<th>Eh (mV)</th>
<th>Acidity (mg/L CaCO₃)</th>
<th>SO₄ (mg/L)</th>
<th>Σ metals (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valdarcas</td>
<td>V3</td>
<td>3.0</td>
<td>1919</td>
<td>15.4</td>
<td>427</td>
<td>850</td>
<td>1089</td>
<td>448</td>
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<tr>
<td></td>
<td>V4</td>
<td>3.1</td>
<td>1681</td>
<td>16.1</td>
<td>432</td>
<td>745</td>
<td>974</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>V5</td>
<td>2.9</td>
<td>1710</td>
<td>16.6</td>
<td>464</td>
<td>765</td>
<td>1012</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>V6</td>
<td>3.1</td>
<td>2289</td>
<td>16.1</td>
<td>404</td>
<td>1337</td>
<td>1763</td>
<td>710</td>
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<tr>
<td></td>
<td>V9</td>
<td>2.9</td>
<td>1585</td>
<td>15.3</td>
<td>457</td>
<td>653</td>
<td>862</td>
<td>214</td>
</tr>
<tr>
<td>São Domingos</td>
<td>PAT 2</td>
<td>2.6</td>
<td>7297</td>
<td>21.9</td>
<td>552</td>
<td>3708</td>
<td>5873</td>
<td>1077</td>
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<tr>
<td></td>
<td>PAT 3</td>
<td>2.7</td>
<td>2877</td>
<td>23.3</td>
<td>517</td>
<td>1274</td>
<td>1608</td>
<td>98.7</td>
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<td></td>
<td>PAT 4</td>
<td>2.7</td>
<td>2655</td>
<td>23.3</td>
<td>555</td>
<td>1228</td>
<td>1728</td>
<td>184</td>
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<tr>
<td></td>
<td>PAT 5</td>
<td>2.5</td>
<td>4035</td>
<td>23.2</td>
<td>538</td>
<td>2841</td>
<td>3155</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td>PAT 6</td>
<td>3.0</td>
<td>1735</td>
<td>23.2</td>
<td>480</td>
<td>811</td>
<td>1002</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>PAT 7</td>
<td>1.7</td>
<td>15133</td>
<td>24.4</td>
<td>517</td>
<td>169610</td>
<td>144352</td>
<td>50177</td>
</tr>
<tr>
<td></td>
<td>PAT 8</td>
<td>2.8</td>
<td>3262</td>
<td>22.2</td>
<td>501</td>
<td>2036</td>
<td>2365</td>
<td>251</td>
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<tr>
<td></td>
<td>PAT 9</td>
<td>2.9</td>
<td>2221</td>
<td>22.2</td>
<td>494</td>
<td>810</td>
<td>1285</td>
<td>87.3</td>
</tr>
<tr>
<td></td>
<td>PAT 10</td>
<td>3.0</td>
<td>2601</td>
<td>20.2</td>
<td>486</td>
<td>774</td>
<td>1564</td>
<td>90.2</td>
</tr>
<tr>
<td></td>
<td>PAT 11</td>
<td>4.4</td>
<td>654</td>
<td>20.9</td>
<td>345</td>
<td>103</td>
<td>255</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>PAT 12</td>
<td>6.4</td>
<td>247</td>
<td>21.2</td>
<td>300</td>
<td>-</td>
<td>33.8</td>
<td>13.0</td>
</tr>
</tbody>
</table>
with low depth (which allows light entry for photosynthesis) and low current speed in the lagoons of São Domingos and the calmer sections of Valdarcas stream appear to be more propitious to fixation of Euglena.

Contrarily to observations made by Wolowski et al. (2008), *Euglena mutabilis* was not found as an abundant alga in the São Domingos mine drainage. The presence of this specie only in PAT3 and PAT10 (Table 1) seems indicative of its survival range, namely regarding pH as stated by Verb and Vis (2000).

In terms of water properties the obtained results points to a minimum pH of 2.7 and metals concentrations until around 20 mg/L as most appropriate conditions for Euglena establishment. Several authors (e.g. Hogsden and Harding 2012) confirm that biota respond differently to the individual stressors. Niyogi et al. (1999) had already reported that AMD hydrochemistry has direct effects on the aquatic ecology. In the same way, Hogsden and Harding (2012) refer that low diversity is related to physiological sensitivity to extreme AMD conditions (high acid and/or high metals). On the other hand, the biomass production may reflect the tolerance of acidophilic algae to different levels of chemical contamination. For example, large biomass production, with blooms of Euglena and filamentous Chlorophyta (e.g.

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**Figure 2** Ficklin diagram revealing different classification for Valdarcas and São Domingos water samples.

**Figure 3** Microscope Image of typical elongated *Euglena mutabilis* clear cells.
Klebsormidium sp.) were reported in extreme AMD conditions (Valente and Leal Gomes 2007). Climate may also act as limiting factor for Euglena survival. Since these algae are attached to humid substrates, at São Domingos they are subjected to additional stress, due to the dryness of the region, with frequent drought episodes (Gomes et al. 2018).

**Conclusion**

The abundance and distribution of *Euglena mutabilis* were analyzed in relation to abiotic chemical and physical factors in two different mining sites. The obtained results emphasize the influence of pH, metal concentrations, hydrology, depth of water column and solar incidence. High solar incidence, lentic, and low depth conditions seem to facilitate the establishment of Euglena communities. Moreover, pH in the small range of 2.8 and 3.0, and a metallic concentration ($\Sigma$ (Fe, As, Cu, Zn, Mn)) around 20 mg/L were found as favorable environments for *Euglena mutabilis*.

Considering the factors analyzed in the two mining sites, the differences in water properties (conditioned by paragenesis and climate), and the hydrological conditions suggest that Valdarcas is more propitious for *Euglena mutabilis* survival and maintenance. At São Domingos this alga has a restrict distribution to some particular lentic environments.

**Acknowledgements**

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Geochemical and Mineralogical Characterization of Precipitates from Sabie-Pilgrim’s Rest Goldfields for the Potential of Acid Mine Drainage

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Abstract
The main aim was characterizing geochemistry and mineralogy of the efflorescent crusts that could further contribute to acid mine drainage of the two abandoned tailings storage facilities (TSFs): at Glynn’s Lydenburg and Nestor mines for that. Soil samples in the mine surroundings were also analysed. The X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses were carried out on the efflorescent salts from both tailings storage facilities and surrounding soils. Secondary minerals such as gypsum and jarosite which have been reported to contribute to further acidification of water were found on the efflorescent salts. The obtained results indicated that quartz and mica are dominant primary minerals at both sites. Nevertheless, dolomite is the major primary mineral in the Glynn’s Lydenburg tailings but is absent in the Nestor tailings storage facility. In the soils surrounding Nestor tailings storage facility, acid producing minerals such as ferricopiapite and fibroferrite and gibbsite were also detected. In addition, the mineralogy of the surrounding soils indicates the presence of smectite and kaolinite. The XRF results showed that in terms of major elements, the chemistry of both sites is dominated by SiO$_2$, Fe$_2$O$_3$, and Al$_2$O$_3$ followed by CaO, MgO. Also occurring in lesser concentrations were K$_2$O, TiO$_2$, Na$_2$O, MnO and Cr$_2$O$_3$. Trace elements such as As, Cu, Cr, Pb, V and Zn which can be hazardous to the environment were also found at both sites.

Keywords: Acid Mine Drainage, Efflorescent Crusts, Tailings Storage Facilities, X-Ray Diffraction, X-Ray Fluorescence

Introduction
Decades of mining in South Africa has resulted in acid mine drainage problem for certain regions. The Sabie-Pilgrim’s Rest Goldfield had been producing gold since 18th century generating wastes in the form of tailings and waste rocks. This area has several mine tailings storage facilities of different ages and sizes.

The key here is that few environmental studies had been carried out on mine tailings; hence this study was focused on the two abandoned tailings storage facilities, Nestor and Glynn’s Lydenburg. The main objective of this study was to determine the mineralogy and the geochemistry of efflorescent salts which can further contribute to acid mine drainage problem.

Location of the study area
The Glynn’s Lydenburg (GL) and Nestor (NS) tailings storage facilities are located in Sabie area, Mpumalanga Province of South Africa (Fig. 1).

Methods
Sampling and Sample Preparation
A total of eleven (11) samples were collected from Glynn’s Lydenburg TSF and seven (7) samples were collected from Nestor TSF. Sampling was focussed on efflorescent salts (solid precipitates) from the TSFs sidewalls (Fig.2). Individual grab samples were taken, collected over regularised areas to a depth of about 5 cm, and as vertical profiles from the surface to the base of exposure (GL1-8 and NS1-3 and NS7). Additional sampling was
done of the surrounding soils (GL9-11 and NS4-6), taken from small dug pits, to assess the contribution from the TSFs as well as for indications of secondary mineral products, or as background samples.

The collected tailings and soil samples were taken to the Council for Geoscience laboratory and submitted for trace element composition and mineralogy using XRD and XRF respectively.

The samples were analysed by X-ray fluorescence spectrometry (XRF) and X-ray diffraction spectrometry (XRD) according to procedures of USEPA (1986). The glass disks and wax pallets were analyzed using a PANalytical wavelength dispersive AXIOS X-ray fluorescence spectrometer that was equipped with a 4kW Rh tube. Both major and minor elements have been determined and reported as oxides and trace elements. Quality control/Quality assurance (QC/QA) was done using the in-house amphibolite reference material (sample 12/76). The X-ray diffraction (XRD) technique employed scanning from 2 to 70° 2θ CuKa radiation at a speed of 0.02° 2θ steps size/0.5 sec, with

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**Figure 1 Location of the Study Area**

**Figure 2** A) Efflorescent crusts on the sidewalls of the Glynn's Lydenburg TSF. B) Efflorescent crust developed on the slopes of the Nestor TSF
a LYNXEYE detector and generator settings of 40 kV and 40mA. Semi-quantitative approximations of the minerals present were based on the relative peak heights to area proportion according to Brime (1985).

**Results and Discussion**

**Geochemistry of tailings precipitates**

The XRF results showed that the chemistry of both sites in terms of major elements is dominated by major elements SiO$_2$, Fe$_2$O$_3$, and Al$_2$O$_3$ (Fig. 3). CaO was highly concentrated in Glynn’s Lydenburg soils (up to 14.22 ppm at GL16) than Nestor (up to 12.68 ppm in efflorescent crusts at NS01) and MgO was only found in Glynn’s Lydenburg (up to 5.09 in efflorescent crusts and 3.06 in soils). Also occurring in lesser concentrations were K$_2$O, TiO$_2$, MnO, Na$_2$O, MnO and Cr$_2$O$_3$ (Fig. 3). Quartz is more dominant in major element in soils of Nestor Mine site (up to 88.48 wt. %) and enriched in efflorescent salts of Glynn’s Lydenburg TSF (up to 60.35 wt. %) compared to soil samples of the respective site. Iron and aluminium oxides are also enriched in soil samples from both sites; Fe$_2$O$_3$ up to 12.84 wt. % in Nestor and 14.14 wt. % in Glynn’s Lydenburg TSF salts with Al$_2$O$_3$ having higher concentrations in Glynn’s Lydenburg TSF efflorescent salts (21.32 wt. %) compared to 20.37 wt. % in Nestor TSF precipitates (Fig. 3).

The sulphate minerals that contain Fe, Al and Mn generally accumulates in the form of efflorescent salts and essentially store acidity and will produce acid when dissolved in water during acid mine drainage formation (Naicker et al., 2003). Both sites are rich in Fe and Al hence likely to further generate acidity to the surrounding environment.

Metals and metalloids were also detected following the sequence As>Zn>Cr>Cu>V>Ni>Pb>Co (Fig. 4). Soils from both sites are dominated by elements Cr, V, Ni, and Co compared to efflorescent salts; suggesting that mineralization might be of sync-Bushveld Igneous Complex age. The precipitates are dominated by As, Zn and Cu compared to soils samples with very high concentration of Pb reaching up to 400 ppm.

The fate of various metals such as Cr, Ni, Cu, Mn, Hg, Cd and Pb and metalloids such as As, Sb and Se is of great concern to the environment (Adriano, 1986; 1992). The USEPA listed metals of major interest in bioavailability study as Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se and Sb (McKinney and Rodgers, 1992). Trace metals such as Cu, Cr, Pb, V and As occur within the efflorescent salts (Table 1) in excess of South African guidelines soil screening, National Norms and Standards.

![Figure 3 Major elemental compositions of Glynn's Lydenburg GL and Nestor (NS) TSFs](image-url)

DWAF (1996) showed that concentration of Cu in water over 30 mg/L results in liver, kidney and blood cells damage. Alloway and Ayres (1997) Cr VI is more toxic than Cr III wherein Cr VI concentration of 0.5 g/ml is considered to have negative effect.

The concentrations of As in both tailings storage facilities and surrounding soils are high and likely to cause As poisoning. A concentration of 100 mg/L As in soil can reduce crop yield by 90% and can lead to As poisoning which can result in diseases such as lung and skin cancer (Harada, 1996). Physically, the crusts showed different colourations with Glynn’s Lydenburg having whitish colour and Nestor had brownish to yellowish colour. This could be attributed to the elevated concentrations of Fe in Nestor compared to Glynn’s Lydenburg.

**Table 1** The distribution of metals and As (range, ppm) average values are given in brackets

<table>
<thead>
<tr>
<th>Metal</th>
<th>Nester TSF</th>
<th>Glynn’s Lydenburg TSF</th>
<th>All land uses, protective of water resources</th>
<th>Informal residential</th>
<th>Standard residential</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.10-0.88</td>
<td>0.06-0.08</td>
<td>5.8</td>
<td>23</td>
<td>48</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5-109</td>
<td>1.5-109</td>
<td>16</td>
<td>1100</td>
<td>2300</td>
</tr>
<tr>
<td>Cr</td>
<td>43.1-114</td>
<td>43.3-301</td>
<td>65</td>
<td>65</td>
<td>13</td>
</tr>
<tr>
<td>Co</td>
<td>15-364</td>
<td>15-364</td>
<td>20</td>
<td>110</td>
<td>259</td>
</tr>
<tr>
<td>Ni</td>
<td>7.7-102</td>
<td>7.7-102</td>
<td>150</td>
<td>150</td>
<td>320</td>
</tr>
<tr>
<td>Pb</td>
<td>9.9-400</td>
<td>9.9-400</td>
<td>240</td>
<td>920</td>
<td>1900</td>
</tr>
<tr>
<td>V</td>
<td>9.7-227</td>
<td>9.7-298</td>
<td>150</td>
<td>150</td>
<td>320</td>
</tr>
<tr>
<td>Zn</td>
<td>1.5-166</td>
<td>1.5-166</td>
<td>240</td>
<td>920</td>
<td>1900</td>
</tr>
</tbody>
</table>

**Figure 3** Major elemental compositions of Glynn’s Lydenburg GL) and Nestor (NS) TSFs

**Mineralogy of tailings precipitates**

The mineralogical composition of efflorescent salts was determined using XRD analysis. The dominant primary minerals in both precipitates materials are quartz and mica. In Glynn’s Lydenburg dolomite is the major primary mineral found within the salts and is absent in Nestor tailings salts (Fig.5).

Soluble secondary salts store acid and metal in their solid phase, hence they are of environmental concern. Their dissolution can result in potentially detrimental flushes of acid and metals into ground and surface water during periods of rainfall or snowmelt (Nordstrom and Alpers, 1999). Plumlee et al. (1995a and b) showed that jarosite is a common salt in many mine waste materials that readily release acid and metals during rain storms or laboratory leach tests. In terms of secondary acid-producing minerals gypsum dominates both sites. Another acid producing mineral jarosite was only found at one Nestor TFS salts sample while
gibbsite was only found on the surrounding soils at both sites. According to Blair et al. (1990); Jambor et al. (2003); Lottermoser (2007); Thornton (1996); Williams (1975) acid mine drainage (AMD) can also acidify and contaminate soils located near mining areas and in floodplains downstream of them. In the soils surrounding Nestor TSF, acid producing minerals ferricopiapite, fibroferrite, jarosite and gibbsite are present (Fig. 5) and the Klein-Sabie river is located just 300m south of the tailings storage facility. The mineralogy of the surrounding soils in both sites indicates the presence of smectite and kaolinite (Fig. 5).

Conclusions
The obtained results indicated that quartz and mica are dominant primary minerals at both sites. Nevertheless, dolomite is the major primary acid-neutralizing mineral in the Glynn’s Lydenberg tailings but is absent in the Nestor tailings storage facility. In terms of secondary minerals, gypsum dominates both sites. In the Nestor tailings, acid producing minerals such as ferricopiapite, fibroferrite, jarosite, and gibbsite were also detected. In addition, the mineralogy of the surrounding soils indicates the presence of smectite and kaolinite. Acid-producing sulphite gibbsite was also found in the surrounding soils at both sites. The XRF results showed that in terms of major elements, the chemistry of both sites is dominated by SiO₂, Fe₂O₃, and Al₂O₃. Also, trace elements such as As, Cu, Cr, Pb, V, and Zn, were also found in elevated concentrations. These elements can be hazardous to the environment in higher quantities. The results principally point to the capacity of crusts to store contaminants.

Acknowledgements
Council for Geoscience is acknowledged for the financial contribution towards this study. To my late colleagues Obed and Tlou rest in peace.

References
Harada M (1996) Characteristics of industrial poisoning and environmental contamination in


Abstract
Geochemical codes are routinely used throughout the world for investigating a wide variety of water-rock interactions including mine site characterization and remediation. Unfortunately, there is an underappreciation for the knowledge that a code user must bring to bear on the interpretation of code output, the limitations of popular codes, and their reliability. Examples of code testing are shown through comparison of calculated and measured Eh, comparison of simulated pyrite oxidation with actual field samples, and mineral saturation indices consistent with field conditions for calcite. Hydrous ferric oxides can appear to be supersaturated because colloids pass through 0.1 and 0.45 μm filter pore sizes. The colloid effect on ferrioxide saturation indices was demonstrated by comparing measured vs. calculated redox potentials, removing non-detects for Fe(III), and recalculating saturation indices. The results show no supersaturation for freshly precipitating iron oxides. Aluminum precipitates occur at the pH where the first hydrolysis constant is reached, making it an easily predictable phenomenon. Other minerals such as barite and anglesite may appear supersaturated because of grain size effects or the lack of disulfato-metal stability constants in the code. Modeling of mass balances is often overlooked and even more important because of its role in the conceptual model of a site. This paper highlights important points of geochemical modeling for mine site characterization and remediation from Nordstrom and Nicholson (2017).

Keywords: geochemical modeling, mine site remediation, code reliability, mineral saturation, redox

Introduction
From the beginning of computerized geochemical modelling in the late 1960s and early 1970s, substantial progress has been made with code development and application. This improvement in code sophistication has led to misunderstandings about the uncertainties and limitations of code application. Models have been confused with codes; model and code assumptions have not been fully understood; “model validation” has been a routine and incorrect phrase for scientific studies; and modelling with proprietary and non-proprietary codes have been used for mine permitting without adequate review (Nordstrom, 2012). In more general terms, modelling of all kinds and consequential failures of predictions have led some researchers to point out that quantitative models cannot be trusted (Pilkey and Pilkey-Jarvis, 2007) and why so many predictions often fail (Silver, 2012). It appears that science and computerized modelling has far outpaced our actual understanding of environmental systems such as the geochemistry of mine sites. In this paper I summarize the main points from our recent publication on Geochemical Modeling for Mine Site Characterization and Remediation (Nordstrom and Nicholson, 2017). This handbook is the 4th in a series of 6 that cover management technologies for metal mining influenced water. The handbook covers hydrogeochemical process such as speciation, mass balances, redox chemistry, hydrologic modelling and reactive-transport modelling.

Main Hydrogeochemical Processes
The main geochemical processes that occur at sulphide-rich metal mine sites are: (1)
sulphide mineral oxidation, (2) carbonate mineral dissolution, (3) gypsum dissolution and precipitation, oxidation and reduction (redox) of several metals, metalloids, and sulfur, (4) iron precipitation, (5) aluminium precipitation, (6) silica precipitation, (7) efflorescent salt formation and dissolution, (8) mixing of waters, and (9) evaporation. Most of these reactions are described by stoichiometric equations found in Plumlee (1999), Lottermoser (2010), Blowes et al. (2014), and Nordstrom and Nicholson (2017). Geochemical modelling of some of these reactions are described below.

**Pyrite oxidation and iron precipitation**

Simulating pyrite oxidation and iron precipitation is a good test for any geochemical code because of its complexity, especially with regard to redox processes. It is also the primary reaction that causes acid mine drainage from sulphide mines. Fig. 1 shows a graphical model of the change in pH with the amount of pyrite oxidized. The calculations were obtained with the PHREEQC code (Parkhurst and Appelo, 2013) and replotted from Nordstrom and Campbell, 2014).

Figure 2 demonstrates the change in pH of field samples before (initial) and after (final) dissolved ferrous iron oxidized compared to the simulation (Nordstrom and Campbell, 2014). This particular fit only works well if the logK\text{sp} = \approx 3 for hydrous ferric oxide (or ferrihydrite) because the crossover point is very sensitive to the logK\text{sp} of the precipitating phase. If the iron phase precipitating is changed, the crossover point changes substantially (Fig. 1). The fact that there are crossover points reflects inflection points in the curves and indicates a buffering reaction. More details can be found in Nordstrom and Campbell (2014).

Supersaturation has frequently been observed for waters precipitating hydrous ferric oxides. This effect seems to be caused by nanocolloids passing through the field filtering system, resulting in Fe(III) concentrations that are higher than those truly dissolved. This effect was discovered by comparing measured with calculated Eh (based on Fe (II/III) determinations and speciation computations). Fig. 3A shows the comparison for more than 1,000 acid mine water samples from the western USA. Many samples agree quite well and others not well. When samples that were below detection limits for Fe(III) (10^{-5.5} molar) were removed, Fig. 3B shows that nearly all the samples remaining now show good agreement (Nordstrom, 2011).

Using only the selected values from Fig. 3B to calculate the ferricydrite saturation indices (SIs), I have demonstrated that supersaturation no longer occurs (Fig. 4B) compared to using all the samples (Fig. 4A).

Hence, supersaturation for hydrous ferric oxides are an artifact of filtration because the colloid concentration is so high compared to the dissolved Fe(III) concentration, it only takes a small amount of colloids to give apparent supersaturated conditions.

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**Figure 1. Simulation of pH from pyrite oxidation.**

**Figure 2. Comparison of field samples**
Aluminum Precipitation

Aluminum has been shown to precipitate when acid mine waters are diluted through mixing or neutralized by buffering up to a pH near the pK1 for Al hydrolysis (5.0). This condition was first reported by Nordstrom and Ball (1986) and has been further confirmed for 1,500 mine water samples across the western USA (Nordstrom, 2011). The key diagram is reproduced in Fig. 5.

The samples plotted in Fig. 5 show undersaturation up to a pH of about 5 and then a limit is reached between 5 and about 7.5. For pH values above 7.5 a downward trend in SI values is very likely related to organic complexing which maintains a constant Al concentration in solution, but the hydrolysis in the code speciation is not accounting for that and causes the SI values to decrease because of increasing activity of Al(OH)$_4^-$ which decreases the activity of Al$^{3+}$ in the SI.

Calcite solubility equilibrium

One of the earliest examples of mineral solubility equilibrium being reached in a groundwater was that of Langmuir (1971) for a shallow limestone aquifer in Pennsylvania. His analytical data were rerun through PHREEQC using the data of Plummer and Busenberg (1982) and the SI values plotted as a function of pH as shown...
in Fig. 6. This is one of the best examples of mineral solubility equilibrium for field data, but it is common for saturation indices to be supersaturated. Reasons can include inadequate thermodynamic data, kinetic inhibitions, lack of metal-organic complexing data, and insufficient analytical quality.

**Barite and Anglesite Mineral Saturation**

It is common to find that the SI values for barite and anglesite are supersaturated by about 0.5 or more. If these minerals are freshly precipitating from the water column, then the supersaturation could easily be a grain size effect on solubility. The other possibility is that these waters contain very high sulfate concentrations which could form double sulfate-metal complexes with barium and lead. These are occasionally suggested in the literature but usually not included in speciation codes. Their exclusion could also cause apparent supersaturation which is not really there.
Mass Balances
Mass balances simply convert the change in water chemistry along some flowpath to an assemblage of minerals that must have dissolved or precipitated to cause the change in water composition. This procedure is adequately explained in many other publications that are cited in Nordstrom and Campbell (2014) and Nordstrom and Nicholson (2017). The main result from studies on acid mine drainage is that no matter what assumptions one makes for the mineral assemblage, iron and silica are always precipitated (Nordstrom, 2011). The iron precipitation is obvious because of visual staining, the silica precipitation is not obvious, but has been confirmed in mineralogical studies (Jambor, personal communication).

Geochemical Models, Test Cases, Codes, and Examples
The examples of testing geochemical models and codes shown above are described in Nordstrom and Nicholson (2017) along with hydrologic modelling fundamentals, reactive-transport modelling for mine sites, a listing of codes and databases, and several case studies. The most detailed, advanced, and exhaustive case study using geochemical modelling at a mine site was done by Glynn and Brown (2012) and their 15-year perspective (reproduced in Nordstrom and Nicholson, 2017) should be read by all geochemical modelers working on mine wastes. Not only are the major limitations described, but the optimal approach for modelling is described.

Conclusions
Geochemical modelling for mine site characterization and remediation is a sophisticated science that requires background and training in chemistry, geology, hydrology, mineralogy, microbiology, mining, and mineral processing. Large uncertainties abound and it is still an area of active research, not a finished routine product. Major advances have been made and there are applications that are worth pursuing, but only for modelers who have sufficient experience with field work as well as with the codes.

Geochemical models (like most models) are not unique, they are not “final,” they do not give exact answers, only approximations. They are helpful tools to understand reactions and processes. Don’t let the sophistication of the model outpace the available field data. A combination of inverse modelling and forward modelling can lead to the most insightful understanding of complex processes at mine sites, as shown most clearly by Glynn and Brown (2012). The core of modelling is the conceptual model and mass balances. Nothing improves our conceptual model of a site more than better field data, which best constrains our modelling conclusions.

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The author thanks the U.S. Geological Survey for the opportunity to pursue research on acid mine drainage for more than 40 years, the EPA for their support of some of my research, and the supportive collaboration of many of my fine colleagues at the USGS and elsewhere.

References


Considering the Ionic Strength and pH of Process Water on Bubble-Particle Attachment of Sulfide Minerals: Implications for Froth Flotation in Saline Water

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Abstract
Due to the current climate of water scarcity in mining areas and the fact that water treatment is costly; the recirculation of process water seems to be a viable option in mineral processing. A consequence of the recirculation of water is the build-up of ions such as Ca²⁺, Mg²⁺, Na⁺, SO₄²⁻ and NO₃⁻ as well as increases in pH. This study thus considers the combined effect of increasing ionic strength and pH of process water on the froth flotation process. These parameters are important to study simultaneously because complex water systems at high pH values, may result in the formation of various hydroxo complexes compromising the flotation efficiency.

Both fundamental bubble-particle attachment tests and microflotation show decreases in attachment and sulfide recovery as the pH is increased to 11. However, at the elevated pH the recovery increases as the ionic strength (water recycles) is increased. This could be due to the compression of the electrical double layer by the indifferent ions as seen by the zeta potential measurements. Zeta potential measurements also show steep increases in the potential of the sulphide minerals at pH 11.

Although this work suggests that process water with a pH as high as 11 will result in decreased mineral recoveries, it has been shown that at increased levels of ionic strength (increased recirculation of process water) higher recoveries can be obtained. Thus, it can be concluded that if the pH of process water was to reach a pH of 11, the combined effect of recirculation of process water would not necessarily have detrimental effects on sulfides flotation performance.

Introduction
Froth flotation takes advantage of a minerals surface properties as a means of separating valuable minerals from non-valuable gangue. When air is introduced into the mineral slurry, the hydrophobic particles (most often valuables) attach to the air bubbles and rise into the froth phase where they are eventually collected. Whereas the hydrophilic, (most often non-valuable) particles stay in the pulp zone (Wills and Finch, 2016).

This process thus depends on the attachment of particles to air bubbles; which makes the bubble-particle attachment sub-process critical in achieving the separation of valuables from non-valuables (Albijanic et al., 2010).

Water scarcities in parts of the world with massive mining industries have led to recycled process water and sea water usage gaining huge interest in the mining industry. These water types are of high ionic strength and therefore their water chemistry is very different to that of fresh water and may negatively affect the froth flotation process (Rao and Finch, 1989). Recycled process water is a combination of varying water streams from the process thus the proportions of dissolved solids will vary and affect the pH of the system (Levay et al., 2001). It is therefore valuable to understand how a change in pH in recycled process water will affect the flotation process.

It has been proposed that upon the addition of electrolytes, the electrical...
double layer is compressed which lead to the accelerated rupturing of the wetting film at the air-water and solid-water interface and in turn assists in faster bubble-particle attachment (Laskowski and Iskra, 1970; Li and Somasundaran, 1993; Harvey et al., 2002; Laskowski and Castro, 2015).

Manono et al. (2017) and Tadie et al. (2016) both reported a decrease in solids recovery with process water at elevated pH values in a flotation system and attributed this to the hydroxo complexes and its possible precipitation on the mineral surface, hence imparting hydrophilicity on the particles. This study thus looks at the simultaneous effect of increasing ionic strength and pH from both a flotation and fundamental bubble-particle attachment perspective in a chalcopyrite and galena system respectively.

**Materials and Methods**

**Mineral Sample**

1 kg of Galena and 1 kg of Chalcopyrite obtained from Ward’s Science was crushed using a hammer to 100% passing 1000 microns. The respective sulphide mineral particles were then pulverized and sieved through 75 and 38 micron sieves to obtain a size fraction between 38 and 75 microns for the microflotation and attachment time tests. The fraction below 38 microns was sieved through a 25 micron sieve and the particles below 25 microns were used for the zeta potential measurements. The two minerals in the 2 size fractions of interest (38-75 microns and <25 microns) split, purged with nitrogen and refrigerated.

**Water Quality**

Standard synthetic plant water (1 SPW) as described by Wiese et al. (2005) was used as the baseline synthetic plant water for the test programme. In order to simulate the recycle, the amount of dissolved solids was increased five and ten times making up 5 SPW and 10 SPW respectively. The ionic concentrations of the three synthetic plant waters are depicted in Table 1.

**Attachment Time Tests**

The attachment timer (ACTA) used in this investigation was developed at Aalto University and has been described by Aspiala et al. (2018) and October et al. (2019). A detailed description of the experimental procedure in terms of particle bed building and running measurements is documented in October et al. (2019). Measurements were taken for each of the water qualities in Table 1. Further, these tests were performed in duplicate for each condition to minimise experimental error.

**Microflotation Tests**

The microflotation cell developed by Bradshaw and O’Connor (1996) was used to perform the microflotation tests in this work. 3 g of the respective sulphide minerals was mixed with 50 mL of the particular water quality under study; the mixture was then ultra-sonicated for 5 minutes to allow for good dispersion of the mineral mixture. The suspension was then transferred to the microflotation cell and the pulp was circulated by a peristaltic pump at 90 rpm. Air was then introduced at the base of the cell at a flow rate of 7 mL/min and concentrates were collected at 2, 6, 12 and 20 minutes of flotation. The tailings and four concentrates were then filtered, dried and weighed. The microflotation tests were performed in duplicate to minimise error.

**Zeta Potential Measurements**

Very dilute mixtures of the particular water type and particles were made up; the dilute mixtures were then equally divided in six

<table>
<thead>
<tr>
<th>Water type</th>
<th>Ca(^{2+}) mg/L</th>
<th>Mg(^{2+}) mg/L</th>
<th>Na(^{+}) mg/L</th>
<th>Cl(^{-}) mg/L</th>
<th>SO(_{4})^{2-} mg/L</th>
<th>NO(_{3})^{-} mg/L</th>
<th>CO(_{3})^{2-} mg/L</th>
<th>TDS mg/L</th>
<th>Ionic Strength mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 SPW</td>
<td>80</td>
<td>70</td>
<td>153</td>
<td>287</td>
<td>240</td>
<td>176</td>
<td>17</td>
<td>1023</td>
<td>0.0241</td>
</tr>
<tr>
<td>5 SPW</td>
<td>400</td>
<td>350</td>
<td>765</td>
<td>1435</td>
<td>1200</td>
<td>880</td>
<td>85</td>
<td>5115</td>
<td>0.1205</td>
</tr>
<tr>
<td>10 SPW</td>
<td>800</td>
<td>700</td>
<td>1530</td>
<td>2870</td>
<td>2400</td>
<td>1760</td>
<td>170</td>
<td>10230</td>
<td>0.241</td>
</tr>
</tbody>
</table>
containers and the pH was adjusted to 2, 4, 6, 8, 10 and 12 with dilute HCl or dilute NaOH. After 15 minutes on the magnetic stirrer the pH was measured again and adjusted where needed. 1 mL of the suspension was then transferred to the Malvern Dip Cell and inserted in the Malvern ZetaSizer where measurements were taken. All zeta potential measurements were performed in triplicate to reduce experimental error.

Results and Discussion

Figure 1 shows the recovery of galena in the microflotation cell for with the various synthetic plant waters at both the natural pH as well as at a pH 11. In terms of the galena recovery at the natural pH it is clear that the recovery increases as the ionic strength of the plant water increases, this can be attributed to the fact that an increase in ions result in the compression of the electrical double layer at the air-water and solid-water interface. This in turn will cause the accelerated rupturing of the film at the air-water and solid-water interface; increasing the attachment of particles to air bubbles (Laskowski and Iskra, 1970; Li and Somasundaran, 1993; Harvey et al., 2002; Laskowski and Castro, 2015). The recovery of galena at the elevated pH reduced drastically compared to at the natural pH. With 1 SPW at a pH of 11 resulting in the poorest galena recovery. Similar results were obtained by Tadie et al. (2016) and this was said to be as a result of the precipitation of hydroxide species on the mineral surface. The recovery does however increase as the ionic strength increases even at the high pH.

Attachment time tests were further done to understand the effect of increasing pH and ionic strength on the bubble-particle attachment from a fundamental perspective, examining both the probability of attachment and the mass recovered through particle-bubble contacts. It is important to note, that the attachment probability is calculated by dividing the amount of bubbles with one or more attached particles by the total number of bubbles, but does not take into consideration how many particles are actually attached to one particular bubble. In certain experimental conditions particles tend to attach to each other and get recovered as clusters. In these cases relatively large mass of particles can be recovered, even when the quantified attachment probability is low.

Figure 2 shows the attachment probability of galena particles to air bubbles with plant water of increasing ionic strength at both the natural pH and elevated pH so as to complement the microflotation results. The attachment contact time apparatus also collects the particles that have successfully attached to the bubbles, the mass recovered of these particles are also depicted in Figure 2.
In terms of the attachment probability, it is clear that the probability of galena particles attaching to air bubbles are dramatically reduced at the high pH. However, the result of the combined effect of increasing ionic strength at pH 11 on the attachment probability is not clear. Therefore, the result showing the mass of particles that successfully attached to the bubbles prove to be useful. As with the microflotation tests, the mass of galena recovered in the ACTA increases with increasing ionic strength at the natural pH. In addition, at pH 11 the mass recovered is also substantially lower than at the natural pH but the mass recovered does increase with water of high ionic strength even at pH 11. Thus, matching the microflotation results.

Figure 3 shows the recovery of chalcopyrite in the microflotation cell for with the various synthetic plant waters at both the natural pH as well as at a pH of 11. The recovery of chalcopyrite at the natural pH is relatively similar with the three water qualities, this is possibly due to the floatable nature of chalcopyrite. However, the recovery of chalcopyrite with the highest ionic strength plant water does give a better recovery, as with galena this is attributed to the compression of the electrical double layer in waters of high ionic concentration. Similarly, as with galena the chalcopyrite recovery at the elevated pH is reduced drastically compared to at the natural pH. With 1 SPW at a pH of 11 resulting in the poorest chalcopyrite recovery. The recovery does however increase as the ionic strength increases even at the high pH.

Figure 4 shows the attachment probability of chalcopyrite particles to air bubbles with plant water of increasing ionic strength at both natural pH and elevated pH as well as the mass of particles recovered at the conditions under study. Both the attachment probability and mass recovered perfectly matches the results of the microflotation. Thus, reinforcing the trend of a decrease in bubble-particle attachment at an increased pH but at a higher
**Figure 3:** Microflotation of Chalcopyrite with various water qualities

**Figure 4:** Attachment Probability (a) and Mass Recovered Chalcopyrite particles under various water qualities
pH the bubble-particle attachment increases with waters of higher ionic strengths in both a flotation system as well as a fundamental bubble-particle attachment system.

Figure 5 show the zeta potential of galena (a) and chalcopyrite (b) under the various water qualities. Both sulfide minerals display a similar trend in terms of charge on the mineral; with the zeta potential becoming less negative with increase in ionic strength of the synthetic plant water. This phenomenon is indicative of the compression of the electrical double layer as the ionic concentration of the water increases (Moignard et al., 1977). This result was also observed by October et al. (2019) in a pyrrhotite system as well as Ikumapayi et al. (2012) in a galena system. These authors attribute this to be due to the increased passivation of the mineral surface by the increasing cation concentration. Upon closer study of these zeta potential results, an increase in potential with all the synthetic plant water is observed between pH values of 10 and 12. Which is said to be because of metal hydroxide precipitation or oxidation at the mineral surface (Harvey et al., 2002; Ikumapayi et al., 2012; Hirajama et al., 2016). Speciation diagrams as shown by Manono et al. (2018) show that at this pH range for these waters, the content of hydroxo species increases substantially with the highest concentration of these species occurring in the 10 SPW plant water at pH values of 11 and above.

A similar study by Manono et al. (2017) looking at the interactive effect of ionic strength and pH on a Merensky ore in a batch flotation system also showed a decrease in recovery at pH 11 and this was attributed to the increase in hydroxo complexes. While, Fuerstenau et al. (1999) proposed that in alkaline conditions metal ions hydrolyze and deposit hydrophilic metal hydroxides on the mineral surface. The decrease in sulfide mineral bubble-particle attachment at pH 11 from this more fundamental study considering pure minerals may also be attributed to the increase in hydroxo complexes deposited on the mineral surface as supported by the zeta potential measurements in Figure 5. This deposition of hydrophilic metal hydroxides on the mineral surface will also hinder the adsorption of the collector on the mineral surface, decreasing the bubble-particle attachment (Rao, 2004).

The bubble-particle attachment results both fundamental and microflotation shows how the attachment of sulfide mineral particles to air bubbles increases with waters of higher ionic strength which is due to the compression of the electrical double layer as reinforced by Figure 5. At a high pH the bubble-particle attachment decreases substantially but however still increases with increasing ionic strength. It would be expected that a high pH and high ionic strength water would result in the poorest performance as the hydroxide concentration is even higher, but this is not the case demonstrating the effect of the compression of the electrical double layer even in alkaline solutions.

Conclusions

Fundamental bubble-particle attachment tests and microflotation tests show a substantial decrease in the attachment of sulfide minerals to air bubbles with synthetic plant water at a pH of 11. This has been attributed to the
increase in hydroxo complexes at this pH, inducing hydrophilicity upon the particles or hindering the action of the collector. This work does however show that increases in sulfide mineral recovery can be attained at a high pH with plant water of high ionic strengths.

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Transformation of the acid mine drainage composition of the Sibay chalcopyrite deposit on the geochemical barriers of the river system

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Abstract
This article focuses on the study of the Sibay copper-zinc deposit (South Urals) acid mine and dump drainage and on its transformation in the Karagaily river system. The runoff of the river is initially formed by underground water, dump drainage and mine drainage. The hydrochemical composition of water and the content of ore metals in bottom sediments have been examined. Special attention has been paid to the phase distribution of metals, which provides information about the forms and intensity of element mobilization into the solid phase. The effect of anthropogenic and natural geochemical barriers on the river self-purification ability has been estimated. It has been shown that the formation of a new artificial geochemical barrier in the river, caused by the discharge of alkaline waters from the treatment facilities, substantially increased the self-purification ability of the watercourse. This led to the fact, that the quality of river water in the lower course almost reached normative indicators.

Keywords: acid mine drainage, bottom sediments, potentially toxic metals, trace elements, geochemical barriers

Introduction
The development of polymetallic sulphide deposits leads to acidification of natural waters and contamination of landscape components with potentially toxic metals.

The mining of chalcopyrite deposits leads to contamination of landscape components with potentially toxic metals (PTM) and to natural water acidification (Liu et al. 2010; Perotti et al. 2017; Balci, Demirel 2018; Opekunov et al. 2018). This influence is especially noticeable for streams directly polluted with mine drainage (Opekunov et al. 2010, Canovas et al. 2017). Cu, Zn, Cd and other chalcophyles are the main elements of secondary dispersion haloes around chalcopyrite deposits. In the hypergenesis zone in presence of oxygen Fe2(SO4)3 and H2SO4 poorly soluble sulfides are transformed into hydrated metal sulfates. As a result of these reactions a sharp decrease in the pH of surface and soil water is observed, accompanied by an increase in Eh (Siegel 2002). The main forms of Cu, Zn and Cd in aqueous solutions are cations, as well as hydroxyl or mixed hydroxyl-sulphate complexes, which, with an increase in pH, pass into the solid phase, leading to a decrease in their concentration in water. This process is especially active on geochemical barriers. The Sibay copper-sulphidean (copper-zinc) deposit, located in the Bashkir Trans-Urals (Southern Urals), has been developed since 1939. Open-pit mining of the Sibay ore deposit (which contains the main reserves of Cu and Zn) was started in 1956. Since 2003 only shaft mining has been performed.

Before the construction began, the upper reaches of Karagaily river, were diverted to Kamyshty-Uzyak, (another small river of the study area) and in the middle stream a new channel has been dug, bypassing the future quarry. (fig. 1). In 2011, wastewater treatment facilities for the nearby Kamagan quarry were constructed. Alkaline wastewater discharge to the Karagaily led to a substantial change in the hydrochemical regime of the watercourse in the middle and lower reaches.

The article discusses the effectiveness of
geochemical barriers in wastewater treatment. All barriers, including an artificial barrier, which arose as a result of the discharge of alkaline waters from treatment facilities, were formed spontaneously. However, their effect on water quality is quite substantial. Studies show that the construction of artificial geochemical barriers is a very effective and cheap way of reducing pollution of sour drainage waters.

Methods

Research on the Karagaily river has been conducted from 2004. During this period, wastewater, mine drainage water, river water and bottom sediments were sampled. Conductivity, pH, main cations and anions content, PTM (Cu, Zn, Pb, Cd, Fe, Mn, Ni, Co) concentration were measured in water samples. A total PTM content and content of their mobile forms were determined in bottom sediment samples. During the research period 30 water samples and 65 bottom sediments samples were analyzed. PTM total content was measured using mass spectrometry with complete acid digestion. PTM concentration in water after filtration and PTM mobile forms content in bottom sediments (extracted with ammonium acetate buffer, with pH 4.8) as well as PTM phases content in bottom sediments were determined using atomic absorption spectrometry («AAS-novAA 300» spectrometer). The ion-cationic composition of water was determined by the titrimetric method. Phase analysis of PTM in 11 bottom sediments samples was done using sequential extraction and included determination of sorbed forms (0.25 mol/l MgCl2), carbonates and non-persistent organic matter (ammonium acetate buffer with pH 4.8), organic matter and sulfate (1 mol/l acetic acid and H2O2), PTM sorbed on iron and manganese hydroxides (hydroxylamine hydrochloride NH2OH-HCl), crystalline (0.3 mol/l HCl), residue (difference in total content and mobile phases content summary). Spatial distribution of PTM in bottom sediments was characterised using a multiplicative index (MI) calculated as a product of the Cu, Zn and Cd content (in%), additionally multiplied by 1000.

Figure 1 The study area
Discussion

Consumption of mixed waters in the summer is 15-30 l/s. At 1 km below the source, quarry waters are discharged into the river bed.

Originally, Karagayly flowed from the ridges of the Irendyk mountain chain. Later the Karagaily upper course was buried under quarry dumps south-west of Sibay, where underground water comes to the surface and mixes with acid dump drainage. Water flow in summer is 15-30 L/s. About 1 km downstream mine drainage water, the volume of which exceeds the river’s volume at this place approximately 1.5 times, is discharged into the river. Hydrochemical characteristics of mine drainage are close to those of dump drainage (table 1). Both are Mg-SO₄, mineralization is from 3,3 to 9,4 g/L. Water hardness is high, the sum of Ca²⁺ and Mg²⁺ reaches 139 mg-eqv/l. Anomalous concentration of Cu, Zn, Cd and other chalcophytic elements was discovered in the river water. Our estimation of Zn, Cu and Cd intake to the river is 53 t/yr, 3 t/yr and 0,1 t/yr respectively (Opekunov et al. 2018). Thus, for a long time the water flow in the upper and middle course of the Karagaily has almost completely been formed by mine and dump drainage.

Nowadays the Karagaily is 11 km long. The river flows through the southern outskirts of Sibay and into the river Khudolaz, which is a tributary of the Ural river. The river bed and floodplain morphology determines different hydrological regimes and sedimentation rate of suspended and dissolved matter. In the upper course near the village of Gornyi the river bed is 2-6 m wide (up to 20 m at maximum in several places). The flow velocity during the summer low-water period is 0,2-0,3 m/s. The River bed is a U-shaped valley, the height of the banks doesn’t exceed 1,5 m. The sediment regime is predominantly accumulative or trans-accumulative. A wide (up to 200m) waterlogged floodplain covered with reed is located in the middle course of the river. In this area a pond has been constructed. It acted as a mechanical and sorption geochemical barrier, where suspended material and PTM accumulated. Downstream (near the tailing pond) the river has a narrow and relatively deep bed. The flow velocity reaches 0,8 m/s and provides a transitional sediment regime. In the lower course the floodplain expands and gets waterlogged again due to road construction. Close to the river mouth (near the village of Kalininskoe) the river bed is mature and the valley is relatively wide and the flow velocity is low (0,2-0,3 m/s). Such conditions determine an accumulative (in some places – erosional and accumulative) sediment regime.

Several natural and anthropogenic biogeochemical barriers have been formed along the river. To some extent they provide self-purification of the Karagaily and protection of the Khudolaz. Downstream from the mine drainage discharge site water acidity slowly decreases due to mixing with natural waters (pH 8,0-8,2) and contact with slightly alkaline soils (fig. 2). Alkaline and

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**Table 1** Hydrochemical characteristics of dump and mine drainage.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Dump drainage</th>
<th>Mine drainage</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.95-6.25</td>
<td>3.32-4.95</td>
</tr>
<tr>
<td>K⁺, mg/L</td>
<td>1.78-2.66</td>
<td>2.20-2.28</td>
</tr>
<tr>
<td>Na⁺, mg/L</td>
<td>69.7-154.3</td>
<td>165.4-176.9</td>
</tr>
<tr>
<td>Mg²⁺, mg/L</td>
<td>461.8-1463</td>
<td>358.9-450.4</td>
</tr>
<tr>
<td>Ca²⁺, mg/L</td>
<td>363.2-369.2</td>
<td>248.7-256.2</td>
</tr>
<tr>
<td>Cl⁻, mg/L</td>
<td>7.25-7.66</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>SO₄²⁻, mg/L</td>
<td>2922-7392</td>
<td>2547-2917</td>
</tr>
<tr>
<td>HCO₃⁻, mg/L</td>
<td>&lt; 1.0-1.84</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Σ ions, mg/L</td>
<td>3828-9381</td>
<td>3342-3783</td>
</tr>
<tr>
<td>Zn, mg/L</td>
<td>12.1-111.0</td>
<td>36.6-49.0</td>
</tr>
<tr>
<td>Cu, mg/L</td>
<td>0.20-21.0</td>
<td>5.4-8.1</td>
</tr>
<tr>
<td>Ni, mg/L</td>
<td>0.025-0.24</td>
<td>0.09-0.12</td>
</tr>
<tr>
<td>Cd, mg/L</td>
<td>0.03-0.59</td>
<td>0.13-0.15</td>
</tr>
<tr>
<td>Hardness, mg-eqv/l</td>
<td>56-139</td>
<td>42-49</td>
</tr>
<tr>
<td>Water type</td>
<td>Mg-SO₄</td>
<td>Mg-SO₄</td>
</tr>
</tbody>
</table>

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
sorption barriers are the most crucial for PTM immobilization.

The first anthropogenic alkaline barrier is located under the dumps, where acid dump drainage mixes with discharged underground water. At sampling point (SP) №1 mix pH reaches 6,0-6,5 (fig. 2). This barrier manifests itself in white powder-like sediment which covers the river bottom over 1 km downstream from the dumps (fig. 3). The white sediment is predominantly composed of hydrated sulfates of metals. The levels of $\text{SO}_4^{2-}$ (19,8%), Cu (1,24%), Zn (1,57%) and Cd (13,3 ppm) substantially exceed background values. Compounds which sediment on the river bottom include copper sulfate, goslarite ($\text{ZnSO}_4\cdot7\text{H}_2\text{O}$), hydrosulfates of Fe, Zn and Cu. Cd is present as admixture. A high ratio of Cu, Zn and Cd mobile forms (33, 26 and 22% respectively) has been noted.

One more anthropogenic alkaline barrier and one more maximum of PTM content in bottom sediments can be found on the acid mine drainage discharge site (fig. 2, SP 3). Here, unlike the first barrier place, mine drainage substantially acidifies the water (pH 4,75-4,85) and inhibits hydrosulfates formation downstream, where PTM are sedimented predominantly by sorption on clay minerals. It is proved by exchangeable forms ratio increase up to 70% for Cu (average – 25-30%), 82% for Zn (average – 50%) and 72% for Cd (average – 35-45%).

Before 2011 river water pH slowly rose downstream, up to 5,2-5,4 in the middle course (fig. 2; SP 11-18) and up to 6,85-7,12 near the mouth (fig. 2; SP 20, 21). This was mainly due to the lateral inflow and the formation of natural geochemical barriers. Changes of PTM concentration in water corresponded to pH changes (fig. 4). Cu and Cd sedimentation in hydrated sulfates forms in the upper and middle course reached 56-86% and 43-60% of total content respectively; however, in the river mouth it dropped to 15 and 7%. Zn hydrated sulfates ratio was lower: 22-29% in the upper and middle course and 9% in the river mouth.

Such a regime existed for about 50 years. There, at the confluence with the river Hudolaz, an alkaline barrier was formed, on which metals precipitated as sulfates and in the adsorbed state on iron oxyhydroxides. Their content in water was

![Figure 2 Changing of water pH and multiplicative index of Zn, Cu and Cd in bottom sediments along the Karagaily (Opekunov et al., 2018, revised and completed)]
reduced to standard values. It all changed in 2011, when wastewater treatment facilities 2,2 km downstream of the river head were put in operation (fig. 2, SP 9). Now wastewater treatment is performed by water liming followed by flocculation. Discharged wastewater pH reaches 10,5. A sharp pH increase has intensified PTM sedimentation and river self-purification (fig. 2, SP 9-16).

Directly at the discharge site (fig. 2, SP 9) PTM are immobilized in sulfate forms. Then iron sulfate is transformed into hydrocarbonate and later into hydroxide: $\text{FeSO}_4 + \text{Ca(HCO}_3\text{)}_2$ $\rightarrow \text{Fe(HCO}_3\text{)}_2 + \text{CaSO}_4$ $2\text{Fe(HCO}_3\text{)}_3$ $\rightarrow$ $2\text{Fe(OH)}_3$↓ + $6\text{CO}_2$. The newly formed $\text{Fe(OH)}_3$ actively adsorbs ore metals. It is the basis for the complex sorption and alkaline barrier, which manifests itself in ochreous color of bottom sediment anomalously enriched with Fe (up to 21%), Cu (0,83%), Zn (1,92%) and Cd (0,0048%). Exchangeable forms content is maximum on the surface and decreases downward 1,3-1,8 times, due to $\text{Fe(OH)}_3$ crystallization and consequential non-availability of PTM for the ammonium acetate buffer. Thus, the artificial barrier, which emerged spontaneously in 2011, causes active accumulation of PTM near discharge site and downstream (fig. 2, SP 10-15).

The high activity of the artificial barrier is proved by comparative data (tab. 2). The increase of PTM total content and exchangeable forms content in bottom sediments after 2011 is shown. However, it is accompanied by a decrease of exchangeable forms percentage. This highlights the role of iron hydroxides in chalcophylic metals sedimentation.

**Conclusion**

The artificial geochemical barrier formed spontaneously as a result of alkaline discharge from wastewater treatment facilities substantially increased the self-purification ability of the Karagaily river.
in regard to sulfate and PTM. The creation of this barrier led to a 5-fold decrease of Zn, Cu and Cd concentration downstream from 4,1 mg/L, 0,059 mg/L and 0,016 mg/L respectively before 2011 to 0,826 mg/L, 0,0125 mg/L and 0,003 mg/L after 2011. After 2011 the quality of water in the mouth of the river Karagaily satisfied the standards for river water for drinking and water supply. It also means that removal of PTM to the Khudolaz river decreased correspondingly in 2011. According to preliminary estimation of the river self-purification ability, before 2011 about 25% of Zn that had come with mine and dump drainage, was carried from the Karagaily downstream to the Khudolaz. After the artificial barrier - wastewater treatment facility - construction this ratio dropped to 5%. For Cu this value changed from 1,2% to 0,3% and for Cd – from 10% to 2%. Simultaneous increase of PTM total content and decrease of their mobile forms ratio in bottom sediments is an important factor (tab. 2). It can be claimed, that after the described changes of physic and chemical conditions the risk of secondary pollution of the river water has decreased.

Acknowledgements

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Metal fluxes from the Tinto River (SW Spain) to the Atlantic Ocean: importance of flood events

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Abstract

Flood events may play a key role in the metal transport fluxes from rivers to oceans. This is especially relevant in semi-arid and arid climate regions, which alternate long drought periods and short but intense rainfall events, when most of the water discharge, dissolved contaminants, and suspended matter transport occurs. This study provides information on the metal transport from the Tinto River to the Atlantic Ocean during high resolution samplings of different flood events (2004/06 and 2017/18).

Keywords: metal transport, flood events, metal pollution, acid mine drainage

Introduction

The Tinto River drains the Iberian Pyrite Belt (IPB), one of the largest polymetallic massive sulfide regions in the world, with original reserves of the order of 1700 million tonnes. The Tinto River springs within the Riotinto Mining District (Fig. 1), the largest sulfide deposit described in the world. As a consequence of historical mining the Tinto River is strongly polluted, showing extremely low pH values and high metal concentrations up to its confluence with the Atlantic Ocean (Cánovas et al., 2007) and transport a huge load of metals into the Ocean, e.g. 5075 t/yr of Fe, 1224 t/yr of Al, 687 t/yr of Zn and 469 t/yr of Cu (Olías et al., 2006). Metal transport takes mainly place during short but intense flood events when most of the water discharge occurs. For this reason, flood rainfall events need to be studied with a high temporal sampling resolution considering the great geochemical and hydrological variability observed in these episodes. These studies should be extended to large data series in order to assess the effect of flood events on metal fluxes upon different hydrological regimes. Changes in metal transport patterns associated with climate and land use changes such as closure or reopening of mines and adoption of remediation measures in mine sites should be also addressed. In this sense, the reopening of the Riotinto mines in 2015 may have changed the metal transport pattern to the Ocean. Thus, this study provides information on the metal transport from the Tinto River to the Atlantic Ocean during high resolution samplings of flood events before (2004/06) and after (2017/18) the reopening of the mines to evaluate the effect on the metal transport to the Ocean.

Methods

A high-resolution sampling were performed during the hydrological year 2017/18 at the stream-gauge station of Gadea (Fig. 1), located approximately 41 km downstream of the Riotinto Mining District and around 20 km upstream of its entry into the Ría of Huelva estuary (Fig. 1). Results were compared to those obtained in similar samplings performed from 2004 to 2006. Sampling was performed using a Teledyne ISCO® autosampler, with a sample container holding up to 24 bottles previously washed in 10% (v/v) HNO₃. Samples were pumped by a peristaltic pump, with a schedule purge stage between samples to avoid cross-contamination. Electrical conductivity (EC), pH, and oxidation-reduction potential (ORP) were measured in situ for all samples using field with portable meters (Hanna Instruments HI 9025 and HI 9033). Samples were filtered through 0.45 µm Millipore®
Teflon filters and acidified to a pH < 2 immediately after collection, and finally stored at 4 °C until analysis. The chemical analyses were undertaken at the Central Research Services of Huelva University using inductively coupled plasma optical emission spectroscopy (ICP-AES: Jobin Yvon Ultima 2) for major elements and inductively coupled plasma mass emission spectroscopy (ICP-MS: Agilent 7700) for trace elements. Detection limits were 0.2 mg/L for major elements and 1 µg/L for trace elements. Rainfall data were obtained from different gauges distributed within the Tinto catchment and water discharge was provided by the Environmental Andalusian Agency.

Results and Discussion
The Tinto River drainage basin is mainly composed of impermeable materials, thus this river has a fast response to rainfalls; river flow can increase up to 1000 times in a short-term scale, i.e. hours to days (Fig. 1). This fast response causes sharp changes in chemical composition of waters through the year. Figure 2 represents the evolution of some physico-chemical parameters and metal concentrations during floods monitored through the hydrological year 2017/2018. The first rainfalls after summer cause the dissolution of evaporitic sulfate salts precipitated on the river banks and mine sites, as well as the transport of accumulated weathering products of sulfide, which is especially intense during the dry period. These soluble sulfate salts may act as temporary sinks for acidity and metals in dry seasons, which are again released during rainfall events in wet seasons (e.g., Bigham and Nordstrom, 2000; Hammarstrom et al., 2005; Cánovas et al., 2008). Therefore, the first rainfalls after the dry period cause a sharp increase in EC values and the highest peak of sulfate and metal concentrations through the year; up to 11.4 mS/cm, 1529 mg/L of Fe and 115 mg/L of Cu were observed (Fig. 2). The washout of these salts also caused a slight decrease in pH values; from 2.4 to 2.1 (Fig. 2). As long as the rainy period continues a progressive depletion of metals and sulfate stored as soluble evaporitic salt minerals and concentrated pore fluids occur, and then dilution by freshwater becomes increasingly dominant. During this period hydrochemical variations are observed by Fe minerals precipitation, relative changes in the sources of AMD (e.g. mine tunnels, spoil heaps, etc.) and to differences in the rainfall distributions along the catchment (Cánovas et al. 2007). However, despite the arrival of large volumes of freshwaters, pH values in the Tinto River remain below 3 most of the time (Fig. 2) due to the buffering effect of Fe(III) precipitation. Only when extreme rainfall episodes take place and Fe is almost depleted, pH may exceed values above 4. Then, the lowest metal concentrations of the year are observed coinciding with high flows (i.e. 60 m³/s), i.e. down to 0.27 mg/L of Fe and 1.3 mg/L of Cu (Fig. 2).

As a consequence of such low pH values and high metal/loid concentrations, the Tinto River carries high loads of pollutants to the Ocean. Table 1 shows the metal/loid loads during the hydrological years 2004/05, 2005/06 and 2017/2018. As can be seen, metal/loid transport is strongly linked to
pluviometry, with higher loads observed during the most rainy years. Thus, around 900-5000 ton of Fe, 500-2250 ton of Al, 110-550 ton of Zn, 110-450 ton of Cu and lesser amounts of Pb, As and Cd are annually transported by the Tinto River.

The most striking fact is the difference of loads transported by the river during different periods with a similar pluviometry (2005/06 and 2017/18); almost 2 times more Fe, Al, Cu and Zn were transported by the Tinto River in 2017/18 (633 mm) than in 2005/06 (639 mm). This increasing loads could be related to rainfall antecedents; when extremely long dry periods are followed by intense rainfalls events, the washout of evaporitic salts and oxidation products accumulated during this long period, leads to dramatic increases in metal/loid concentrations and loads (Cánovas et al. 2008). However, this seem not to be the reason behind such anomalous metal/loid transport. The preceeding years of October 2005 were not especially rainy, 769 and 307 mm were collected during the hydrological years 2003/04 and 2004/05, respectively. However, more intense rainfalls were recorded during the previous years to March 2018 flood event; 730 and 647mm were collected during the hydrological years 2015/16 and 2016/17. Therefore, hydrological factors seem not to be the responsible of such increasing loads, which may be instead probably related to intense mining operations after the reopening of Riotinto mines in 2015. Such mining operations also seems to have caused hydrochemical changes in the Tinto River. Figure 3 shows the Cu/Zn and Cd/Zn mass ratios during the flood events monitored in 2006, and in 2017, before and after the reopening of the mines. It can be clearly seen that Cu/Zn and Cd/Zn ratios have changed after the reopening of the mine; while Cu/Zn and Cd/Zn ratios are close to 1 and 5 before the reopening the mine, after that, noticeably lower values are observed (around 0.5 and 3; Fig. 3), except during extreme rainfall episodes, when ratios increase (especially Cu/Zn). This change in chemical composition

<table>
<thead>
<tr>
<th>Rainfall (mm)</th>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004/05</td>
<td>307</td>
<td>485</td>
<td>0.87</td>
<td>0.51</td>
<td>109</td>
<td>869</td>
<td>5.8</td>
</tr>
<tr>
<td>% October Floods</td>
<td>49%</td>
<td>50%</td>
<td>57%</td>
<td>42%</td>
<td>36%</td>
<td>33%</td>
<td>90%</td>
</tr>
<tr>
<td>2005/06</td>
<td>639</td>
<td>1133</td>
<td>2.3</td>
<td>1.3</td>
<td>240</td>
<td>2311</td>
<td>13</td>
</tr>
<tr>
<td>% October Floods</td>
<td>19%</td>
<td>30%</td>
<td>28%</td>
<td>39%</td>
<td>35%</td>
<td>43%</td>
<td>3.3%</td>
</tr>
<tr>
<td>2017/18</td>
<td>633</td>
<td>2254</td>
<td>3.8</td>
<td>1.7</td>
<td>453</td>
<td>4983</td>
<td>16</td>
</tr>
<tr>
<td>% March Floods</td>
<td>55%</td>
<td>62%</td>
<td>27%</td>
<td>57%</td>
<td>67%</td>
<td>57%</td>
<td>97%</td>
</tr>
</tbody>
</table>

**Figure 2** Evolution of pH, electrical conductivity (EC) values and the concentration of Fe and Cu during flood events monitored in the Tinto River during 2017/18
of the Tinto River waters may be related to change in proportion and composition of mine waters released into the river after the mine reopening. Therefore, further studies are needed to confirm this hypothesis.

Despite its short-time span (hours to days), flood events play a key role in annual metal transport in semi-arid regions affected by sulfide mining. Table 1 shows the relative contribution of monitored floods in the annual metal/loid transport in the Tinto River. These events are caused by intense rainfalls, i.e. between 19 and 55% of annual rainfalls collected in the drainage basin, and may deliver between around 30 and 70% of the annual metal/loid load to the Ocean. In the case of Pb, a metal which is mainly delivered from mine sites during extreme rainfall episodes (Cánovas et al., 2008), these events can contribute up to 98% of annual Pb carried by the river.

In order to evaluate the differences in metal loading during both periods (i.e. pre and after mine reopening) monthly metal loads are represented against the monthly precipitation. As can be seen, monthly loads of As and Fe seem to be higher after mine reopening than before in those months with a similar pluviometry. For instance, Fe loads after mine reopening double that observed before at monthly rainfalls around 50 mm. These increasing loads are even more evident for As; monthly loads are between 3 and 5 times higher for these months.

**Conclusions**

Flood events play a key role in annual metal transport in semi-arid regions affected by sulfide mining. This is the case of the Tinto River, probably the more AMD-affected river in the world, due to the intense mining activity in the Riotinto mine since ancient times. Changes in metal transport patterns associated with climate and closure or reopening of mines and adoption of remediation measures in mine sites can take place in these systems and therefore should be studied. This study provides information on the metal transport from the Tinto River to the Atlantic Ocean during high resolution samplings of flood events before (2004/06) and after (2017/18) the reopening of the mines.

Metal/loid transport is strongly linked to pluviometry, with higher loads observed during the most rainy years; i.e. around 900-5000 ton of Fe, 500-2250 ton of Al, 110-550 ton of Zn, 110-450 ton of Cu and lesser amounts of Pb, As and Cd are annually transported by the Tinto River. The importance of flood events in the annual flow and metal/loid fluxes to the Ocean is evidenced by the high delivery of metal/loid in such short events; between around 30 and 70% of the annual

Figure 3 Tinto River at the Gadea gauge station before (a) and after (b) flood events in 2017 (Cd/Zn ratio expressed as µg/L/mg/L).
metal/loid load to the Ocean is carried by floods. In the case of Pb, these events can contribute up to 98% of total amount carried by the river.

The most striking result is the difference of loads transported by the river during periods with a similar pluviometry (2005/06 and 2017/18); almost 2 times more Fe, Al, Cu and Zn were transported by the Tinto River in 2017/18 (633 mm) than in 2005/06 (639 mm). Hydrological factors seem not to be responsible of such increasing loads, but probably related to hydrological changes induced by the reopening of Riotinto mines in 2015, which seem to have changed the geochemical signature of waters. Further studies through the time are needed to confirm this hypothesis.

Acknowledgements
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References

Figure 4 Relationship between monthly metal/loid loading and precipitation before and after the reopening of the Riotinto mine.


Mobility Control Of Uranium And Other Potentially Toxic Elements In Mine Waters By Ochre-Precipitates

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Abstract

Mineral-water interaction in mine drainage often results in the formation of iron-rich precipitates, called ochre products. They often comprise particles in the nanoscale, known by their strong reactivity. The present study focuses on these nanoprecipitates formed in streams that receive water from a U-Ra mine. Water and the ochre-precipitates that cover the streambed were sampled for geochemical and mineralogical characterization. Results indicate low crystallinity and variety of morphology of the ochre product, which is mainly composed by ferrihydrite in coexistence with minor hematite. The work concludes by noting the potential relevance of these nanophases in fate and transport of elements that pose major environmental concern, namely in uranium-rich mine waters.

Keywords: Uranium-mine waters, ochre-products, ferrihydrite, nanoparticles

Introduction

Degradation of water quality by mining activity is a typical environmental problem worldwide. Although acid mine drainage (AMD) is the typical effect associated with metallic exploitations due to mobility of metals and arsenic at low pH, circumneutral mine waters may also affect ecosystems. Potentially toxic elements (PTE) may occur in high concentrations in neutral and alkaline waters as documented by several authors (e.g., Lottermoser 2010). As referred by Lindsay et al. (2015), conditions of circumneutral pH favors mobility of PTE, like As, Se and U in the form of (hydr) oxyanions that may be responsible for contamination of the streams that receive mine discharges. Moreover, development of other typical indicators of mine water effect, such as deposition of ochre products, occurs in such water systems. These ochre-precipitates have been documented in other mining sites as strongly reactive due to small grain size and high specific surface area (Valente et al. 2012). They have dual and opposing effects. On one side they may disturb aquatic organisms and induce toxicity (Seo and Kwo, 2010) but on the other hand they may act as sinks for PTE.

The present work focuses on this last aspect, studying the result of mineral-water interaction in circumneutral mine water from a U-Ra mine. Therefore, hydrogeochemical and mineralogical studies were performed in a small stream that receives water from a mine located in the Argozelo area (Ribô Boco mine, Guarda, Central Portugal). The ore deposit is mainly of supergenic nature with dominant mineralization in authonite and torbernite. The regional geology is characterized by smoky and zoned quartz veins and basic rocks with pitchblende, sulphides, and secondary uranium minerals (Cameron 1982). Underground exploitation resulted in waste rock dumps with high concentration of radionuclides. High levels of radiation have been reported in the surrounding water and soil (Carvalho et al., 2014).

Surface runoff and mine water are discharged into a small creek (Boco creek), which displays typical features of
mine contamination, such as deposition of yellow-reddish precipitates (Figure 1). Characterization of these products is a complex task due to small dimensions and, generally, low crystallinity of the phases (Valente et al., 2016). Therefore, the present work intends to (i) obtain mineralogical identification, morphology, and chemistry of the ochre-precipitates; (ii) elucidate about the nanoscale properties and ability to retain and constrain mobility of uranium, thorium, and other potentially toxic elements (PTE).

**Methods**

The mine is included in the Uraniferous Region of the Beiras-Central Portugal (Cotelo Neiva, 2003). It was selected as representative of other small U-Ra mines, with similar paragenesis and that generate neutral and reduced iron-rich effluents. Samples of ochre-precipitates were collected in a small pond formed by the accumulation of water discharged through the gallery. Six water samples were also collected, spatially distributed along ≈ 500 m of the small stream that receive this mine water (Boco creek). The first sample was obtained in the same site of the ochre-precipitates (at the exit of the gallery).

Temperature, pH, Eh, and electrical conductivity (EC) were measured in situ using a multiparameter HANNA HI929828 model. The water samples were filtered through 0.45 µm pore size membrane filters. Those for the determinations of major and trace elements (e.g. Ca, Mg, Fe, U, Th, As, Co, Cd, Pb, Cu, Zn, and Mn) were acidified with suprapur HNO₃ at pH 2 and analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using a Horiba Jovin Yvon JV2000 2 spectrometer. Anions were determined in non-acidified samples by ion chromatography with a Dionex ICS 3000 Model. Duplicate blanks and laboratory water standards were analysed for quality control.

At the same site, ochre-precipitates were collected and stored in polyethylene containers protected from light until transport to the laboratory. The ochre samples were wet-sieved to obtain the fraction < 20 µm, using ultrapure water (Milli-Q) in order to remove impurities, and then dried at 40°C. Colour was analysed in dry samples by using Munsell system. The mineralogy was obtained by X-ray powder diffraction (XRD) using CuKa radiation at 40 kV and 30 mA. The ochre-precipitates were also submitted to heating at temperatures between 350 and 950°C following the procedure described in Brindley and Brown (1980) and applied by Valente et al. (2012). The morphology of the particles was studied by field emission scanning electron microscopy (FESEM), using a FESEM Jeol JSM-7001F microscope, equipped with an Oxford EDS light element detector at an acceleration voltage of 15 kV, after coated with chromium film. The chemical elements analysed in water were also determined in the ochre-precipitates by ICP-OES after digestion with aqua regia.

Blanks, replicates and stock solutions were used to assess quality control of the results. The accuracy of the methods was verified using certified patterns and the measurement...
precision was greater than 5% RSD. The chemical composition of water and ochre-precipitates represents an average of three replicate determinations. Metals and arsenic were analysed in the “Department of Earth Sciences, University of Coimbra, Portugal.”

**Results and discussion**

**Water chemistry**

Table 1 shows the properties of the water at the exit of the gallery and at the receiving creek. The first is circumneutral and reduced mine water with high concentration of Fe (18%). This high content of Fe is in accordance with the reducing nature of the source gallery (-61 mV). In general, the water creek reflects a decreasing trend relatively to the mine water, which is very clear for some elements, like Fe. The Eh values increase considerably (-61 to 125 mV), which can be associated with oxidation and hydrolysis of iron. As a consequence there is a strong decline in iron concentrations, associated with the precipitation of the ochre-products that are highly abundant immediately at the exit of the gallery.

**Ochre-precipitates**

XRD analysis reveals the low crystallinity of the ochre-precipitates (Figure 2-a). The XRD pattern allows identification of ferrihydrite, with the two weak and broad bands, at 2.56 and 1.47 Å, with the stronger band for the 11 and 30 hk reflections of 2-line ferrihydrite (Schwertmann and Cornell 2000, Schwertmann et al. 2004). Colour reference in the Munsell system (air dry conditions) was light brown, 5YR 5/6, which is in the range indicated for ferrihydrite (Dixon et al. 1977).

The thermal treatments are often used to understand transformation induced by dehydration on the iron phases. The sequence of XRD patterns in figure 2a-b shows such transformation. Ferrihydrite transforms in a poorly crystalline hematite at 350°C, which,

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**Figure 2** XRD patterns of ochre precipitates. a) Sequence of transformation until 550°C. b) Crystalline hematite (750°C) and Th-phase (750-950°C)

**Table 1** Water properties of the mine water (at the exit of the gallery) and downstream at the creek.

<table>
<thead>
<tr>
<th>Sample site</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>Eh (mV)</th>
<th>Fe (%)</th>
<th>Cu (µg/L)</th>
<th>Zn (µg/L)</th>
<th>Cd (µg/L)</th>
<th>Pb (µg/L)</th>
<th>As (µg/L)</th>
<th>U (µg/L)</th>
<th>Th (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallery</td>
<td>6.1</td>
<td>315</td>
<td>-61</td>
<td>18</td>
<td>10.46</td>
<td>22.75</td>
<td>79.23</td>
<td>17.43</td>
<td>64.77</td>
<td>43.99</td>
<td>19.66</td>
</tr>
<tr>
<td>Creek (n=6)</td>
<td>6.5</td>
<td>60</td>
<td>125</td>
<td>0.05</td>
<td>12.19</td>
<td>36.17</td>
<td>18.19</td>
<td>18.81</td>
<td>49.75</td>
<td>17.00</td>
<td>17.55</td>
</tr>
</tbody>
</table>
as expected, is finally perfectly crystalline at 950°C. Moreover, as observed by Valente et al. (2012), heating may lead to the formation of other compounds evolving due to specific elements that are adsorbed on the surface of the natural ochre-precipitate. In the present case, in coexistence with hematite at 950°C, the assay leads to the appearance of reflections compatible with the XRD pattern of a P and Th phase, specifically thorium nitride phosphide (PDF file 24-1321). This result is in accordance with the identification of the phosphorus element in the EDS spectrum obtained by FESEM (Fig. 3-a). Therefore, the EDS analysis confirms a composition compatible with an iron oxyhydroxide with minor amounts of phosphorus.

The images in figure 3 illustrate morphological aspects that suggest some structural order of the very small grained phases (<100 nm). There are globular aggregates, typical of ferrihydrite (Figure 3-a), but also filamentous and tubular structures, like hollow tubes with iron particles on their surface, as shown in Figures 3b-c. These tubular structures were previously documented for biogenic iron-rich precipitates (Peng et al., 2013, Ishihara et al., 2014), including schwertmannite in AMD (Valente and Leal Gomes, 2007). Figure 3-d shows also the presence of spherical nano-particles. Therefore, though XRD study indicates only the presence of natural ferrihydrite, FESEM images expose varied shapes, including the typical spherical morphology of hematite.

As stated by Fisher and Schwertmann (1975) nucleation of hematite from ferrihydrite is favored over goethite at neutral pH, which justifies the absence of this phase in the ochre precipitates. Thus, ferrihydrite in the ochres may represent different aging stages, and hematite could develop at expenses of the ferrihydrite aggregates.

Enrichment process
Table 2 presents the chemistry of the ochre-precipitates, indicating the dominance of

Figure 3 Morphology of ochre-precipitates. a) Globular aggregates typical of ferrihydrite and the EDS spectrum. b) General view of different morphologies. c) Detail of tubular structures marked in b). d) Detail of an area with spherical and globular morphology.
iron, in accordance with the presence of the iron-rich phases indicated by XRD and FESEM. The ratio between the dissolved elements and Fe in both water and ochre is also shown in table 2. Combining data in table 2 with the water chemistry (Table 1) it is possible to infer about the role of the ochre-precipitates in retaining PTE. An enrichment factor (EF) was also calculated through the relation between the concentrations in the solid and in the water (Munk et al. 2002). The EF, represented in Figure 4, shows that some dissolved elements, like U, may have strong affinity to the ochre-precipitates, occurring with concentrations up to tens of thousands orders of magnitude. High EF was also detected for Th and Pb (=7000). This affinity is in accordance with the ratios presented in table 2. Such results suggest the scavenging/sorption of PTE by the ochre. Also, co-precipitation of PTE like As and Cd along with iron may be occurring as a result of changes in redox conditions.

**Conclusion**

Ochre-precipitates from a U-Ra mine water are mainly composed by nanoparticles of ferrihydrite as revealed by XRD and FESEM. The analyses indicated a variety of morphologies, including tubular structures typical of biogenic iron products. Moreover, the study showed the coexistence of hematite, probably formed from evolution of ferrihydrite. In addition to Fe, other elements present in the mine water are enriched in the ochre-precipitates. Some of them show affinity to the ochre, as indicated by the high values of EF. Furthermore, the development of a crystalline Th, P-host phase, through heating experiments, suggests the possible adsorption/co-precipitation of these elements on the surface of the ochre-precipitates. In conclusion, the mixture composed of nanoparticles of ferrihydrite and hematite acts as sink of U and Th, as well as other PTE, like Pb and Zn, controlling their mobility in the mine water affected-system.

**Acknowledgements**

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| Table 2 Concentration of Fe (%) and PTE (mg/kg) in the ochre, and ratio (%) between PTE and Fe |
|----------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Fe     | As    | Cd     | Pb     | Zn     | Th     | U      |
| Concentration | 38    | 37.52  | 95.03  | 118.4  | 95.49  | 142.37 | 713.8  |
| ratio (water)   | -     | 0.346  | 0.423  | 0.093  | 0.121  | 0.105  | 0.235  |
| ratio (ochre)   | -     | 0.009  | 0.025  | 0.031  | 0.025  | 0.037  | 0.199  |


Hydrogeochemical and water cycle features of groundwater at a western arid coal mine in the Ordos Jurassic coal province, China

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Abstract
Xiaojihan coal mine, located in the east of the Ordos basin, is typical of the regional hydrogeologic background and commenced coal mining in 2014. To investigate water quality and water cycle features, 21 water samples were collected from underground aquifers for water quality tests, 14 samples for isotopes of D/18O and T tests, and 6 samples for 14C tests. The characteristics of the Jurassic aquifers are neutral pH, enriched in Na+, high concentration of SO42−, large TDS, and polluted with B and F. It was drawn that coal mining was inducing a much higher water connected zone than as expected and coal mining was dewatering and increasingly enlarging the depression cone in the Jurassic aquifers. It is urgent to limit the maximum height of water interconnected zone and control the further expansion of depression cone in the Jurassic aquifers.

Keywords: Hydrogeochemical, water cycle, the Ordos basin, China

Introduction
Nowadays, the Ordos Jurassic coal province of China is becoming the central bases of China coal industry (National Development and Reform commission 2016). Located in the arid western China, the Ordos basin is charactuerized as water scarce and ecologically fragile. The practical coal mining in the Ordos basin in the past decade encountered a series of challenges, including flowing sand catastrophes, unexpected coal-layer-aquifer water inrush, excessively large inflow drainage, super-thick overlying aquifers, etc. The disclosed mining hydrogeologic conditions are actually not as simple as it had been expected.

Xiaojihan coal mine, located in the east of the Ordos basin, is typical of the regional hydrogeologic background and commenced coal mining in 2014. Intially, the Xiaojihan cal mine had been viewed as hydrogeolical simple, but it was then classified as hydrogeologically medium complexity owing to a series of coal-fissure-aquifer water inrush. So far, it was frustrating the engineers again with a ceaselessly increasing mine water drainage. It is urgent to investigate the actual water cycle at the Xiaojihan coal mine. The purpose of this paper is to use hydrogeochemical methods to explore the signatures of groundwater and find the reasons for increasingly complicated hydrogeologic conditions at Xiaojihan coal mine.

Geologic settings
The main minerable coal beds at the coal mine lie in the upper part of the middle Jurassic Yan’an Formations (J2y), which are overlain by the middle Jurassic Zhiluo Formations (J2z) and Anding Formations (J2a), the lower Cretaceous Luohe Formation (K1I) and the Quaternary sand deposits. As reported by the detailed coal exploration, the type of mining hydrogeologic coditions at the Xiaojihan cola mine was calssified as simple with a limited mine water inflow from the overlying Jurassic sandstone aquifers.

However, as the earlier mine construction engineerings, including the ventilation shaft, main roadways and first trial longwall face etc., were drawing near or passing through the J2y cola layer, there unexpectedly happened a seires of serious waterburst. The maximum inflow from the fissured coal-layer aquifer at that time was up to 800 m3/h and the Xiaojihan coal mine was then re-classified as hydrogeologically medium complexity with a potential risk of rare fissured-coal-layer aquifer water inrush.
Nowadays, as more longwall faces were excavated and the mining panel went further western and deeper, the total mine water inflow didn’t decrease as expected but dramatically rose up from about 700m³/h in 2013-2015 to 1200m³/h in 2018. The practitioners were confused where the extra inflow was running out, especially worrying about whether the water-enriched K1l aquifers have hydraulic relationship with the underlying water-scarced Jurassic aquifers.

**Methods**

To investigate water quality and water cycle features, 21 water samples were collected from the underground aquifers for water quality tests, 14 samples for isotopes of D/18O and T tests, and 6 samples for 14C tests.

**Results**

Characteristics of water quality of the semicemented Jurassic aquifers at the Xiaojihan coal mine: (1) Neutral pH; The average pH of groundwater in the J2a, J2z and J2y aquifers was 7.5-7.7, obviously less than that in the K1l aquifer of 8.3; (2) Enriched in Na⁺; The Na⁺ concentration in the J2a, J2z and J2y aquifers was up to 330 ~ 550 mg/L, much higher than that in the overlying K1l aquifers of 31mg/L; (3) High concentration of SO₄²⁻; The concentration of SO₄²⁻ in the J2a, J2z and J2y groundwater was excessively rise up to 1000 ≈ 2800mg/L, accounting for 95% of its anions in meq and 60-70% of the TDS in mg/L; In comparison, the concentration of SO₄²⁻ in the K1l aquifer was only 18mg/L; (4) Large TDS; The TDS of groundwater in the J2a-J2y aquifers was high up to 1600-4300mg/L, whereas that in the K1l aquifers was no more than 350mg/L; (5) Scarce in Fe²⁺, Mn²⁺, H₂S and NH₄⁺, indicating an hydrogeologically oxygenic status in the J2a-y aquifers; (6) Uniform and narrowly ranged water type (Figure 1); The water samples in the J2a, J2z and J2y aquifers fell into the water types of Na-Ca-SO₄, Ca-Na-SO₄, and Na-Ca-SO₄ repsectively, distinctively different from the water type of Ca-Na-Mg-HCO₃ in the K1l aquifer and that of Ca-Mg-HCO₃ in the Q4 aquifer; (7) Apart from Na⁺ and SO₄²⁻ pollution, the water in the J2a, J2z and J2y aquifers was also with F (maximum of 1.77mg/L) and B maximum of 1.23mg/L pollution.

D/18O signature of 21 groundwater samples: (1) The δD of groundwater samples from the J2a , J2y, and J2y sandstone aquifers averaged -81‰, -83.5‰, and -84.5‰ respectively, and the δ¹⁸O of them averaged -10.28‰, -10.72 % and -10.78%; (2) the D/18O plot of these water samples from the J2a to the J2y aquifers was δD$_{v-SMOW}$ = 7.80·δ¹⁸O$_{v-SMOW}$ + 0.12 with R²=0.98, which was almost parallel with and beneath the local precipitation line; (3) The water samples from the J2a to the J2y aquifers was also with F (maximum of 1.77mg/L) and B maximum of 1.23mg/L pollution.

*Figure 1 Piper plot of the water samples from the Xiaojihan coal mine.*
The Jurassic aquifers are neutral pH, enriched in Na\(^+\), high concentration of SO\(_4^{2-}\), large TDS, and polluted with B, F and Mn\(^{2+}\). The hydrogeochemical reactions mainly include plagioclase weathering, carbonate rock weathering, gypsum dissolution, cation exchange, etc. It is the arid, oxygenic, and interpolate-lake sedimentary environment that was basically predominating the hydrogeochemical occurrence in the basin.

Water cycle features of the ground water at the Xiaojihan coal mine: (1) The J\(_2\)a, J\(_2\)z and J\(_2\)y formations stored more paleo-water, had a common/similar water origin, and had no direct hydraulic relationship; (2) The Jurassic aquifers actually stored much more amount of water than as expected; Though all the aquifers of the Jurassic had only very weak hydraulic connection, current coal mining was drastically dewatering the storage in the lower J\(_2\)z and J\(_2\)y aquifers, or even draining the upper J\(_2\)a aquifers as well; (3) From the hydrogeochcmical evidence, the K\(_1\)l aquifers have no direct hydraulic connection with the underlying Jurassic formations.

Being hard and fissured made the Jurassic coal layer the rather preferential water reservoir even than coarse sandsone. As Mining, much higher water connected zone was unexpectedly induced. More naturally inact aquifers got involved in the anthropogenically mining drainage. The depression cone of drainage aquifers was still unpredictably expanding.

**Conclusions**

The characteristics of the Jurassic aquifers are neutral pH, enriched in Na\(^+\), high concentration of SO\(_4^{2-}\), large TDS, and polluted with B, F and Mn\(^{2+}\). The hydrogeochemical reactions mainly include plagioclase weathering, carbonate rock weathering, gypsum dissolution, cation exchange, etc. It is the arid, oxygenic, and interpolate-lake sedimentary environment that was basically predominating the hydrogeochemical occurrence in the basin. Coal mining was inducing a much higher water connected zone than as expected, and coal mining was drastically enlarging the depression cone in the Jurassic aquifers. For the purpose of mining safety, it is urgent to limit the maximum height of water interconnected zone and control the enlarging depression cone in the Jurassic aquifers.

**Acknowledgements**

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References
PIT LAKES
Abstract

There are over 200 pitlakes in South Africa due to over two centuries of coal mining. The aim of this study is to determine if pitlakes are a sustainable coal mine closure option in South Africa. The study investigated the water balance, chemistry, limnology and bacteria of three selected pit lakes. The pitlakes occur in the three major coal basins of South Africa and are as a result of different mining methods. The major factors driving the water balance of the pitlakes are rainfall, runoff, groundwater and inflow from historical mine workings. The major losses from the pitlakes are evaporation or discharge of water on surface. The study proved that pitlakes can be designed to be terminal sinks and as a result a sustainable closure option in terms of the water balance. The groundwater chemistry showed the pitlakes to be stable with alkaline pH, mostly a sodium sulphate type water with total dissolved solid content of less than 3 000mg/L. The phytoplankton and microbiological data showed that the pitlake supported aquatic life. The study proved that with the correct design, coal mine pitlakes are an environmentally sustainable closure option for South Africa coal mines. A suggested design manual was developed to aid mine planners, owners and regulators to develop sustainable coal mines pitlakes as a closure tool.

INTRODUCTION

South Africa has been mining coal since the early 1800’s initially by conventional underground methods, but since the 1950s, the majority of the coal production has been from open cast mines. Coal supplies 95% of the South Africa’s power supply and this is predicted to continue into the latter half of the 21st century. South African coal production for power generation, export and domestic consumption is estimated at 255 million tonnes per annum. Open cast coal mines generally leave a final void because of the mining method, insufficient overburden to fill the voids created by removal of the coal and/or to manage water. Once mining operations cease these voids fill with water forming a lake which is generally referred to as a “pitlake”. The author has estimated that there are over 200 pit lakes in the three major South African coal fields namely the Witbank, Kwa-Zulu Natal and Waterberg Coalfields. The study evaluates the environmental sustainability of using pitlakes as a closure option for existing and proposed new coal mines in South Africa.

The major factors that determining environmental sustainability of pitlakes are the water balance and water quality. Positive water balances result in discharge of water from the pitlake onto surface. A further environmental sustainability consideration is the chemical and biological nature of the water in the pitlake. Pitlake water quality varies depending on the geology, mining method and catchment characteristics. In general, pitlake water quality may not comply with legislated catchment water quality standards resulting in potential threats to the overall catchment water quality. This investigation concentrated on the two major drivers of pitlake sustainability, whilst investigating 3 different pitlakes.

The pitlakes studied were selected on the basis that they are representative of the major South African coal fields considering variances in geology and climatic conditions. The factors affecting pitlake water balances (and as a result the variation in water levels) are groundwater, direct rainfall and
runoff, while the losses from the pitlakes are evaporation, surface discharge and flow into the surrounding aquifers. The water balances of each of the pitlakes were evaluated to determine the major inputs and losses. The major input free draining rehabilitated mines was found to be groundwater either from the aquifer or backfilled material. To a lesser extent water balance inputs were from runoff and direct rainfall. The major losses from the pitlakes was found to be evaporation. Pitlake morphology, volumes and surface area are the major design considerations to prevent discharge of pitlake water into the catchment. The chemical and biological evolution of the water quality in a pitlake determines the long-term ecological sustainability of pitlakes. The chemistry study concentrated on the water quality and vertical stratification. The vertical variation in pH, temperature, dissolved oxygen and the redox potential was measure at numerous points in each of the pitlakes. The organic study determined the phytoplankton, chlorophyll –a and the microbiology of each of the pitlakes.

The outcome of this study is that pitlakes can be environmentally sustainable if they are designed correctly and that the potential to discharge water into the catchment area is managed. The organic and inorganic water quality in the pitlakes showed that the pitlakes are alkaline and have elevated total dissolved solid contents (mainly calcium sulphate) when compared to the natural surface and groundwater in the catchment. The pitlakes support life in terms of chlorophyll-a, phytoplankton, microbiology (bacteria), vegetation and aquatic life.

The current South African mining and environmental legislation states that all pitlakes should be backfilled for the mine to achieve closure. This has considerable financial liabilities for old and ownerless mines, closed mines and current operations. Environmentally stable pitlakes offer a sustainable closure option and may avoid the expense of continual water treatment. A fundamental change in the current South Africa legislation is required to accept pitlakes as an environmentally sustainable solution. Enough data was collected in the study to allow for the development of a guideline for the design of coal mine pitlakes in the Southern African coal fields.

**PITLAKE WATER BALANCES**

Pitlake water balances in South Africa are largely controlled by evaporation as evaporation exceeds precipitation by a factor of 2 to 3. As a result, if the inflow into a pitlake is managed it is highly unlikely that it will discharge onto surface and into the catchment. The water balances of the pitlakes were calculated based on a generalized mathematical expression after Gammons et al., 2009)

\[
\Delta S = (P + SW + GWin) - (E + (T) + SWout + GWout)
\]

Where :\(\Delta S\) is change in storage which is the volume of water in the lake, \(P\) is the precipitation falling onto the pit lake, \(SW\) is the sum of any surface water inputs which includes runoff and diverted streams, \(GWin\) is groundwater entering the lake (which includes groundwater flow from historical workings), \(E\) is the evaporation the lake, \(T\) is plant transpiration which is often negligible, \(SWout\) is surface water discharge from the pit lake and includes pumpage, \(GWout\) is the groundwater leaving the pit lake. In the above equation if \(SW\) is managed by minimising runoff into the pitlake and \(GWin\) is minimised (by allowing groundwater levels to rebound). If evaporation exceeds the sum off all inflows into the pitlake and the pitlake will be a terminal sink.

**PITLAKE WATER QUALITY**

A major consideration is the final pitlake water quality after the closure of a mine. The pitlake water quality effects on the environmental classification and as a result the environmental sustainability of the lake. Conceptual models of pit lake geochemistry are described by external and internal processes, of which many of the internal processes are mediated by algae and microbes (Gammons et al., 2009). External processes are described as wall rock runoff and wall rock leaching. The quality of the inflows into the pitlake also affects the evolution of the pitlake water quality. Figure 1 summarises the processes that determine the chemistry in pit lakes.
CASE STUDIES
This study concentrated on 3 case studies namely Mafutha, Kriel and Rooikop pitlakes and the characteristics of the pitlake are shown in Tables 1 and 2 and Plates 1, 2 and 3.

Mafutha is single open pit where 250 000 tons of material was removed from a single 90m deep open pit. The pit is surrounded by an undisturbed aquifer and surface runoff into the pit is largely to runoff from the side walls. The pitlake has reached equilibrium where groundwater inflow and direct rainfall equal evaporation resulting in very minor seasonal variations in pitlake levels. The pitlake water in Mafutha is alkaline with a TDS of 1 000mg/L sodium chloride water.

The Kriel site comprises several hydraulically linked open pits due to extensive extent of the open cast mining. The pitlakes are hydraulic connection due to the highly permeable backfilled open cast material between the lakes. In this system the major inflows are due to direct rainfall, runoff and substantially greater recharge through the overburden spoils. Inflow exceeds evaporation and groundwater outflow, resulting in periodic outflow onto surface. The pitlake water is alkaline with a TDS of 3 500mg/L and is largely a sodium calcium sulphate water.
The Rooikop pitlake is hydraulically connected to the underground workings. Inflow is from groundwater recharge to the 100ha underground workings. The other major component of inflow is direct rainfall and runoff. The pitlake is alkaline with a total dissolved content of 1 200mg/L and water is calcium sulphate. The pitlake has a positive water balance and outflow occurs in the subsurface along the coal seam into pollution control dam which then discharges into a stream. The discharge into the stream does not comply with the water quality objectives of the stream.

<table>
<thead>
<tr>
<th>Table 1: Pitlake Physical Characteristics</th>
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<tr>
<td></td>
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<tr>
<td>Mafutha</td>
</tr>
<tr>
<td>Coalfield</td>
</tr>
<tr>
<td>Nature of pitlake</td>
</tr>
<tr>
<td>Mining method</td>
</tr>
<tr>
<td>Age yrs.</td>
</tr>
<tr>
<td>Surface Area (m²)</td>
</tr>
<tr>
<td>Pitlake Volume (m³)</td>
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<tr>
<td>Dominant inflows</td>
</tr>
<tr>
<td>Dominant outflows</td>
</tr>
<tr>
<td>Morphology (%)</td>
</tr>
<tr>
<td>Depth (m)</td>
</tr>
</tbody>
</table>

Plate 3: Rooikop Pitlake Nov 2017.
**Table 2: Comparison of pit lake chemistry, phytoplankton and microbiology (2016-2017)**

<table>
<thead>
<tr>
<th>Pit lake</th>
<th>Mafutha</th>
<th>Kriel</th>
<th>Rooikop</th>
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<tr>
<td>pH</td>
<td>8.4</td>
<td>8.4</td>
<td>7.9</td>
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<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>27.2 (epilimnion; summer)</td>
<td>20.6 (summer)</td>
<td>20 (summer)</td>
</tr>
<tr>
<td></td>
<td>18.6 (hypolimnion, summer)</td>
<td>13.5 (winter)</td>
<td>15.3 (winter)</td>
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<td></td>
<td>18.6 (whole pit lake, winter)</td>
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<tr>
<td>Dissolved oxygen (mg/l)</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>7.53 (Epilimnion summer)</td>
<td>R44: 2.03 (summer) &amp; 8.3 (summer)</td>
<td>7.9 (winter)</td>
</tr>
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<td></td>
<td>1.3 (hypolimnion summer)</td>
<td>5.7 (winter)</td>
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</tr>
<tr>
<td></td>
<td>6.95 (whole pit lake winter)</td>
<td>R42: 4.9 (summer) &amp; 8 (winter)</td>
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<td>TDS (mg/l)</td>
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<td>1208</td>
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<tr>
<td>Total Hardness (as mg/l CaCO₃)</td>
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</tr>
<tr>
<td></td>
<td>186</td>
<td>1210</td>
<td>712</td>
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<td>Sodium (mg/l)</td>
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</tr>
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<td></td>
<td>301</td>
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<tr>
<td>Total alkalinity (mg/l)</td>
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</tr>
<tr>
<td></td>
<td>326</td>
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<tr>
<td>Sulphate (mg/l)</td>
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<td></td>
<td>94</td>
<td>1930</td>
<td>608</td>
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<tr>
<td>Chloride (mg/l)</td>
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</tr>
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<td></td>
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<td>Nitrate-NO₃ (mg/l)</td>
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<tr>
<td></td>
<td>9.7</td>
<td>0.24</td>
<td>&lt;0.1</td>
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<td>Water type classification</td>
<td>Na-Cl</td>
<td>Na/ Ca-SO₄</td>
<td>Ca-SO₄</td>
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<tr>
<td>Chlorophyll-a (µg/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.5</td>
<td>3.7</td>
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<td>Trophic state classification</td>
<td>Oligotrophic</td>
<td>Mesotrophic to Eutrophic</td>
<td>Oligotrophic to Mesotrophic</td>
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<tr>
<td>Phytoplankton (Dominating Phylum, Genus)</td>
<td>Chlorophyta, Ankistrodesmus</td>
<td>Cryptophyta, Cryptomonas and Chlorophyta, Ankistrodesmus</td>
<td>Chlorophyta, Chlorella</td>
</tr>
<tr>
<td>Phytoplankton (Dominating Phylum, Genus)</td>
<td>Chlorophyta, Ankistrodesmus</td>
<td>Cryptophyta, Cryptomonas and Chlorophyta, Ankistrodesmus</td>
<td>Chlorophyta, Chlorella</td>
</tr>
<tr>
<td>Microbes (Dominating Phylum; Genera)</td>
<td>Proteobacteria; Acinetobacter, Synechococcus</td>
<td>Proteobacteria; Hydrogenophaga, Chlorobaculum, Pseudomonas, Nodularia</td>
<td>Bacteriodetes; Flavobacterium, Luteolibacter</td>
</tr>
<tr>
<td>Stratification &amp; mixing</td>
<td>Strong thermal stratification (October to March/ April) Turnover (late autumn/ winter)</td>
<td>Weak thermal stratification (October to March/April) Turnover (late autumn/ winter)</td>
<td>Weak thermal stratification (October to March/April) Turnover (late autumn/ winter)</td>
</tr>
<tr>
<td>Classificationa</td>
<td>Slightly alkaline, low TDS, Holomictic, monomictic</td>
<td>Slightly alkaline, high TDS Holomictic, monomictic</td>
<td>Circum-neutral, low-TDS Holomictic, monomictic</td>
</tr>
</tbody>
</table>

---

*a Trophic state classification according to De Lange et al. (2018). Only September data for Rooikop and Kleinfontein.

b Classification of pit lakes according to Eary (1999) and Boehrer and Schultze (2008)
The chemistry of the three pitlakes is shown in Figure 1.

DISCUSSION

The pit shape is important from a water balance and water quality point of view based on the following reasons:

- Large surface area compared to mean depth, linear/elongated pit lake morphology. These pit lakes are more prone to effects of evaporation and evapo-concentration. Larger surface areas provide larger areas for evaporation, with lower potential for discharge/overflow and ensure a groundwater gradient towards the pit lake, to act as a hydrological sink. This is evident in the Mafutha pitlake where the pitlake is in equilibrium between inflow and outflows. See Figure 2.

- Small surface area to mean depth ratio or cone shaped pit lakes. These pit lakes tend to form an isolated bottom layer, called the monimolimnion, with inferior water quality to the rest of the lake. If the chemistry and physical structure of the pit lake is stable, the isolated layer may be beneficial to detain potentially toxic metals. Conversely, an isolated layer may not be desirable, as sudden storms events may erode the chemocline and cause this layer to turnover together with the top layers, and mix poor, metal rich water through the whole water column with deleterious effects on overall water quality.

ARE SOUTH AFRICAN COAL MINE PITLAKES AN ENVIRONMENTALLY SUSTAINABLE CLOSURE OPTION?

The use of pitlakes in the South African coal mine as an environmentally sustainable closure option must consider the following aspect which should be incorporated into the closure design.
Water Balance

It is critical that the sum of the inflows into the pitlake is less than evaporation to prevent major changes in pitlake water levels. Positive pitlake water balances result in discharge onto surface. Negative water balances result in pitlake being a terminal sink. As a result, a carefully designed pitlake where the inflows equal the outflows will result in a stable pitlake which will not discharge onto surface. The morphology is a critical factor in determining the environmental sustainability of a pitlake.

Water Quality

The South African pitlake studied are all alkaline with variable dissolved solids contents which support phytoplankton, microbes, vegetation and aquatic life. Although the water quality may not comply with the catchment water quality objectives, the pitlake is environmentally sustainable. Pitlakes are an environmentally sustainable closure option in South Africa if designed to have a marginally negative water balance to act as a sink. The water quality

Summary of Pitlake water balances

<table>
<thead>
<tr>
<th>Pitlake</th>
<th>Inflow</th>
<th>Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mafutha</td>
<td>Groundwater 90% Runoff 2% and direct rainfall 8%</td>
<td>Evaporation 100%</td>
</tr>
<tr>
<td>Kriel (average of 4 pitlakes)</td>
<td>Groundwater 43% runoff 17% direct rainfall 40%</td>
<td>Evaporation 100% for most years</td>
</tr>
<tr>
<td>Rooikop</td>
<td>Groundwater 58% Runoff 11% direct rainfall 37%</td>
<td>Evaporation 90% discharge 10%</td>
</tr>
</tbody>
</table>

Figure 2 Mafutha Pitlake: Water level rebound and chemistry
shows that the pitlakes are stable and able to support aquatic life.

CONCLUSION
The surface area of a pitlake is vitally important in order to maximise evaporation which directly affects the water balance. In addition, surface runoff should be controlled to avoid excess flow into the pitlake during storm events that may lead to a temporary positive water balance and uncontrolled discharge into the catchment. Should the pitlake to suitably design it forms a water sink to prevent uncontrolled discharge from the mining operations.

The water quality in the pitlakes are alkaline with evaluated dissolved solid content but is able to support chlorophyll-a, phytoplankton and bacteria. Although this may not comply with catchment water quality standards is support a stable ecosystem.

Correctly design coal mine pitlakes are a sustainable closure option for South African coal mines in South Africa. It is recommended that the current South African legislation be reviewed in order to accommodate pitlakes as a sustainable closure option.

REFERENCES


Sedimentation Rates In Two Pit Lakes: Implications For Riverine Flow-Through As A Closure Strategy.

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Abstract
Lack of organic matter inputs into a pit lake inhibits ecological development. Connecting a river to a pit lake should add organic matter to the lake. Sedimentation traps and sediment sampling was undertaken in two co-occurring pit lakes: one with river flow-through (Lake Kepwari) and one without (WO5H) in Collie, Western Australia.

Carbon in the sediment did not vary between lakes or depths. Sedimentation rates did not vary between lakes during low/no river inflow periods. River inflow did increase sedimentation but without increasing allochthonous inputs of C. Even with river inflow C accumulation in the lakes remains very low.

Keywords: carbon, organic matter, succession, AMD

Introduction
Blanchette and Lund (2016) proposed that natural evolution of pit lakes towards becoming lake ecosystems was dependent on carbon accumulating in the lake faster than it was being lost. When natural lakes form through asteroid strike, flooding of craters or from glacial action, the initial sediment at the bottom of the lake is largely devoid of organic matter, similar to the material at the bottom of pit lakes. As newly created natural lakes evolve they accumulate organic materials from external (allochthonous) or internal sources (autochthonous) that as it settles out at the bottom creates sediment. The organic materials in the sediment provide food sources for microbial activity, binding and release sites for nutrients and alter the physico-chemical properties of the sediment. In pit lakes, the development of sediment is similarly important, however low nutrient concentrations, potentially toxic waters, and low pH can all individually or together limit primary production within the lake. Further, small catchments and poorly developed riparian zones reduce external sources of organic matter (Lund and McCullough 2015). Despite studies examining carbon accumulation in sediment of pit lakes such as Laskov et al. (2002), the effect of increased catchment size on allochthonous inputs of carbon into pit lakes has not been measured. This study aimed to test whether river flow through a pit lake, which can effectively dramatically increase the lakes catchment, results in increased carbon input into the sediments – which were examined through sediment sampling and measurement of sedimentation rates.

Methods
Study Sites
The Collie coal basin in Western Australia contains over 10 pit lakes formed from prior open-cut coal mining (Lund et al. 2012). The largest of the Collie pit lakes is Lake Kepwari (98 ha, 65 m deep), it is circumneutral and slightly saline (≈2.4 mS cm$^{-1}$) (Lund and Blanchette 2018b). The Collie River South Branch had been diverted to allow mining to occur. The lake water level was established under a rapid fill programme whereby river water was diverted to the mine void during periods of high flow. This had the added advantage of managing acidification of the lake by preventing further oxidation of sulphides in the exposed coal seams. The lake water level was then to be maintained by seasonal top-up of the lake under high river flow conditions, with no discharge
from the lake. Following an accidental river inflow (McCullough et al. 2012) government approval was given to connect the river to the lake, initially as a 3-year trial. A key conclusion of the trial was that flow through is the preferred closure strategy for Lake Kepwari. A revised closure plan includes backfilling of the diversion channel and permanent uncontrolled inlet and outlet structures to allow the river to flow unimpeded through the lake. WO5H is the second largest Collie pit lake and the deepest (44 ha, 85 m deep). WO5H is used to manage water runoff from the mine site and is used as third party water supply; discharge is prevented by use of lake water by a nearby power station for cooling. Water levels within WO5H can vary by 1 m over short periods. WO5H is acidic (pH 2.6-3.5), and slightly saline (≈2.4 mS cm$^{-1}$). Both lakes have had their catchments revegetated and contourd. Neither lake has riparian vegetation (although some is starting to grow in Lake Kepwari), although in WO5H planting of upland vegetation below the final water level (now dead) probably improves bank stability.

Collie is situated in an area of Mediterranean climate, with hot, dry summers (range 11.7–30.5°C) and cool, wet winters (range 4.2–16.3°C) (Commonwealth of Australia, Bureau of Meteorology (BOM) 18/5/2018). Seventy-five percent of the rainfall occurs during the five months from May to September (Figure 1). The 100-year mean annual rainfall for the Collie Basin is 933.1 mm, (BOM) 18/5/2018), although this has decreased to an average of 731 mm over the last 15 years. Evaporation rates for the
area are not routinely measured by the BOM weather stations in the region, but it supplies an atlas of potential evaporation rates.

Total annual rainfall in Collie between 2004 and 2018 ranged between 390 mm (2010) and 902.2 mm (2005) (fig 1).

**Sampling**

A single set of sediment traps made of plastic cylinders were deployed in centers of WO5H and Lake Kepwari for 30 days in September 2016, 42 days in September/October 2017, and 23 days in September/October 2018. Groups of 3 duplicate cylinders (0.98 m long, 80 mm dia.) sealed at the bottom were attached to a 50 m rope, at depths of 10 m, 25 m and 40 m representing top, middle and bottom of the water column (Bloesch and Burns 1980). The vertical cylinders were attached so as to maintain a distance of approximately 0.2 m from each other thereby minimising contamination from any algal growth that might occur on the rope. The rope was anchored to the sediment with approximately 15 kg of weights, and a buoy was mounted about 2 m from the water surface to hold the cylinders vertically in the water column. A second free-floating buoy on the surface allowed the traps to be located (fig 2). Additionally in 2018, at 3 approximately equidistant sites around the edge of each lake, a set of 3 duplicate sediment traps were set at a 5 m depth in a water depth of 10 m – they were treated and designed as per the central tubes. At the end of the experiment, the entire set of traps was removed from the lake and each cylinder was immediately capped upon collection.

After collection, each cylinder was shaken for 10 seconds in order to homogenise any captured sediment and then a subsample of 0.5 L was filtered through 0.5 µm pre-weighed glass fibre filter paper (Pall Metrigard, USA) for later determination of dry weight (DW) according to methods described by APHA (1998). Once dry the filter papers were burnt for 1h at 550 °C to allow for determination of loss on ignition (LOI). Carbon content was estimated from LOI by dividing by 2 as per Pribyl (2010).

Five random (approximately equidistant) sediment samples were collected from <10 (shallow), 10-20 m (intermediate) and >20 m (deep) water depths in each lake. Sediment was collected in 2016 using an Ekman dredge and Peterson sampler (Wildco, Fl, USA) and in 2018 using a Standard Ponar sampler (Wildco, Fl, USA). Sediment samples consisted of ~0.5 L of the top 100 mm of sediment. In the laboratory, the sediment sample was manually homogenised and then ~25 ml of sediment (3 duplicates) was taken and dried to constant weight at 60 °C and then burnt for 1 h at 550 °C for determination of LOI.

**Data Analysis**

Groups of three cylinders were averaged (where data for a cylinder varied by >50% from the other cylinders for dry weight or LOI that data was excluded from the average as an outlier). There was no replication of the central cylinders so no statistics were undertaken, however edge samples were replicated and tested for difference using One way ANOVA (SPSS v24, IBM). Three way ANOVA (fixed factors) was used to compare sediment C between depths, lakes and years. Data was transformed as required to achieve homoscedasticity as determined by the Levene’s Test (for the sediment C, homoscedasticity was not...
Results and Discussion

The carbon content of sediments from Lake Kepwari and WO5H were measured in 2016, and 2018, there was a significant difference (P<0.05) between years and depths, but not between lakes and the interaction (years x depth) was also significant. The estimated marginal means for depth and lake show that the interaction occurred as C content in deep sediment decreased slightly between 2016 and 2018 (respectively for WO5H and Lake Kepwari %C was in 2016, 6.8±0.5 and 5±0.9 and in 2018, 6.4±0.5 and 3.8±0.9), while increasing in the shallow (0.5-0.7 to 3.4-3.8 %C 2016 to 2018) and no real change in the intermediate zone (3.4-4.6 %C in 2016 to 3.7-4.1 %C in 2018). In 2012, the shallow zone of Lake Kepwari had a mean of 1.1%C, which was the lowest of another 4 Collie pit lakes sampled (2.0 -12.0%C)(Lund et al. 2014). The 2012 sediment samples were collected by diving and focused on the surface layer, therefore provide a more accurate assessment of C content, as compared to the bulk collections used in 2016 and 2018 where surficial organic matter can get washed out of the sampler as it is being hauled to the surface and the top 100 mm was homogenised together potentially lowering the %C measured. Therefore the difference in shallow sediment %C from 2012 to 2018 probably represents an important increase in organic matter accumulating. Since partial river flow through Lake Kepwari commenced in 2013, submerged plants (predominantly Chara spp) were observed in the shallows and are likely to be contributing to C accumulation in the sediment (Lund pers. Obs.).

The similarity between lakes, in %C in the sediments did not appear to reflect the observed organic layer visible on the surface of Lake Kepwari sediments. WO5H sediments were also found to contain coal.

![Figure 3](image-url)

**Figure 3** Sedimentation in WO5H and Lake Kepwari pit lakes in September/October of 2016 - 2018, as mean (based on 3 duplicates) a) dry weight (g m⁻² d⁻¹), b) carbon content (g m⁻² d⁻¹) and c) organic matter (%LOI) at three depths.
fines (which were removed when possible) but this may also have increased the %C in these sediments. Estimating from the accumulations of sediment in the sediment traps at 40 m deep, there appears to be a depositional rate of approximately 0.5 mm per month in both lakes. Therefore the depth of sediment that is likely to have accumulated since river inflow started is 20 to 30 mm. The sediment collection methodology integrated at least the top 100 mm together effectively diluted the organic accumulation by a third which may explain why no significant difference was found between lakes. Further investigation of the pit lake sediments identifying sources and lability of the carbon such as the approach of Laskov et al. (2002) may be useful in separating the lakes.

In a study of 40 natural wetlands in Perth (Western Australia), %C as determined from LOI ranged between 0.8 to 40.8% with a mean of 16% suggesting that the pit lakes while at the lower end of %C range were within the range of natural lakes (Davis et al. 1993). The lack of anoxia in the bottom of both lakes during stratification (Lund, unpublished data) may also limit C accumulation in the sediment as the carbon may be consumed by oxidative processes (see Radbourne et al. 2017).

The lakes were stratified at the time of sampling, however it was just re-establishing after the annual mixing (warm monomictic) and the epilimnion extended to about 7 m with the hypolimnion starting at 10 m in both lakes (unpublished data; Lund and Blanchette 2018a). Sedimentation rates (DW) were generally lower with water depth in both lakes and years, indicating little re-suspension of bottom sediments (fig 3). Low re-suspension is not surprising given the substantial water depth (Bloesch, 1995). Rainfall during deployment of the sediment traps could be responsible for differences between years as suggested by Axler et al. (1998). In 2016, there was 94 mm (daily maximum of 11.8 mm) of rainfall, in 2017, 104.8 mm (max. 34 mm) and in 2018, 44.4 mm (max. 17.6 mm). Aside from the direct effect of rainfall on surface runoff, additionally in Lake Kepwari this would also increase river inflow (which was minimal in 2018 during the sampling period). River flow through in 2016 and 2017 does appear to generally result in higher rates of sedimentation in Lake Kepwari compared to WO5H (fig 3a). In 2018, there was no apparent difference between the two lakes and overall sedimentation was lower than previous years. The intense rainfall event of 2017 were associated with lower rates of DW sedimentation compared to 2016, and in WO5H there was no difference apparent between DW sedimentation rates in 2017 and 2018 suggesting that rainfall was not directly responsible for altering sedimentation rates assuming that particles settle quickly so that antecedent conditions are not important.

Sedimentation rates (DW) were low compared to Kalin and Wheeler (2013) who found DW sedimentation rates for a circumneutral uranium pit lake in Canada to be 28.7 g m⁻² d⁻¹ in 1992 before dropping to 2 g m⁻² d⁻¹ in 1999. However, in shallow Polish natural lakes, DW deposition rates of 0.521 g m⁻² d⁻¹ (equivalent to 2-3 mm deposition per year) were recorded (Gąsiorowski, 2008) which are similar to those noted in Collie. In a pit lake used for aquaculture (Twin City-South pit lake, MN, USA) sedimentation ranged from 0.5-6 g m⁻² d⁻¹ with the highest values associated with localised flooding (Axler et al. 1998). In April 2013, Lund et al. (2014) using identical sedimentation sampling methods as this study measured very similar rates of DW sedimentation between WO5H and Lake Kepwari and over depth at 0.15 – 0.45 g m⁻² d⁻¹. April 2013 was a very dry month in Collie with 0.4 mm rainfall during sample deployment and no river inflows into Lake Kepwari, suggesting that these DW sedimentation rates are due to wind induced erosion of the banks and pit lake side walls, airborne particulates from soil erosion, and biological production. In 2017, the 40 m deep sample in Lake Kepwari had a very high sedimentation rate at 6.1 g m⁻² d⁻¹ compared to other depths and WO5H, this was not matched by a high organic matter (OM) content so that algal biomass was not responsible – the cause is not known. Lund and Blanchette (2018a) noted for Lake Kepwari (2014-2016) that Total N concentrations in the river inflow compared to river outflow whilst similar differed in that the inflow was
dominated by organic/particulate N and the outflow by NOx suggesting deposition of those particles within the lake. OM content of the depositional material was high variable between years and lakes, there appears to be no difference between WO5H and Lake Kepwari in terms of OM content. There is no evidence that river inflow has resulted in a substantial increase in autochthonous C production through inputs of nutrients.

The 2018 edge samples were not significantly different (P<0.05) between lakes for OM, %C and DW, with OM content similar to the centres of the lakes at 20.0±2.2 and 21.6±2.6 % for WO5H and Lake Kepwari respectively. Edge sedimentation as DW was similar to the centre of WO5H (10 m) at 2.1±0.6 g m⁻² d⁻¹ but higher than the centre of Lake Kepwari at 1.9±0.5 g m⁻² d⁻¹, with C showing the same trend at 0.2±0.1 g m⁻² d⁻¹ for WO5H and Lake Kepwari. The higher surface area of Lake Kepwari increases wind fetch potentially increasing resuspension in the shallows compared to the centre of the lake.

In WO5H and Lake Kepwari, although sediment depositional rates were low, it has been previously speculated by Phillips et al. (2000) that sedimentation may be sufficient to continually bury secondary minerals reducing the chances of re-oxidation. Axler et al. (1998) found that organic matter produced by aquaculture in a pit lake was rapidly buried following localised flooding, allowing the lake to recover from the eutrophication effects of aquaculture. Sedimentation rates and accumulation of organic matter in the sediments are important drivers of aquatic processes in pit lakes and warrant further investigation.

Conclusions

Rates of sedimentation in Collie pit lakes are similar to those identified in other pit lakes worldwide, however river flow through in Lake Kepwari resulted in higher rates. The higher rate of sedimentation during river flows appears to be predominantly associated with inorganic particulates rather than the river catchment substantially contributing to an increase in allochthonous C. Despite the neutralisation of Lake Kepwari by river flow through and the continual input of nutrients from river water this does not appear to have resulted in a substantial change in autochthanoous C production, except in the littoral area. This experiment suggests that despite river flow-through it will take many years before C levels in Lake Kepwari are sufficient to substantially alter the biology of the lake.

Acknowledgements

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Acid Mine Drainage Pollution at the Tharsis Mines (Iberian Pyrite Belt): A Serious Environmental and Socioeconomic Problem

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Abstract
The Tharsis mining district belongs to the Iberian Pyrite Belt (IPB), which is rich in massive sulphide deposits. Large-scale mining began in 1866 and continued until 2001, leaving a large area of sulphide-rich dumps, soils affected by mining and 4 pit lakes containing 5.2 hm$^3$ of acidic waters. The acid mine drainages (AMDs) generated in this area cause a serious environmental and socio-economic problem by producing severe pollution of 115 km of river courses, 58 hm$^3$ of reservoir waters and compromising the water quality of another large reservoir (246 hm$^3$) under construction. Measures to reduce the pollution levels should be taken.

Keywords: Water pollution, sulphides, abandoned mines, pit lakes

Introduction
The Tharsis mining district is located in the IPB, specifically in the province of Huelva (SW Spain). The area has gentle relief, with altitudes between 150 and 362 m. The climate is Mediterranean, with an average rainfall close to 600 mm. Most rainfall occurs in autumn and winter while summers are hot and dry. There is also a great interannual variability in rainfall. The most important streams are the 1) Aguas Agrias creek, which drain to the east and flow into the Oraque River and 2) various streams flowing to the south joining finally the Meca River, regulated in its final reach by the Sancho Reservoir (58 hm$^3$ capacity). Both the Meca and Oraque Rivers belong to the Odiel River basin.

The IPB is very rich in massive sulphide deposits; among them the Tharsis mines is one of the most important, with estimated original sulphide reserves of 133 Mt (Tornos et al. 2009). Exploitation began, on a very small scale, around 4500 years ago. During the Tartessian civilization and the Roman period, extractions were increased through underground mining. After the Roman period followed a long time with little mining activity until 1866, when mining suffered a great development, on an unprecedented scale in the region, in order to obtain copper. At that time, open-pit mining began in Filón Norte and later in Sierra Bullones and Filón Centro (Fig. 1). Underground mining also continued, mainly in the Sierra Bullones area. From the beginning of the 20th century, once the Cu-rich enrichment zone was exhausted, the main objective of exploitation became sulphur for the manufacture of sulphuric acid. In addition, between 1937 and 1964 exploitation of the gossans from Filón Sur to extract gold and silver by cyanidation took place (Tornos et al. 2009). In 1966 the underground mining in Sierra Bullones was definitively abandoned, after 100 years of intense exploitation. From then on, open-pit mining restarted in the Filón Norte open pit until the end of the 90s. Finally, between 1990 and 2000 exploitation resumed in Filón Sur to obtain gold and silver from the gossan. The Tharsis mines have been the second most important of the IPB, after the Río Tinto mines. Since 1866, 40 Mt of sulphides have been extracted (Tornos et al. 2009), to which should be added another 5 Mt from Roman and pre-Roman times (Moreno González et al. 2018).

The sulphide-rich wastes generated in the area produce numerous acid leachates in contact with rainwater and atmospheric
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oxygen. These acidic waters end up in the streams of the area causing their pollution. The main goal of this paper is to show a global perspective of the serious problems that exist in this zone, after the total cessation of mining activity in 2001 and propose some lines of action to improve the situation.

Methods

A cartography of the surface affected by mining has been made, classifying dumps based on pollutant potential. Two samplings in different hydrological conditions (dry and wet periods) were carried out in the mining area to collect acidic leachates from the main AMD sources. When possible, the discharge of the sources were measured with a current meter. Two small reservoirs located in the mining area and the flooded open pits (Fig. 1) have also been sampled. Samples were filtrated through 0.45 μm Millipore Teflon filters, acidified with HNO₃ suprapur to pH<2, and kept in the dark at around 4°C until analysis. Temperature, electrical conductivity (EC), redox potential and pH were determined in the field with portable meters. The instruments were calibrated and checked against certified standards. Analyses were performed using ICP-OES and ICP-MS. Different elements were determined but here only Al, Cu, Fe, Mn, Zn, As, Cd, Co, Pb and sulfate will be shown.

Results

There is an area of 3.94 km² affected by mining, mainly covered by spoil heaps (2.44 km²), open pits (0.85 km²) and mine soils (0.54 km²). The dumps have been classified into 5 different types:

1. Spoil heaps composed mainly of sulphides (Fig. 2), the most important being to the northeast of Filón Norte and to the east of Corta Esperanza (Fig.1). They are very large, with altitudes of up to 80 m, and produce the higher loads of acidic waters.
2. Mixed dumps with different types of materials, including sulphides. They are smaller in size and also have less polluting potential due to their lower sulphide content.
3. Dumps of roasted pyrite ashes, wastes coming back from factories where the

Figure 1 Map of the Tharsis mining district showing the affected streams and the main AMD sources.
ore was transported for the extraction of sulphuric acid. These dumps have some isolation measures and generate relatively few acid leachates.

4. Gossan heap leaching wastes from the treatment of gossan by cyanide to obtain gold and silver. They are located to the east of the mining area and do not produce substantial acid leachates.

5. Revegetated spoil heaps, located to the east of the urban area. Its original topography has been remodelled to give them a more natural appearance and has been covered with soils that allows the growth of vegetation. Visually these areas are in good condition. However, there are no isolation measures to prevent the infiltration of rainwater and the influx of atmospheric oxygen, so that some AMD sources exist (Fig. 1).

Besides that, in the area there are 5 open pits, one of which is filled by mining wastes (Corta Esperanza, Fig. 1). The other 4 are partially flooded with acidic waters with high concentrations of metals and metalloids (Sánchez España et al. 2008). The water level in the Filón Centro and Filón Sur pit lakes is stabilized, while in Filón Norte and Sierra Bullones, connected by underground galleries, is rising at an average rate of 2.8 m/year (Moreno González et al. 2018). The volume of stored acidic water was 5.2 hm³ in 2016, most of it (3.6 hm³) is found in Filón Norte. In total, the dissolved metals in the pit lakes are close to 9000 t of Fe, 1000 t of Al and Zn, etc. (Moreno González et al. 2018). On the other hand, in the mining area there are also two shallow reservoirs that are slightly affected by acid leachates and have pH values between 4 and 5. The largest is the one located to the north, with a surface area of 0.27 km² (Fig. 1).

There are about 30 AMD sources which cause the severe pollution of surrounding streams (Fig. 1), although some are temporal and dry out during the summer. Table 1 summarizes the values obtained from the samplings. Flow rates ranged from less than 0.1 to 13 L/s in the wet season, while in the dry season the maximum flow rate was 2.5 L/s. The average pH values are close to 2.5, with some values close to zero or even negative (-0.2). The EC values are between 1 and 70 mS/cm, with mean values between 12 and 14 mS/cm and median between 6 and 9 mS/cm. The concentrations of metals and metalloids are also very high, with maximum values of 194 g/L of Fe, 11 g/L of Zn, 8 g/L of Al and 2.3 g/L of As. These extreme values are reached in seepages from dumps composed almost exclusively of sulphides, which give rise to precipitates with spectacular melanterite crystals. More representative are the median data, with values of 668 - 412 mg/L for Fe (dry and wet samplings), 494 - 369 mg/L for Al and 0.3 - 1.3 mg/L for As (Table 1). Median concentrations are higher in the dry period sampling except for As and Pb, which have higher values in the wet sampling.

During periods without rainfalls, especially during the summer, the evaporation of acid waters with high concentrations of metals and sulfate produces the precipitation
of large amounts of evaporative salts throughout the mining area (Fig. 2) and on the margins of the affected courses (Valente et al. 2013). These salts are washed quickly with rainfalls following a prolonged dry period, causing a large increase in the concentration of metals and metalloids in the water.

Figure 3 summarizes the pollutant loads released by the AMD sources. The highest loads are found in winter, when flows are much higher. The amount of pollutants released by some of these sources is extreme (e.g. up to 6.8 t/day of Fe, 1.3 t/day of Al and 39 kg/day of As). The median values, although notably lower, are also very high for the wet period sampling.
The largest pollutant loads come from the large sulphide-rich dumps located to the east of Corta Esperanza and, especially, to the northeast of Filon Norte (Fig. 1). These contributions have a profound effect on the Aguas Agrias creek, which flows westwards into the Oraque River, which also receives pollutants from other mines located in its basin (Olías et al. 2011). On the other hand, acid leachates from AMD sources in the south and west of the area flow southwards through several streams and join the Meca river (Cánovas et al., 2017). As a result, 115 km of watercourses are heavily polluted, in most cases with pH values of less than 3 and high concentrations of metals and metalloids.

The Meca river is regulated by the Sancho reservoir, the largest in the Odiel basin with a capacity of 58 hm$^3$. Due to the acid contributions received, the water stored in this reservoir has a pH close to 3.5 and substantial concentrations of toxic elements (e.g. 4.4 mg/L of Al and 1.9 mg/L of Zn). In addition, there is a trend of worsening attributed to the rebound effect after the mine closure in 2001 (Cánovas et al. 2016). There is a great interest for using this water for irrigation, but the necessity to build a neutralization plant and its high maintenance cost compromise its feasibility.

Downstream of the confluence between the Oraque and Odiel Rivers, a new reservoir of 246 hm$^3$ of capacity is being built. Both the Oraque and Odiel rivers are heavily contaminated by AMD. According to the reservoir project, the water will have a neutral pH and good quality. However, according to estimates by Olías et al. (2011), if measures are not taken to eliminate the main sources of acidic waters, the reservoir will have conditions similar to or worse than those of the Sancho reservoir.

The acidic waters of the Tharsis mines finally flow into the Odiel River, also contaminated by other mines, which in turn flows into the estuary of the Huelva Estuary. The estuary receives a large quantity of metals and metalloids transported by the rivers Tinto and Odiel, consequently producing an important contamination in this coastal system (Nieto et al., 2007).

In summary, the Tharsis mines constitute one of the most polluting in the IPB, producing a total degradation of the Aguas Agria creek, a tributary of the Oraque river, and of numerous streams of the Meca river basin, and contribute to the important contamination by metals and metalloids of the estuary of the Ria de Huelva. In addition, acidic waters compromises the possibility of using the water of the reservoirs in the area. Consequently, actions are urgently needed to improve conditions and to reduce the levels of pollutants emitted.

The very high concentrations of metals in the Tharsis AMD sources mean that the passive treatment methods usually used to treat AMD (wetlands, anoxic limestone drains, reducing systems and alkalinity producers, etc.) cannot be applied. For these waters, with extreme concentrations of Fe, Al and other metals, the DAS –Dispersed Alkaline Substrate- technology has been developed (Ayora et al. 2013). This method is based on passing the acidic water through reactive tanks filled with a mixture of: 1) fine grained limestone, in order to obtain a high specific surface area and avoid the passivation by a layer of iron precipitates, and 2) an inert material (wood shavings) to give a high porosity and permeability to the system, to avoid clogging problems due to the precipitation of the large quantity of metals contained in the acidic waters (Ayora et al. 2013). The accumulation of rare earth elements and yttrium (REY), elements of high technological and strategic interest in a specific part of the reactive tank when pH values are close to 5, could contribute to financing, at least partially, the maintenance costs of DAS plants (Ayora et al. 2016).

This technology is being successfully used in two passive treatment plants built at the Esperanza and Concepción mines, also located in the Odiel basin. However, the high flow values together with the high concentrations of metals from the AMD sources of the Tharsis mines would require the construction of huge reagent tanks or frequent replacement of the limestone-wood shaving mixture. It would be therefore necessary to combine the construction of DAS
plants with the isolation of the most sulphiderich tailings to reduce the amounts of acidic waters generated. Another possibility would be the construction of an active neutralisation plant, but this option does not seem viable due to its high maintenance costs, which would have to be paid indefinitely.

Conclusions
The extractive activity in the Tharsis mines ceased completely in 2001, but the acidic waters generated by the waste generated during 140 years of mining continue to pose a serious environmental and socio-economic problem in the area. The affected surface is close to 400 ha. Different types of spoil heaps have been differentiated, the ones with the greatest polluting potential are those that are fundamentally constituted by sulphides, some of which are up to 80 m high. There are around 30 main sources of acid mine drainage with discharges between 0.1 and 13 L/s, pH values lower than 3, electrical conductivity values ranging from 1.0 to 71 mS/cm and high concentrations of Fe (up to 194 g/L), Al (up to 8.1 g/L), As (up to 2.2 g/L), etc. The load of pollutants released from the mining area varies depending on the rainfall regime, reaching values in some sources of up to 6.8 ton/day of Fe, 1.3 ton/day of Al, etc. In addition, in the area there are 4 flooded open pit, with a volume of acidic water close to 5.2 hm³. The water level in two of these pit lakes has not yet stabilized and continues to rise.

The acid leachates generated produce the degradation of 115 km of water courses of the Meca and Oraque Rivers, both belonging to the Odiel River basin. In addition, the Meca River basin is regulated by the Sancho reservoir (capacity of 58 hm³), which has a pH close to 3.5 and substantial concentrations of toxic elements, so the water must be treated before being used for the supply to an industrial facility. Other acidic leachates join the Oraque River, where downstream the confluence with the Odiel River a new reservoir (capacity of 246 hm³) is currently under construction. However, this reservoir will store acidic waters if remediation measures are not taken. Finally, acidic leachates from the Tharsis mines also contribute to the important pollution of the Ría of Huelva estuary.

A strategy based on the isolation of the most pollutant spoil heaps combined with the construction of DAS-passive treatment plants is proposed for the reduction of contaminant emissions from Tharsis and the improvement of the surrounding water bodies.

Acknowledgements
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Groundwater Quality Formation at Drinking Water Intakes Near a Flooded Pit (Middle Urals, Russia)

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Abstract
Mineral is often accompanied by dewatering. Groundwater extracted by drainage wells outside of a pit usually has good quality and meets the requirements for drinking water. In the Middle Urals, water is supplied to some cities from such sources. However, after mining ceases and mine workings flood, the groundwater quality at such water intakes gradually deteriorates. Using the Lipovsky water intake as an example, a mass balance analysis indicated that dissolution of secondary sulfates in the internal dump was causing the contamination.

Keywords: secondary sulfates, mass balance, technogenic aquifer, dissolution, internal dump

Introduction
The availability of drinking groundwater resources and groundwater usability in areas disturbed by mining operations is determined by both natural and industrial factors, including the type of mineral being mined, the land remediation method, and water intake design (Palkin et al., 2011). Unlike deposits of solid minerals, groundwater is a renewable resource and a dynamic system: groundwater extraction leads to changes in existing and development of new hydrodynamic and hydrogeochemical conditions, redistribution of the system's balance constituents, and engagement of new sources in the formation of a deposit's resources (Rybnikova et al., 2017).

Fresh groundwater deposits within mining sites are continually exposed to changes in the groundwater balance structure by mining and even more so, by mine closure. In the post-mining phase, wet closure of the mine typically leads to redistribution of usable groundwater recharge sources, changes to the boundaries and area of the groundwater deposit, and emergence of new contaminating factors or entrapment of existing ones into the catchment area. Nevertheless, many water intake facilities are still operating due to the availability of a decades-long infrastructure (Rybnikova and Rybnikov, 2016).

The objective of this study was to assess the resource potential and patterns of change in drinking groundwater quality after the flooding of a nickel open pit mine, using the Lipovsky groundwater deposit as an example.

Case study and methods
The Lipovsky nickel silicate deposit is located on the eastern slope of the Middle Urals within the transition zone between the Folded-Mountain Urals and the Western Siberian Lowland, on the left-bank slope of the Rezh river valley (Sverdlovsk Region). The area has a continental climate with an average annual air temperature of 0.2°C and a winter that lasts about 5 months. The dewatering system of the Lipovsky mining pit served two functions: it protected the pit against flooding and served to supply drinking water to the town of Rezh (about 50 000 residents). To this end, a 20 km water supply line was constructed from the pit to the town (fig. 1).

The Lipovsky nickel silicate deposit is associated with development zones in the Mesozoic weathered crust formation atop the Paleozoic basement. The thickness of the weathered crust is greatest (up to 200 m) at tectonically disturbed contacts of serpentinites with marbles and at contacts of thin dikes of marbles with serpentinites and marbles. The main nickel carrier minerals are decomposed serpentine, nontronite, nepouite, garnierite, montmorillonite, kerolite, iron oxides of the goethite-hydrogoethite series, psilomelane...

From 1961 until the early 1990s, the peripheral drainage system of the Lipovsky nickel ore pit ensured safe mining of the mineral. It had two water drainage intake structures (on the western and eastern edges of the pit), each having three to five 200 m deep extraction wells.

The most water-flooded types are carbonaceous rocks, limestones and marbles. The pre-mining groundwater level was at +220 m elevation. By 1991, when the mine was abandoned, the level was drawn down 127 m from the static level (elevation +93 m) by an average annual discharge rate of 250 L/s. The total recharge area is estimated to be about 100 km², and the area of the active part of the depression cone about 30 km². The mined-out space is 51 million m³. Mining was accompanied by the filling of the pit’s eastern part with overburden rock and substandard ore.

After mining ceased, water withdrawal decreased to 100 L/s, which resulted in a partial recovery of the groundwater and the formation of a 120 m deep pit lake. In natural conditions, the groundwater was of hydrocarbonate-calcium and calcium-magnesium type, with a salt content of up to 0.2 g/L, a sulfate content of not more than 10-15 mg/L, and a chloride content of not more than 5–7 mg/L. The groundwater had a pH of 6.8 to 7.9 and an Eh of 239 to 310 mV.

The metallogenic characteristics of the area, represented primarily by a broad development of ultrabasites and nickel-bearing minerals, determine the presence in the groundwaters of a certain group of metals, such as nickel, cobalt, beryllium, arsenic, copper, zinc, cadmium, and chromium. However, the natural background concentrations of these elements are substantially lower than the standard values for drinking water. In particular, the natural background value for nickel is 0.002-0.004 mg/L against the permissible level of 0.02 mg/L. The characteristic feature is the presence of sulfides as dispersed mineralization in hydrothermal ore formations and in karst cavities (as pyrite, pyrrhotine, and marcasite). The deposit displays signs of recent mineral formation processes; the weathered serpentinites have water-soluble sulfates forming on them, such as epsomites and melanterite (Bizyaev, 2012).

Research results and discussion
Over the 30-year period of water drainage and intake until 1991, the groundwater quality changed, with most of the indicators increasing 1.5–2 times compared to their
natural levels (fig. 2). It should be noted that the concentrations of the groundwater components on the western and eastern edges did not differ before water withdrawal decreased and the pit lake began to fill. Subsequently, the concentrations of the marker components (i.e., dissolved sulfate and nickel) increased considerably, particularly in the wells on the eastern edge of the pit, where the sulfate content increased 14-16 times (to 140–160 mg/L) and nickel increased 25-30 times (to 0.1 mg/L). In the wells on the western edge, this process was less rapid and the sulfate content increased 6-8 times (to 62–85 mg/L) and the nickel content 10-15 times (to 0.03 mg/L).

Previous research has demonstrated that the sulfate and nickel content water in the pit lake increases slightly with depth, from 79 mg/L (at a depth of 10 m) to 85 mg/L (at a depth of 70 m), and 0.19 mg/L (at 10 m) to 0.23 mg/L (at 70 m), respectively (Palkin and Palkin, 2002).

An essential geomigration estimate may be obtained based on a tentative mass balance calculation using sulfate ion content as the main marker (indicator) of change in groundwater quality. For the western water intake, the fraction of resources coming from the pit lake \( Q_{wp}/Q_{wi} \) may be estimated using the following balance equation:

\[
Q_{wi} \cdot C_{wi} = Q_{wp} \cdot C_{wp} + Q_{wn} \cdot C_{wn},
\]

where \( Q_{wp}, Q_{wp}, Q_{wn} \) represent water discharge rates at the western intake and recharge resources from the pit lake and aquifer in the area of resources formation, with the corresponding concentrations \( C_{wp}, C_{wp}, C_{wn} \) in the water intake, pit lake and aquifer in the resource formation area. Then for the concentrations \( C_{wi} = 60, C_{wp} = 80 \) and \( C_{wn} = 10 \) mg/L, we obtain \( Q_{wp}/Q_{wi} = 2/3 \).

If we assume that the discharge rate of the eastern intake \( Q_{ei} \) is also formed at the expense of withdrawing pit lake waters (not less than half of \( Q_{ep} = Q_{en} = 0.5Q_{ei} \)), then in this case:

\[
Q_{ei} \cdot C_{ei} = Q_{ep} \cdot C_{ep} + Q_{en} \cdot C_{en}; C_{ei} = 0.5C_{ep} + 0.5C_{en}, C_{ep} = 2C_{ei} - C_{en}
\]

and for \( C_{ei} = 140 \) and \( C_{en} = 10 \) mg/L, the sulfate content of the water from the pit lake would amount to \( C_{ep} = 260 \) mg/L, which is 3.5 times higher than what is formed in the pit lake itself.

The wells of the eastern intake are located on the pit edge, which was filled with overburden and substandard ore with dispersed sulfide mineralization during the mining of the main orebody (fig. 3).

Decreased water withdrawal after 1991 led to the filling of the cone of depression, flooding of the pit, rising of the water level in the pit lake and, as a consequence, formation of a unified aquifer between the pit lake and the eastern intake, including a

\[\text{Figure 2} - \text{Changes in the sulfate-ion contents of the groundwaters in the wells on the eastern and western edges of the Lipovsky fresh groundwater deposit. The blue arrows point at pit flooding stages: } +93 \text{ m} – \text{beginning of flooding; } +150 \text{ m} – \text{beginning of tecnogenic aquifer formation in the internal dump.}\]
technogenic aquifer within the filled part of the pit. A rise of the groundwater table in the technogenic aquifer to +150 m and higher (after 1994) with free access of oxygen has led to active geochemical weathering of the sulfide-containing minerals and dissolution of secondary sulfates, which accounts for the increased concentrations of sulfate, nickel and other components in the groundwater intake on the eastern edge of the pit. The technogenic aquifer has thus become a supplier of sulfate salts.

Conclusions

Thus, the recharge sources of the Lipovsky groundwater deposit have fundamentally changed. Two thirds of the discharge are formed at the expense of recharge from the open technogenic reservoir, whose water has a sulfate-ion concentration of $K_c=8$. In the process of groundwater quality formation at the eastern intake, the recharge water from the pit lake is additionally enriched in the course of filtration through
the technogenic aquifer. The waters coming into the wells on the eastern edge of the pit have a sulfate-ion concentration coefficient of $K_c=26$. The main process by which the waters are enriched with sulfate, nickel, etc. is the dissolution of the secondary sulfates that formed as a result of chemical weathering of the sulfide minerals in the unmined ore and in the overburden and substandard ore used to fill the eastern part of the pit. Such processes have been observed at other mineral deposits as well (Appelo and Postma, 2005).

In recent years, the nickel content has been persistently higher than the permissible level: 20% higher at the western intake and 500% higher at the eastern one. The operation of this water intake facility continues since it is the only source of water supply for the town of Rezh.

Not denying the significance of hydrochemical activity in weathering crusts (particularly in karst sinkholes) for the formation of groundwater chemistry (Bizyaev, 2012), it should be pointed out that this factor apparently played the main role during the period when water drainage was operating, the technogenic aeration zone was forming, and oxidation processes were intensifying due to free oxygen access. As a result, the conditions in the pit were favorable for the development of soluble secondary sulfates. The pit lake and technogenic aquifer in the remediated part of the flooded pit became the main contaminant sources after 1991 at the operating water intake facility. Although some researchers believe that the basic processes of hydrogeochemical transformation at the Lipovsky geotechnogenic system are over (Palkin and Palkin, 2003; Bizyaev, 2012), the hydrogeochemical situation is far from being stable, as demonstrated in fig. 2. Considering the limited supply of oxidized minerals within the technogenic aquifer, we may assume that in the future, the quality of the groundwater withdrawn by the intake wells will improve. This process, however, may take dozens or even hundreds of years (Rybnikova and Rybnikov, 2017).

References


EXTRACTING OF VALUE ELEMENTS OF MINE WATER AND TAILINGS
Cavitation of Acid Mine Drainage-Magnesite Mixtures: A Promising Acid Mine Drainage Treatment Technology

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Abstract
Cavitation of AMD-magnesite mixtures was induced using a sonotrode and the chemical species removal, and neutralization potential of the magnesite evaluated. This process was repeated using the conventional agitation by a magnetic stirrer. SEM images showed new morphologies indicating formation of new mineral phases while XRF results indicated increased concentration of Fe, S, Al and Mn in residues indicating formation of Fe, S, Al and Mn bearing mineral phases and deposition on unreacted magnesite grains. Contact of magnesite with AMD for 60 mins with conventional agitation led to increase in pH to 9.4. Al, Mn, Fe and Zn were removed to levels > 99% while SO\(_4^{2-}\) were removed to levels ≥ 50 %. Cavitation treatment of the same AMD-magnesite mixtures for 60 mins led to an increase in pH to 8.6 and sulphate removal ≥ 90%. Cavitation treatment was observed to induce fast kinetics, final alkaline pH was attained in a shorter time than conventional shaking and was also superior in terms of sulphate removal. Cavitation seems to introduce superior mechanical aspects that enhanced sulphate removal and can be enhanced through seeding with various salts for recovery of beneficial salt products.

Keywords: Acid Mine Drainage, Metal Species, Sulphate, Magnesite, Cavitation, pH, precipitation

Introduction
South Africa is endowed with large quantities mineral deposits. These include gold, diamond, platinum, manganese, copper, coal and chromium among others. However exploitation of these mineral deposits have positive and negative effect. Exploitation of these mineral have deposits contributes to social and economic development. However, the mining processes generate waste that could have negative effect on the environment if not adequately managed (Name 2014). Acid mine drainage (AMD) is an inevitable waste effluent resulting from the mineral deposit exploitation, its strongly acidic in nature and contains substantial levels of inorganic contaminants such as Fe, Al, Mn, Zn, Pb and SO\(_4^{2-}\) ions. Acid mine drainage results from oxidation of sulphide rock in presence of water during mineral deposit exploitation, the oxidation in presence of water and oxygen leads to formation of sulphuric acid (Watten 2015). Release of these effluents to the environment can have negative effect on surface and groundwater resources. Most government have regulations that require these effluents to be treated to acceptable levels before release into the environment. Many treatment technologies that are currently in use have limitations which include, cost factor, treatment inefficiencies, implementation inconveniences and material availability (Masindi 2016). There is thus a constant search for cheaper and more efficient technologies for effective management of AMD. Moreover for the technologies to be sustainable, the treatment process needs to include material recovery from the treatment process in addition to using locally available liming agents. Magnesite, a locally available liming agent was used in this study. Magnesite (MgCO\(_3\)) occurs in two forms crystalline and cryptocrystalline. The application of cryptocrystalline magnesite for treatment of AMD has been reported in our previous work (Masindi 2016) which reported
effective removal of inorganic contaminants. This study was designed to develop a novel technology that uses ultrasonic technology to drive the mass transfer kinetics between magnesite and the AMD during the mixing process. Due to the ability of ultrasonication to create cavitation phenomena, it was envisaged this aspect will introduce superior mechanistic aspects that will lead to more efficient and faster treatment process. This would result in less contact time and liming agent required for the treatment process. Our previous work using jet loop reactor that employs cavitation and impingement provided superior mixing that enhanced the treatment process leading to a more efficient contaminants removal (Madzivire 2013). An attempt was also made to compare the efficiency of this new novel technology with the conventional agitation of the reaction mixtures.

Methods

Magnesite was collected from Folovhondwe magnesite mine Limpopo province, South Africa. The magnesite was crushed using a hammer and milled into fine powder. The samples were kept in a zip-lock plastic bag until use.

A simulated AMD solution was prepared as described by Gitari [15]. The AMD was formulated by dissolving the following quantities of salts in 1000 mL of MilliQ water (18MΩ), 0.895g FeSO₄·7H₂O, 2.685g FeSO₄, 0.494g Al₂(SO₄)₃·18H₂O, 0.08015 g MnCl₂·4H₂O, 1.1393g MgSO₄·7H₂O and 0.03 ml H₂SO₄. This was expected to give 250 mg/L Fe³⁺, 540 mg/L Fe²⁺, 40 mg/L Al³⁺ and 35 mg/L Mn²⁺, 230 mg/L Mg²⁺, 660 mg/L Ca²⁺, 20 mg/L Zn²⁺ and 524 mg/L SO₄²⁻ in solution.

The milled magnesite and the AMD-reacted magnesite were characterized using XRF. Magnesite powder pellets were prepared by pressing the powder mixed with 15-20 g boric acid as a binding agent in a Die set of 40 mm diameter. The pellets were then placed in plastic cups for XRF analysis (S2 Ranger, Bruker Bench top XRF). The morphology of the raw magnesite and AMD-reacted magnesite was examined using scanning electron microscopy (SEM) and SEM-EDX at the University of Cape Town, South Africa.

Table 1 presents the chemical composition of magnesite, magnesite residues, AMD and product water.

Temperature, electrical conductivity and pH of aqueous samples were measured using an Orion multi-parameter analyser. Simulated and treated AMD samples were divided into two, the first half was acidified with 3 drops of concentrated HNO₃ to prevent aging and immediate precipitation of Al, Fe, Mn and SO₄²⁻ ions and stored in a refrigerator at 4 °C until analysis for cations using ICP-MS and the second half left unacidified and stored in a refrigerator at 4°C until analysis for anions using metrohm professional 850 IC.

To evaluate the chemistry and kinetics of the treatment process several operational parameters were evaluated. These were agitation time, sonication time, amplitude and cycle time of sonicator and liming agent dosage. For the effect of agitation time 9 samples of 100 mL each of the simulated AMD were pipetted into 9 HDPE bottles of 250 mL and 1g of magnesite added to each. The mixtures were agitated for 1, 5, 10, 15, 30, 60, 90, 120 and 180 minutes at 250 rpm using the Stuart reciprocating shaker. To study the effect of sonication time 9 samples containing 100 mL of the simulated AMD solution were pipetted into 9 bottles of 250 mL and 1g of magnesite was added to each sample. The mixtures were sonicated for 1, 5, 10, 15, 30, 60, 90, 120 and 180 minutes at 60% amplitude and a cycle time of 50%, using the ultrasonic processor UP400S. The mixtures were then filtered through 0.45μm pore membrane filters and analysed for cations and anions as previously described.

Results and discussions

Physicochemical characterization of magnesite, magnesite residues, AMD and product water.

Table 1 presents the chemical composition of magnesite and AMD treatment residues. MgO is a major component of the magnesite while SiO₂ and CaO occur in minor quantities. After AMD treatment a decrease in MgO was observed. This is as a result of MgCO₃ dissolution on interaction with the acidic media. There was an increase in Mn, Al and Fe oxides in an AMD reacted magnesite. An increase in Fe, Ca, Al and Mn indicates the precipitation of Fe, Al, Mn bearing mineral phases such oxyhydroxides, oxyhydroxysulphates and carbonates.
The increase in Ca could be attributed to the formation of gypsum due to the high concentration of $\text{SO}_4^{2-}$ in the simulated AMD. Our previous studies reported formation of these mineral phases on interacting Fe, Al, Mn, Ca and sulphate rich AMD with highly alkaline and Ca rich fly ash (Gitari 2006). For trace components Ni, S, Zn and Cr had the highest concentration in raw magnesite and were also observed to increase in the residues. This is again an indication of formation of new mineral phases bearing these elements. Of notable importance is the substantial increase in S and Zn content in the residues. Sr, Yb, Ba and Zr were observed to decrease in the residues as compared to the raw magnesite indicating their release into solution. Our previous studies reported release of such chemical species on reacting AMD with highly alkaline and Ca, Ba, Sr rich coal fly ash (Gitari 2006). This would be of concern in this treatment technology and would require detailed investigation.

**Morphology of the raw and reacted magnesite by Scanning Electron Microscope and Scanning Electron Microscopy Energy Dispersive Spectroscopy**

Figure 1 shows the SEM and SEM-EDS spectra of raw magnesite and AMD reacted magnesite residues.

### Table 1 Chemical composition of magnesite and residues

<table>
<thead>
<tr>
<th>Major oxides (% w/w)</th>
<th>Magnesite</th>
<th>Residues</th>
<th>Trace element (mg/kg)</th>
<th>Magnesite</th>
<th>Residues</th>
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<td>MgO</td>
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<tr>
<td>SiO2</td>
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<td>Sr</td>
<td>279.6</td>
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</tr>
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<td>3.44</td>
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<td>2136.5</td>
</tr>
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<td>10.08</td>
<td>Yb</td>
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<tr>
<td>Al2O3</td>
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<td>Ba</td>
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<tr>
<td>TiO2</td>
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<tr>
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<td>Cr</td>
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<tr>
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<td>MnO</td>
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**Figure 1** SEM Images (a) raw magnesite, (b) AMD reacted magnesite residues, (c) SEM-EDS for raw magnesite and (d) SEM-EDS of AMD reacted magnesite residues.
The SEM images reveal that magnesite has a leafy like-petals like morphology and with rod shaped hedges. The leafy like structures are folded to form a confining like structure (bowl like depth). The surfaces of these structures appear smooth (fig. 1a). After contact with AMD, new structures with completely different morphology appear to be deposited on the flower like structures. A substantial portion of the original magnesite morphology are still present (fig. 1b). This indicates that only a small portion of the magnesite appear to have reacted, majority of it remaining unreacted. The SEM-EDS gives surface elemental composition of a material. In figure 1c and d we see new chemical species present in AMD appearing the surface of the AMD reacted magnesite indicating possible incorporation of mineral phases bearing these elements on the surface of the magnesite. This was also confirmed through bulky analysis of the raw magnesite and AMD reacted magnesite residues by XRF (tab. 1). There is emergency of Fe, Si, S and Ca peaks that were not present in the raw magnesite (fig.1b) confirming deposition of mineral phases bearing these chemical species on the surfaces of the unreacted magnesite.

**Contaminants removal trends as a function of operation parameters**

**Effect of contact time**

Figure 2a and b shows the % metal removal and change in pH as a function of shaking and sonication time respectively.

An increase in pH was observed for both treatment systems, for the conventional agitation the pH stabilized at ~9.8 after 60 minutes (fig.a) while for the sonication system it stabilized at ~8.97 after 1 minute (fig b). This indicates the superior mechanistic aspects introduced by sonication of the reaction mixtures. This rapid increase in pH is accompanied by rapid removal of the metal contaminants Fe, Al, Zn and Mn to near ~100 % within 5 minutes. The removal of the metal contaminants is attributed to precipitation as metal hydroxides, oxyhydroxides and oxyhydroxysulphates. Ca removal followed the same trend as the metal contaminants which could suggest incorporation in the metal bearing mineral phases. Our previous studies have shown the formation of Fe, Al oxyhydroxides and oxyhydroxysulphates when AMD solutions were treated with high alkaline coal fly ash (Gitari 2008). In addition gypsum precipitation was observed to account for removal of Ca and sulphate too. We note the enhanced removal of Ca and sulphate in the sonication system as compared to the conventional agitation system. Experiments conducted using lime to treat AMD through the conventional agitation and sonication didn’t show any difference in terms of pH and metal removal trends (data not shown). Its interesting to note that experiments conducted with limestone to treat AMD through conventional agitation and sonication system showed similar trends to those of magnesite. Both magnesite and limestone are form of carbonates and are less soluble than lime, during treatment of AMD with limestone and magnesite armoring accurs which renders further contact of reactive surface with AMD impossible hence no release of alkalinity. Its
our hypothesis that sonication disrupts this phenomena leading to increased contact of AMD with fresh surfaces of magnesite and limestone particles. This is still subject of our continued investigation.

Conclusion

Acid mine drainage treatment with magnesite liming agent was evaluated using a conventional agitation of the reaction mixtures and compared to a sonication system. Solid residues from both agitation systems showed increased concentration of Fe, S, Al and Mn indicating formation of Fe, S, Al and Mn bearing mineral phases and deposition on unreacted magnesite grains. Contact of magnesite with AMD at S/L of 1g/100 mL for 60 mins of conventional agitation led to an increase in pH to 9.4 while for sonication pH increased to 8.97 within 1 minute. Al, Mn, Fe and Zn were removed to levels > 99% with both systems. However Ca and sulphate removal with agitation system was low as compared to sonication. For sonication system metal contaminants were removed to levels > 99% with 1 minute of treatment. Cavitation treatment was observed to induce fast kinetics, final alkaline pH was attained in a shorter time than conventional shaking and was also superior in terms of sulphate removal. Cavitation treatment was observed to introduce superior mechanistic aspects that enhanced sulphate removal and can be enhanced through selective seeding with various salts to enhance sequential chemical species removal and recovery of beneficial salt products. This will be the subject of further investigation in this project.

Acknowledgements

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Supergene Gold in the Gold-Bearing Wastes of Sulfide Deposits

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Abstract
The dumps of the pyrite-barite-polymetallic deposits of the Ursk ore field (Salairsky Ridge) have been studied by author. As a result of research, it was found that secondary gold enrichment horizon was formed at the bottom of the dump, and it consists of supergene gold. Gold morphology was studied using scanning electron microscopy. This research makes an attempt to prove that this gold is newly formed, bearing traces of growth and consolidation. In addition, factors that contribute to the formation of this gold are considered. The obtained results are the evidence of the high mobility of the dissolved forms of gold in an acidic medium, followed by their deposition on the geochemical barrier.

Keywords: supergene gold, dumps, the secondary enrichment horizon

Introduction
Scientists often investigate the behaviour of gold, namely, distribution, genesis and morphology from supergene zone (Hong Tie 2005; Kalinin et al. 2009; Reith et al. 2012; Osovetsky 2015; Shuster et al. 2017). However, they investigate the gold migration ways from wastes of gold-bearing deposits to prove high mobility of gold in nature and technogenic supergene zones (Myagkaya et al. 2016; Kirillov et al. 2018; Wierchowiec et al. 2018). Besides, the cycle of gold depends on the vital activity of microorganisms (Kuimova Moiseenko 2006; Reith et al. 2006; Shuster Reith, 2018).

It is known that in the supergene zone of sulfide deposits, as well as in the weathering crust, a horizon of secondary enrichment is formed (Smirnov 1951; Kreiter et al. 1958; Roslyakov 1981). The horizon of secondary enrichment is a zone highly enriched with metal, which is formed as a result of physical, chemical, biological and mechanical processes of differentiation and integration of substance in the supergene zone.

The author, in the example of the dumps of the Uruk ore field, studies the gold-bearing wastes and also explain reasons to the formation of supergene gold.

Materials and methods
The Ursk ore field is located in the northern Salair Ridge (Kemerovo region, Russia). The ore field includes the Novo-Ursk, Belokluch, Samoilov and a number of ore formations. It is the pyrite-barite-polymetallic type of mineralization. The structure, morphology, and composition of the ore bodies, the sequence of mineral formation, and the history of mining have been studied and described by many researchers; thus, a brief description of the ore field is given in this articles (Bolgov 1937; Cherepnin 1953; Kovalev 1969).

The material was selected from the wastes of the Novo-Ursk and Belokluch deposits. The samples were collected from vertical sections in different “lithological” interlayers and were enriched by the gravity method by using a pan.

The tailings preserves wastes from cyaniding auriferous pyritic and complex ores (primary ore and ore from the gold-bearing weathering profile) of the Novo-Ursk deposit. Dumps have a height of 10-12 m. The ore mineralogy consists of pyrite, sphalerite, chalcopyrite, galena, arsenical pyrite, fahlite, cinnabar, as well as quartz, barite, calcite, chlorite-group minerals, sericite, albite,
graphite, rutile, and fluorite (Myagkaya et al. 2016).

Samples were collected from two dumps. In the section of oxidized ores, three lithologically different layers (horizons) are distinguished (from top to bottom, Fig. 1A): 1. gray-blue clay horizon (30 cm) with sufficiently hard rocky material (with quartzite geodes, shale); 2. dark brown clay horizon (2-4 cm) containing a large amount (30-40%) of wood (such as wood chips); 3. light brownish horizon (30-40 cm thick), lying directly on the soil. The total number of samples – 19, 15 kg each. In the heap of primary ores, four samples were taken from a brown-ocher cemented horizon, lying directly on the soil (60-80 cm thick). The two dumps are separated by an “acidic” stream that was formed as a result of infiltration of atmospheric water through these dumps.

The wastes of the Belokluch deposit have a height of 10 m. In a vertical section, three lithologically distinct layers can be distinguished (from top to bottom) (Fig. 2A): barite material (60 cm); pyrite material (2 m); oxidized zone (> 60 cm). The total number of samples was eight, with a volume of 15 kg each.

Studies of the chemical composition of samples were conducted in the Analytical Center of multi-elemental and isotopes research SB RAS (Novosibirsk). The concentration of gold and silver was determined by the atomic absorption analysis (analyst Ilina V.N.). The main results are obtained by a scanning electron microscopy (SEM) a LEO VP 1430 (Carl Zeiss, Germany) INCA Energy SEM 350 (Oxford Instruments), spectrometer in the JEOL 01430VP. The finenesses of gold as well as its impurities was obtained by the microprobe analysis.

Results

According to the atomic absorption analysis (analyst Ilina V.N.), the gold content for oxidized and primary ores varies in the range of 0.4 – 1.2 mg/kg at the Novo-Ursky tailing dump. We have found about 50 particles of nugget gold from horizon 1 from the dump of oxidized ores (Fig. 1A). Gold is fine, size <0.2 mm. Predominant grains are the grains of the crystalline form, elongated and rarely flattened. The surface combines a variety of sculptures. For example, there are nano- and micro-particles of gold in the form of growths on the surface of gold (Fig. 1B, C), in films of iron and manganese hydroxides, clay minerals, and also on the surface of barite grains. Often, gold particles have accumulations of nano- and micro-particles form spongy formations (Fig. 1B, C). Another characteristic of grains is the step structure of growth (Fig. 1D, E).

According to the microprobe analysis, gold of medium finenesses (703–984 ‰), silver impurities are presented – 12–27%.

Figure 1 The Novo-Ursk deposit: A – structure of dump; B – sponge gold of crystalline form; C – increased fragment B; D – the step structure of growth gold; E – increased fragment D
mercury – up to 5%. High-grade gold (990) and grains with mercury impurity (up to 7.9%) were found. Gold is homogeneous in composition; no zonal structure or residual "cores" were noted.

According to the atomic absorption analysis, the distribution of gold at the Beloklyuyskoye deposit is even; the content varies from 0.12 to 0.17 mg/kg (average 0.15 mg/kg). We found 18 particles of gold from the horizon of oxidized ores. Gold is mostly fine, grade <0.2 mm. It is represented by crystalline gold particles with distinct edges, elongated prismatic crystals of tabular form. Morphological types of native gold, represented by aggregates of lumpy grains, have an irregular shape. The vertices of the faces are smoothed, and the edges of the particles are curved. A specific characteristic of the studied particles is the presence of mineral inclusions inside them, both on the surface and particles trapped inside (Fig. 2B). Sculptures of particles' surfaces are very diverse. Almost all particles of gold have growth steps (Fig. 2B, C) and cross-hatching on the faces. Gold has a microlayers as well. In addition, a grain with a porous surface was found, which is filled with rounded aggregates of gold (Fig. 2D, E).

Gold has a homogeneous composition. The fineness varies from 826 to 901 ‰, silver impurities are presented – 9-16 ‰; mercury – up to 0.4 ‰. The inner (central) part of the gold has, predominantly, a fineness higher than the edges. Fineness of gold decreases in the peripheral part of the gold, having a smooth, gradual transition. For grains of smaller classes (0.25–0.1 mm), curved edges were noted.

Discussion

Physical, chemical and biological processes are bounded together and their influence determines the morphology of gold particles, as well as the distribution of gold concentrations. Biological and chemical processes in combination with climate and geological conditions determine the physical and chemical conditions in the environment and they control the processes of dissolution, migration and growth of gold. By the geological conditions author means not only the geological structure of the field and the form of gold, but also methods of its extraction and methods of storage of the substance. The importance of solving the gold substance of the supergene nature appeals to the analysis of its typomorphic features, such as granulometry, morphology, and chemical composition.

The Novo-Ursk and Beloklyuksk deposits belong to pyrite-barite-polymetallic type,
which has a powerful oxidation zone with free native gold. Endogenic gold mainly is in a bound form, in sulfides (Bolgov 1937; Cherepnin 1957; Kovalev 1969). Size of gold is 0.016 mm, gold found in chalcopyrite and pyrite (Bolgov 1937; Kovalev 1969) and also in argentite and quartz, tellurides of gold and silver – altaite and hessite (Cherepnin 1957). During the formation of the oxidation zone, gold was released. The highest concentrations of gold are in the oxidized zone. Barite zone, relative to primary ores, is enriched with gold (7-10 times), silver (5-7 times) and arsenic (2-3 times) (Bolgov 1937). In addition, the oxidation zone is characterized by high concentrations of mercury, presented both in the native form and in the form of cinnabar (Kovalev 1969).

Fields have been discovered since the early 1930s. Gold mining was carried out from the oxidation zone, using cyanide. After enrichment, waste ores were stored directly on the soil layer in a specially designated area. Dumps have been stored there for over 80 years.

As a result of the research, it was found that grains of native gold are presented in the secondary enrichment horizon, which was formed at the contact of rock and soil. Since the studies were conducted on individual sections and the distribution of gold is extremely uneven, it is difficult to unambiguously determine the thickness of this horizon.

Gold is supergene, newly formed, as evidenced by the presence of particles of nano- and micron size, which form various growth structures, such as spongy gold or step forms.

We consider the possible conditions for the formation of gold in the secondary enrichment horizon. Sulfide wastes are stored in the open air undergoes weathering processes using water and wind, creating (bio)oxidative conditions. As a result of the oxidation of sulfides, “acidic drainage waters” (AMD) are formed. AMD has a high concentrations of metals and toxic elements. (Myagkaya et al. 2016; Yurkevich et al. 2017; Kirillov et al. 2018). The process of sulfide oxidation involves several stages, which reflects a gradual increase in the degree of sulfur oxidation. Therefore, acid drainage (AMD) contains abundant sulfate anions and other sulfur ions, such as tetrathionate ($S_4O_6^{2-}$) and thiosulfate ($S_2O_3^{2-}$).

Gold in the dump can migrate in dissolved form or in the form of particles in a stream. Since the acidic environment prevails in the dumps, the dissolved gold is presented mainly in the composition of S-complexes, as well as in the form of mixed Au complexes. (Myagkaya et al. 2016; Yurkevich et al. 2017; Kirillov et al. 2018). Then, these complexes migrate with acidic drainage waters and precipitate on geochemical barriers, due to changes in the physico-chemical parameters of the environment, forming a secondary enrichment horizon with supergene gold.

Elements released using AMD waters are reprecipitated as ocher minerals, such as goethite, ferrihydrite, lepidocrocite, jarosite, schwertmannite and hydrogoethite. Therefore, a variety of ocher minerals predominates in the dumps, which form clusters, they are located in the horizon of secondary enrichment. Minor changes in pH-Eh can trigger a rapid changes in minerals, including dissolution, re-precipitation and structural changes (Marescotti et al. 2012).

In addition, microorganisms, bacteria and fungi are actively involved in the remobilization of gold, as well as in the gold formation, which accelerates the dissolution and transformation of sulfide minerals, as well as the processing, migration and deposition of gold and the formation of new gold (Kuimova Moiseenko 2006; Reith et al. 2006; Shuster Reith 2018).

Conclusions
Thus, during more than 80 years, at the base of the dumps of the Novo-Ursk and Beloklyuisk deposits, the secondary enrichment horizon was formed with visible supergene gold. The abundance of sulfide minerals, as well as the size of the grains (about 0.2 mm), affected faster oxidation and release of gold.

The presence of gold particles of nano- and micron size, newly formed phases on the surface of earlier particles, as well as skeletal forms, indicate that gold grew in the wastes.

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Hydrogenic processes of autigenic mineralization of native gold of the Ural placers

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Abstract
In the article the processes of formation of “new” autigenic native gold are considered. The forms of manifestation of noble-metal mineralization in the Ural placers are also taken into consideration. The studies of gold deposition at cryogenic and evaporative geochemical barriers (Australia, New Zealand, Canada) are exemplified. The influence of microorganisms, bacteria and fungi on the processes of gold dissolution, transfer and accumulation are shown as well. The history of the Urals during the formation of Mesozoic weathering crusts and the development of peneplain with the formation of laterites is demonstrated. The mechanism of modern processes of technogeogenesis is given.

Key words: native gold, autigenic gold, cryogenic barrier, evaporative barrier.

Introduction
The natural processes of formation of “new” autigenic native gold are quite widespread, but it is difficult and ambiguous to identify them. Earlier it was noted that in the Ural gold-platinum placers noble-metal mineralization is almost always present in the several facies (forms of manifestation) - clastogenic and autigenic. The clastogenic mineralization is observed in the form of rounded clastic particles of native gold and platinoids. The nature of allotogenic clastogenic gold is determined by its mechanical release from hydrothermal veins of gold-quartz low-sulphide formation, from gold-bearing ores of gold-sulfide low-quartz formation at the orogenic and post-orogenic stages of formation of the folded system of the Urals. The autogenic form of precious metals is represented by gold pellicles passively growing on the clastic particles, and keliphite borders, metasomatically replacing clastic gold particles (Khazov et al., 2010). Authigenic gold is formed from the mineralized water due to the destruction of ores of the gold-sulphidic low-quartz and gold-pyrite formations. In some cases, the autogenic mineralization of gold is manifested in the form of independent clastogenic aggregates of nano- and micro-gold or growths on the surface of gold particles and platinoids; microorganisms, bacteria and fungi are involved in its formation. The mineralization was established for the territory of the Upper-Kama depression (Naumov et al., 2003; Naumov, Osovetsky, 2013; Osovetsky, 2012, 2013) and the gold particles from technogenic-mineral formations and zones of noble-metal mineralization of the Ural placers (Naumov, 2010; Naumov, etc., 2011).

The problem of gold in the hydrosphere and the relationship of the liquid phase of hydrogenic gold with the solid phase placer gold is not new. The problem of “growth” and “destruction”, the dissolution and deposition of gold in placers, many studies are devoted and there are different opinions. The background and anomalous distribution of gold concentration in the surface and groundwater is uneven. The gold content in the hydrosphere for all types of fresh water is stable and makes up 3.0×10⁻⁹ %. The increased content of the dissolved gold is found in slightly acidic, neutral or slightly alkaline bicarbonate and sulfate waters. In recent years, the works on the higherhydrogenic mineralization with the gold of surface and groundwater of the gold ore and gold placer
areas in the permafrost development zone, have appeared (Amosov, 2000; Alexandrov, 2007; Fedoseeva, 2000).

In the hydrochemical studies of the influence of cryogenic processes on the formation of water flows of gold scattering by A. V. Plyusnin and his colleagues (1979) is shown that its concentration in ordinary water is $6.6 \times 10^{-7} \text{ g/L}$, increases to $11.2 \times 10^{-7} \text{ g/L}$ in melt water and reaches $15.0 \times 10^{-7} \text{ g/L}$ in the waters subject to pre-freezing to the temperature of -6° C. The increased acidity of the solutions contributes to the dissolution, migration of gold. Under certain geochemical conditions, it is deposited. The gold deposition is controlled by geochemical barriers: oxygen, reducing, sulphate, carbonate, alkaline, carbon, sulfide, evaporative, cryogenic, sorption or their combinations.

Different bioforms, microorganisms and fungi also participate in the process of dissolution, transfer and accumulation of gold. An example of this is the study by Jeremiah Shuster and et al. (2012). They studied gold in Australia (Queensland) and found that biogeochemical processes stimulate the cyclization of gold through dissolution and re-deposition reactions that lead to the conversion of gold into near-surface media. It was found that the microcracks on the surface of the grains are filled with organic and clay minerals, in which gold colloids and octahedral gold plates of nano- and micro-size are embedded. The formation of these secondary gold structures is explained by the deposition of gold due to the action of reducing agents such as microbiota, residual organic matter and clay.

The study of S. M. Zhmodik and others (2012) obtained new data on the role of micromycetes in the concentration and distribution of gold and platinum in the iron-manganese nodules of the world ocean. Inside the colony of fungi there are three forms of distribution of gold and platinum: 1) in the form of point concentrators (mainly for gold); 2) scattered without a clear dependence on the structure of the colony (manifested poorly for gold); 3) scattered with the concentration in the peripheral parts of the colonies and in spores (common for platinum).

The biogenic factor in the formation and transformation of gold-bearing eluvium is undoubtedly included, but its role is still debatable. Some researchers believe that the participation of microorganisms in the transformation of matter, including native gold in the hypergenesis zone, is insignificant (Dilabio et al., 1988), others - emphasize its important role (Shkolnik et al., 2004; Southam et al., 2009; Mayorova et al., 2010; Bluman, Ibrahimova, 2010, etc.).

For arid conditions in the eight regions of Australia L. Fairbrother et al. (2012) investigated the influence of biogeochemical processes on the conversion of gold grains. In the subtropical and tropical climate there is a continuous processing, isolation and dispersion of gold and the subsequent deposition of gold nanoparticles to form biofilms on gold grains. In these parts, the availability of water and nutrients is limited and sporadic. Therefore, abiogenic evaporative mechanisms control the formation of secondary gold and especially gold nanoparticles. The biofilms able to transform grains of gold, are occasionally developed on the grains of gold in dry conditions. Their research shows that the processes involving microorganisms play an important role in the transformation of gold grains and contribute to the dissolution and deposition of gold. Microorganisms affect the formation of geochemical anomalies in arid conditions.

Frank Reith et al. (2012) studied the gold sampled in the six locations in the southern New Zealand. Based on the fact that biogeochemical processes lead to the transformation of gold in surface conditions, they evaluated the connection between the morphology of the surface of gold grains and the processes of converting of supergen, paying special attention to the formation of gold nanoparticles in temperate climates. Signs indicating the dissolution of gold and silver were found, for example, dissolution of grain boundaries was observed on all grains, as well as a high content of tumors and gold aggregates. They revealed that climatic conditions with high rainfall enhance the transformation of gold grains (coating with bio pellicles, secondary gold, silica and carbon deposits on the surface of
In the early Mesozoic (Triassic), in the period of intensive tectonic movements at the final stage of Hercynian orogenesis, erosion-denudation activity in the form of mechanical destruction and removal of material (physical weathering) substantially prevailed over the processes of chemical weathering. The release of the useful component from the bedrock was incomplete. The increased concentrations of gold were not formed. The average gold content in the terrigenous strata of the lower Mesozoic is close to its average content in eroded indigenous sources.

In the late Mesozoic tectonic stabilization of the territory and humid climate provided the predominance of chemical weathering processes, which led to intensive corrosion (peneplenization) with a very perfect mechanical sedimentary differentiation. Mainly alluvial placers were formed.

In the terms of humid climate and intensive chemical weathering the favorable conditions for the working out of erosion nets are created. The tectonically weakened zones of high-permeability faults, tectonic thrusts, ledge and other dislocations are the least resistant to the exogenous processes; zones of lithologic and stratigraphic contacts are represented by different physical properties of the rock complexes — development areas of carbonate, sandstone and shale strata. The distribution of linearly weakened zones is subordinated to the meridional elongated Hercynian structures of the Urals. Therefore, the primary late Mesozoic river network began to form on them and has a meridional orientation (longitudinal valleys), often spatially coinciding with the zones of development of indigenous gold-platinum mineralization. The erosion-structural depressions are formed in the negative structures. They are filled with the late-Mesozoic terrigenous complexes of genetic series from eluvium to alluvium and preserved complex gold-platinum placers. Due to the substantial duration of these processes, Mesozoic erosion-structural depressions accumulated a substantial amount of released metal.

In the Cenozoic, especially in Pliocene-Quaternary time, as a result of the evolution of the river network and river interception transforming gold grains) and in the soil. Also they cleared up that the dissolution of gold in seawater and bio-mineralization with the participation of microorganisms are important factors affecting the change of gold in the sediments of beach placers. They found that the surface morphology of gold grains from New Zealand is the result of supergenic transformations occurring in modern conditions. The formation of gold nanoparticles, which was previously thought to be caused by evaporation occurring in high rainfall conditions, is likely to occur as a result of other mechanisms such as biomineralization.

**Methods**

Structural-tectonic and geomorphological analyzes were used at the regional and local levels to identify zones and areas favorable for the development of placer gold-bearing (Sigov, 1969; Naumov, 2010). Gold concentration studies have been conducted at placer development sites. Sampling, gravitational enrichment and extraction of free gold, including small and thin classes, were carried out according to the methods of Perm University (Lunev, Osovetsky, 1979; Lunev et al., 2000; 2003; Naumov et al., 2010). For particles of free gold and films, the mineral and chemical composition, structure, and structure were determined, including electron microscopy. Theoretical analysis and experimental work were carried out to determine the conditions and mechanisms for the dissolution, transfer and accumulation of gold-bearing phases in the evaporation and cryogenic barriers. (Naumov et al., 2010; Naumov, Husainova, 2017; Naumov, Osovetsky, 2017).

**Results**

The formation of natural gold placers in the Urals began at the post-construction stage of the folded system. The Mesozoic placer cycle clearly emerged, which appeared in the hot era of crust formation. The placers of gold of this time are characterized by increased productivity. A substantial role of the influence of the evaporation barrier, enlargement and formation of clastogenic gold particles is likely.
the transverse (relative to the Urals) valleys were being formed. In the process of erosion of Mesozoic deposits, there was a redeposition of useful components and their accumulation in the young strata of the Paleogene-Neogene-Quaternary age, often with the formation of industrial placers. Such placers linked with transverse valleys spatially coincide with the Eastern zone, which is the continuation of the Chusovskaya structural-erosion depression. Pliocene-Quaternary alluvial deposits (PP. Wilva, Srednyaya and Severnaya Rossoha, Bolshaya and Malaya Saldinka) - Promyslovsko-Kushvinskaya group, are distinguished by a good sort of gold and platinum, by large size, and are set in modern valleys Gornozavodskii district (Kopylov et al., 2015).

During seasonal freezing of alluvial precipitation in the Quaternary and in connection with the stages of glaciation and interglacial, the processes of authigenic mineral formation and the formation of golden crust and raids are probably also intensified. An example is the study conducted in Canada. Several Quaternary glaciations in the Yukon have been described, which are divided into three stages, commonly known as pre-RAID, Reid, and McConnell. The covers of pre-RAID glaciation are overlain by deposits, which are known in the Yukon as the White Channel Gravel and localized along the streams Hunker and Bonanza. Taking into account the morphology and nature of the surface, four types of gold particles are distinguished. First type are dense massive grains with rounded edges, numerous inclusions of quartz grains and geometrically correct replicas. The last ones record the location of the quartz crystals or gold of the next generation. The gold of this type is characterized by the relatively smooth surface. Its peculiarity is revealed in the presence of numerous thin-platy and lamellar bevels. This type of surface may appear in the result of the formation of gold from supersaturated gold-containing solutions at the cryogenic geochemical barrier. The formation of gold films on the grains of heavy and light fraction minerals in the white Chanel Gravel deposits was previously noted by different researchers (Patyk-Kara, 2008).

For the development of these concepts the mechanism of cryogenic gold deposition in glacial conditions is proposed. It manifests itself in the form of a “capture” by the gold matrix of grains of other minerals or by filling the voids with gold in the primary matrix of a heterogeneous material, where gold acts as cement and performs the intergranular space. On the surface of gold grains of this type there are raids, primers and aggregates of hypergenic minerals (Naumov et al., 2010).

The parallel geochemical bound process of crusts and raids formation of iron and manganese hydroxides is the result of surface interaction of gold-bearing phases with ore solutions enriched with these elements. Iron-manganese phases form raids and crusts on gold, act as cement, forming larger aggregates.

Modern processes of technogeogenesis are manifested in the areas of working out of copper gold-copper porphyry and related epithermal gold deposits. Man-made waste water enriched in siderophilic and chalcophile different elements are formed. They enter the horizons of groundwater and surface water. Along with them is dissolved gold in low concentration.

As a result of such activities, solutions enriched with metals are formed, which are obtained during the leaching of ores during the technological processes of their enrichment. At the same time, they spend substantial energy resources to extract the rock from the Deposit, transport the ore to the ore-processing plant, conduct crushing, abrasion of the ore, and obtain gravitational and flotation concentrate. Then process the concentrate with transferring metals into the liquid phase and only after that extract the metals. Under waste and man-made waters actions on destruction, transfer and transfer metals in solutions are carried out by natural geological agents, activated by human technical activities. Thus formed solutions are human-activated hydromineral raw materials of different metals. When processing large volumes of hydromineral raw materials, it will be economically advantageous to extract it on an industrial scale using artificial geochemical barriers.

In the history of the Urals during the formation of Mesozoic weathering
crusts and the development of peneplains laterites are formed, within which for a much longer period of time such processes happened (destruction, transfer and metal accumulation). This mechanism of deposition and consolidation of gold can be illustrated by analogy while observing the salt evaporation from the drop of water saturated with different salts.

**Conclusions**

Based on the conditions of formation and transformation of gold-bearing phases due to the changes in tectonic, climatic and hydrochemical conditions of sedimentation, for gold-containing objects of the Urals can be concluded as follows.

1. Authigenic gold precipitated from solutions is represented by gold pellicles passively growing on detrital particles, and kelyphitic borders.
2. Authigenic pellicles and microcrusts cover the surface of detrital particles of both rocks and various minerals.
3. Native gold is formed not only in the hydrothermal process, but also the authigenic pellicles and shells are grown on, in the hot climate, in the tropical zone (evaporation barrier) and while freezing “cold” waters (cryogenic barrier) in the exogenous conditions (Khazov et al., 2010). The geochemical barriers (evaporative and cryogenic) contributed to the early (MZ-KZ) formation of increased concentrations of gold in the placers of the Urals in the form of authigenic and clastogenic gold and outgrowths on clastogenic gold.

The knowledge and accounting of natural processes of authigenic formation of gold from “ore-bearing man-made” solutions formed while working out sulfide ore deposits will allow to involve man-made ore, in-ground waters in the technological process of their enrichment and purification while ensuring the environmental safety of mining. The surface and underground waters of a number of waste deposits of gold-sulphide and gold-pyrite formations should be considered as a promising hydromineral raw material.

The creation of artificial geochemical barriers in various areas of working out gold-sulphide and gold-pyrite formations will allow to extract gold from solutions. It is necessary to search for appropriate sorbents, extractants and other systems of gold deposition from solutions. It is necessary to search for sites and conditions for independent deposition of gold in modern technogenic and mineral formations.

**Funding**

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**References**


Mineral Precipitation Sequence During Evaporation of Lake Katwe Brine

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Abstract

Traditional salt mining techniques are the dominant salt extraction methods at Lake Katwe in Uganda. In this work, the effect of temperature on the mineral precipitation sequence during evaporation of lake brine was studied to foster the design of a commercial salt extraction process. Isothermal evaporation experiments at different temperatures were undertaken. PHREEQC was used to predict the precipitation sequence. The precipitates were characterised by the XRD and SEM techniques. Halite is the most abundant mineral, with Thenardite, Trona and Glaserite following, respectively. Halite will be best extracted at higher temperatures whereas the lower temeratures will favour sulphate based minerals.

Keywords: Lake Katwe, Evaporation Temperature, PHREEQC, Precipitation, Brine

Introduction

In Uganda today, salt for both domestic and industrial use is mainly imported from neighbouring countries. The salt import bill is steadily increasing as the country develops which is increasingly straining the country’s merger resource envelope. To avert this, the salt deposit at Lake Katwe need to be fully exploited. This salt lake has been a source of salt for a long time. However, the salt produced from the lake does not meet the required purity standards for table salt and the chlor-alkali industry (Kirabira et al. 2013; Kasedde et al. 2014).

Currently at the lake, salt is recovered by traditional means; brine is channelled from the lake into salt pans. In the salt pan, the salt crystallizes due to solar evaporation producing two salt grades of different qualities. Grade I which is averagely about 93% Halite (NaCl) is the best these rudimentally techniques can produce. Grade II is harvested after Grade I with an average composition of about 65% Halite. The third grade is obtained by hacking the lake bed with iron bars; this has a composition of about 50% halite. Due to their composition, these three salts attract low prices as the demand for them is low (Kasedde et al. 2014).

A salt plant was established for industrial processing of the Lake Katwe brine. The plant never performed to its design expectations and the components were heavily corroded (Driver and Tukahirwa 1990). This led to its abandonment without ever producing any meaningful products. Plans for commercial exploitation of the brine commenced with the characterisation of brine and phase chemistry experiments. The brines are highly alkaline and rich in Na⁺, K⁺, Cl⁻, SO₄²⁻, CO₃²⁻, and HCO₃⁻ showing an intermediate transition between Na-Cl and Na-HCO₃ water types (Arad and Morton 1969; Kasedde et al. 2014).

An isothermal laboratory evaporation experiment at 30°C revealed precipitation of commercial salts such as Thenardite (Na₂SO₄), Anhydrite (CaSO₄), Mirabilite (Na₂SO₄·10H₂O), Burkeite (Na₂CO₃·2Na₂SO₄), Hanksite (9Na₂SO₄·2Na₂CO₃·KCl), Gypsum, Trona (Na₂CO₃·NaHCO₃·2H₂O), Halite, Nahcolite (NaHCO₃), Soda ash (Na₂CO₃), and Thermonatrite (Na₂CO₃·H₂O) from the brine of Lake Katwe. Moreover, the mineral salts crystallize in the order following the sequence starting with sulfates, followed by chlorides and carbonates, respectively (Kasedde et al. 2013) with a rich source of mineral salts. The present work aims at...
evaluating possibilities of future salt extraction from the lake deposit. An isothermal evaporation experiment was conducted on the lake brines. The precipitated salts were characterized by X-ray diffraction (XRD). Fractional crystallisation is often times used to extract most of the aforementioned salts from brine. This, therefore necessitates investigating the precipitation sequences of minerals from Katwe brine at different temperatures in order to facilitate the design a commercial salt extraction process.

Methods and Materials

Laboratory experiments
The rainy season surface brine was sampled from Lake Katwe and stored in 1.5 L plastic bottle at room temperature prior to the evaporation study. Using 10 ml of the original brine from Lake Katwe, the polythermal evaporation experiment was run at five different temperatures (30, 40, 50, 60 & 70°C). These were chosen because they are easily achievable on a commercial scale with less material selection problems and the evaporation process is faster compared to lower temperatures. Before evaporation was started, both the biological and organic materials were filtered off using a 5 µm membrane. The filtrate was then poured into a 50 ml beaker which was then placed in a Labcon thermostatic water bath at 30°C. The formed precipitates were filtered off using a 5 µm membrane and then left to dry overnight in open air on an aluminium foil. This procedure was repeated for the other study temperatures (40, 50, 60 & 70°C).

Characterization of the precipitates
To determine the mineralogy of the precipitates, the powder X-ray diffraction method was used. A Phillips diffractometer PW3050 with a X-ray source of Cu Kα radiation (λ = 1.540598 Å) was used. The scan step size was 0.013°, the collection time 1s, and in the range 2θ CuKα from 1° to 90.5°. The X-ray tube voltage and current were fixed at 45 kV and 40 mA respectively. The Crystallography Open Database (COD) powder diffraction database was searched by QUALX2.0 search–match identification software for phase identification (Altomare et al. 2015). The morphology of the precipitates was determined by a Zeiss Supra 55 VP Field Emission Scanning Electron Microscope (FEG-SEM); all samples were carbon coated before SEM analysis in order to make them electrically conductive.

Table 1 Brine Composition

<table>
<thead>
<tr>
<th>pH</th>
<th>Brine Temp (°C)</th>
<th>Density (g/ml)</th>
<th>EC (us/m)</th>
<th>Na (g/L)</th>
<th>K (g/L)</th>
<th>Mg (g/L)</th>
<th>Ca (g/L)</th>
<th>Cl (g/L)</th>
<th>Br (g/L)</th>
<th>SO₄ (g/L)</th>
<th>HCO₃ (g/L)</th>
<th>CO₃ (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.72</td>
<td>25.2</td>
<td>1.15</td>
<td>14109</td>
<td>69.6</td>
<td>11.6</td>
<td>0.0519</td>
<td>0.0048</td>
<td>44.2</td>
<td>0.461</td>
<td>32.7</td>
<td>18.2</td>
<td>38.8</td>
</tr>
</tbody>
</table>

Figure 1 XRD Pattern of mineral precipitates (Gl-Glaserite, Th-Thenardite, Ha-Halite, Tr-Trona, B-Burkeite, Na-Natron, Th-Thermonatrite, H-Hanksite).
Thermodynamic modelling

To model the precipitation sequence during the evaporation of the Lake Katwe brine, PHREEQC code (Parkhurst and Appelo 2013) version 3.4.0 was used. Due to the high concentration and ionic strength of brine, the geochemical calculations were done using the Pitzer ion interaction approach with a modified version of the pitzer.dat thermodynamic database distributed with the PHREEQC code. Evaporation was simulated in steps, 51 moles of water in 102 steps was removed (92% of the initial water was evaporated). The sequence of the modelled mineral precipitation at the study temperatures during the evaporation was noted. The major ions in Lake Katwe brine as shown in Table 1 were used as PHREEQC input (Kasedde et al. 2014).

Results and Discussion

Mineralogical analysis

Fig.1 illustrates a representative X-ray diffractogram of evaporation precipitates. X-ray diffraction results show a dominance of the carbonates and sulphates of calcium and magnesium (Calcite, Tychite, and Dolomite) in the first precipitates as predicted by Arad and Morton (Arad and Morton 1969). This is attributed to their low solubilities within the study temperature range.

Table 2 shows the mineral composition of the precipitates at the different study temperatures. Four samples are analysed at each temperature and these were collected as soon as crystals appeared. At all the study temperatures, Halite emerges as the most abundant mineral as the phase is observed in almost all the samples. This is also evident by the dominance of its microstructures in Fig.2.

At 30°C, apart from Halite, Trona is the most abundant mineral followed by Thenardite and Natrite. Halite, Burkeite, Glaserite and then Hanksite is the order of prominence at 40°C with Thenardite appearing as a trace. The sodium carbonate and bicarbonate minerals dominate the precipitates at 50°C with traces of Arcanite and Thenardite. For 60°C as well, the

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Calcite, Magnesite, Tychite, Halite Glaserite</td>
<td>Calcite, Thermonatrite, Burkeite, Thenardite, Halite</td>
<td>Calcite, Anhydrite, Magnesium Sulphate, Burkeite, Thermonatrite, Halite, Glaserite, Sylvite</td>
<td>Anhydrite, Dolomite, Thenardite, Burkeite, Hanksite, Trona, Natrite, Halite, Glaserite, Sylvite</td>
</tr>
<tr>
<td>40</td>
<td>Calcite, Anhydrite, Magnesite, Magnesium Sulphate, Thenardite, Trona, Natron, Halite, Glaserite, Arcanite, Sylvite</td>
<td>Calcite, Magnesite, Halite</td>
<td>Magnesite, Dolomite, Thenardite, Burkeite, Thermonatrite, Halite, Glauberite, Glaserite, Sylvite</td>
<td>Burkeite, Hanksite, Halite, Glauberite, Sylvite</td>
</tr>
<tr>
<td>50</td>
<td>Anhydrite, Magnesite, Dolomite, Trona, Thermonatrite, Halite</td>
<td>Calcite, Magnesite, Thenardite, Trona, Halite</td>
<td>Calcite, Magnesite, Dolomite, Gaylussite, Burkeite, Hanksite, Trona, Thermonatrite, Natrite, Halite, Glauberite</td>
<td>Calcite, Anhydrite, Dolomite, Thenardite, Burkeite, Hanksite, Nahcolite, Thermonatrite, Halite, Glaserite, Sylvite</td>
</tr>
<tr>
<td>60</td>
<td>Calcite, Magnesite, Halite, Sylvite</td>
<td>Magnesite, Dolomite, Halite</td>
<td>Calcite, Magnesite, Dolomite, Trona, Natrite</td>
<td>Anhydrite, Dolomite, Burkeite, Hanksite, Natron, Halite, Sylvite</td>
</tr>
<tr>
<td>70</td>
<td>Calcite, Magnesite, Magnesium Sulphate, Dolomite, Thenardite, Halite, Thermonatrite, Glaserite, Sylvite</td>
<td>Calcite, Magnesite, Dolomite, Trona, Halite, Sylvite</td>
<td>Calcite, Anhydrite, Magnesite, Dolomite, Halite, Sylvite</td>
<td>Anhydrite, Magnesite, Dolomite, Gaylussite, Thenardite, Natrite, Halite, Glauberite, Sylvite</td>
</tr>
</tbody>
</table>
sodium carbonate and bicarbonate minerals dominate the precipitates with the sulphates and chlorides of sodium precipitating as Hanksite. Natrite and Hanksite are observed to be the most dominant phases at 70°C. The XRD results are supplemented by the SEM results.

**Microstructual Analysis**

Fig. 2 shows the SEM micrographs of the precipitates observed during the brine evaporation. Four samples were filtered off at each study temperature with Sample A first, followed by B and lastly C. The SEM micrographs reveal distinctive microstructures of the dominant mineral phases that precipitate out of the brine. At all the study temperatures, precipitation of Halite is observed.

The waxy massive form (Fig. 2, (70° (A))) which is due to the hygroscopic nature of the salt (Eswaran et al. 1980; Mees and Tursina 2010) and the sharp cubic crystals (Fig. 2 (60°(C))) (Abdel-Wahed et al. 2015) are typical Halite morphologies. Massive forms of Halite are also observed as coatings composed of anhedral crystals (Fig. 2 (70°(B))) (Mees and Tursina 2010) on top of salt (rice) cake normally a fitting description for Thenardite crystals (Yamamoto and Zhu 1997; Warren 2016). The aforementioned is evidence of mineral stratification and co-precipitation; the latter needs to be minimised if pure salts for industrial use are to be produced. Trona is observed as blade like (Kasedde et al. 2014) and columnar massive (Warren 2016) crystals (Fig. 2 (50°(A)), on top of Thenardite (salt cake) (Fig. 2, (70°(C))) and sandwiching Halite crystals (Fig. 2 (40°(A), 50°(B) & 50°(C)). Hexagonal prismatic crystals of Hanksite are also observed as one of the precipitating mineral phases (Fig. 2, (40°(B)) (Kasedde et al. 2014; Warren 2016). Similar microstructures were identified by Kasedde and co-workers (Kasedde et al. 2013) in an isothermal evaporation study.

As temperature increases, the mineral phase stratifications become more distinct unlike at lower temperatures were phases are more mingled up. This is attributed to the increasing difference between the solubilities of the constituent minerals; as the temperature increases, the difference in the saturation with respect to the mother solution of the different minerals increases as well.

**Thermodynamic modeling**

At 30°C, 40°C, and 50° evaporation temperatures, the major salt precipitation sequence starts with Thenardite followed by Trona, Halite and lastly Glaserite (Fig. 3). This is in agreement with the previous isothermal evaporation study at 30°C conducted by Kasedde et al. (Kasedde et al.
2013) and Lwanyaga et al. (Lwanyaga et al. 2018). However in this study, Sylvite does not equilibrate with the brine and therefore doesn’t precipitate unlike in the previous phase developments study by Kirabira and co-workers (Kirabira et al. 2015).

When the temperature is increased to 60°C, Glaserite does not equilibrate with the solution and therefore does not precipitate. Further increase temperature to 70°C, results into the precipitation of only Thenardite and Halite. At all the study temperatures,
Thenardite precipitates first and later with increasing evaporation dissolves into the solution. The Saturation Index (SI) of Soda ash, a mineral of interest in this study, increases with increasing evaporation temperature. This observation predicts precipitation of this mineral at temperatures higher than 70°C.

From the model results as seen in Fig.3, Halite posted the highest amount of precipitate, followed by Thenardite, Trona and lastly Glaserite. This is consistent with previous studies (Arad and Morton 1969; Kasedde et al. 2014; Lwanyaga et al. 2018) which ascertained that, at the salt lake, brine are comprised of more sodium, chloride, Carbonate, sulphate, Bicarbonate, & Potassium salts.

There are noticeable differences between the actual precipitated salts from the evaporation experiment and the PHREEQC results. The XRD and SEM results confirmed existence of more double salts and hydrates compared to the PHREEQC model. This variation is due to the fact that the PHREEQC model mainly considers the thermodynamic aspects and not the kinetics, yet, the actual setting considers the kinetics thus some minerals might precipitate from the model and not observed by XRD and vice versa.

**Conclusions**

In this work, the effect of temperature on the precipitation and crystallization sequence on the Lake Katwe brine during evaporation was investigated. Increase in temperature fostered the evaporation rate and therefore it took less time to precipitate minerals at higher temperatures than at lower ones. XRD and SEM results confirmed the presences various commercial salts. Halite is the most abundant mineral at all the study temperatures. Other minerals include, Thenardite, Trona, Burkeite, Hanksite and Natrite. carbonates and sulphates of calcium and magnesium (Calcite, Tychite, and Dolomite) precipitate first. These are in low quantities and therefore will have to be removed first in the extraction process to avoid contamination of Halite. From this study, Halite of table salt grade will be best extracted at higher temperatures (60 & 70°C).

**Acknowledgements**

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**References**


Lwanyaga JD, Kasedde H, Kirabira JB (2018) Thermodynamic modeling of Lake Katwe brine
Ferric Sulphate Produced From Pyrite Concentrate of Coal Tailings to Water and Wastewater Treatment

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²Universidade Federal do Rio Grande do Sul, Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e Materiais, LTM- Laboratório de Tecnologia Mineral e Ambiental, Porto Alegre, RS, Brazil.

Abstract
Coal mining produces large amounts of wastes rich in pyrite (FeS₂), which in contact with water, oxygen and bacteria generate acid mine drainage (AMD). Due to its composition and the major environmental problem caused by the AMD, the objective of this work was the production of the coagulant ferric sulfate (Fe₂(SO₄)₃) from the oxidation of pyrite contained in the tailings of coal. The methodology was based primarily on the characterization of the pyrite concentrate, obtained by reprocessing the waste, both collected in the coal mine of Figueira-PR. Later, leaching tests were conducted for four weeks in two columns. After the four week, the solutions were filtered and evaporated to reach levels close to 12% of iron in the solution. The coagulant chemical quality was evaluated in terms of concentration of Fe, other metals and sulphate. The coagulant produced in previous stages, was tested for the treatment of water to human consume, proving its effectiveness, given the parameters required by water legislation. Thus, the production of ferric sulfate by pyrite leaching was shown to be effective and can add value to a residue that still causes a major environmental liability.

Keywords: tailings, coal mining, pyrite

Introduction
Coagulants used for treatment of both water and wastewater are predominantly inorganic salts of ferric iron and aluminium. Aluminium salts, including aluminium sulphate (AS) and aluminium chloride (AC), in addition to pre-hydrolysed metal-ion reagents such as poly-aluminium sulphate (PAS) and poly-aluminium chloride (PAC), are the coagulants most widely used for water treatment (Bratby 1980; Tchobanoglous et al., 2003). However, the presence of residual amounts of aluminium in drinking water has been controversially implicated to neurological diseases (ACWA 2000; Becaria et al. 2006; Campbell et al. 2001; Rondeau et al. 2000; Walton, 2006). A possible alternative is to use iron based coagulants, such as ferric chloride (FC), ferric sulphate (FS), or poly-ferric sulphate (PFS) instead of the aluminium salts (Jiang et al. 1996; Jiang and Graham 1998). Iron based coagulants are commonly produced by acid dissolution of iron scraps or iron ore (Tchobanoglous et al., 2003).

Recent studies showed that is possible to produce ferric sulphate coagulant from the pyrite present in coal tailing by a biohydrometallurgical process (Colling et al., 2011). The main advantage of the process is that it is not necessary acid addition, which is very favourable in terms of production costs. The acidophilic bacteria, e.g. Acidithiobacillus ferrooxidans, can increase the rate of pyrite oxidation and dissolution by several times (Kontopoulos, 1998; Brett and Jillian, 2003; Johnson and Hallberg, 2003) and that they can be substantial in the bio processing of coal tailings for the production of ferric coagulants.

However, the leaching process of the pyrite can dissolve undesirable elements present in the sedimentary rock associated to the coal tailings. The aim of this work was to produce a ferric sulphate solution
from different coal pyrite tailings. The main variable studied was the concentration of pyrite in the material and its influence in the purity of the coagulant.

**Materials and Methods**

**Coal Tailings Samples**

A pyrite concentrate from coal tailings obtained by jigging from “Cambuí Mine”, Paraná State, Brazil, with 65 % FeS2 (FS B/CT – 65% FeS$_2$), were used in this work. The materials were crushed and sieved, and the size fraction between 2 mm and 6 mm was used in the leaching columns.

The material were characterized considering the following parameters: total sulphur, pyritic sulphur, sulphate sulphur, organic sulphur, elemental analysis of CHN (carbon, hydrogen, nitrogen). X-ray diffraction analyses were also conducted to assess the mineral composition of the samples.

**Reagents**

All the reagents used for analytical procedures and pH adjustment additives in water treatment tests were of analytical grade. Distilled water was used for the preparation of all solutions. Commercial poly-ferric sulphate (PFS), produced from scrap iron by sulphuric acid digestion, was obtained from “Sulfato Rio Grande” (RS/Brazil).

**Leaching Experiments for Ferric Sulphate Production**

The leaching experiments were carried out using a laboratory column constructed as packed bed reactor, with a sprinkling system, in a close circuit (Figure 1). The recirculation of the water was performed by a peristaltic pump and flexible silicone hoses. The cylindrical glass column was 30 cm high and 7 cm in diameter, and was filled with 1 kg of non-sterilized coal tailings.

After four weeks of leaching (period where the concentration of suspended cells of *A. ferrooxidans* population reached $1 \times 10^{11}$ cells mL$^{-1}$ and maximum extraction of iron and sulphate was performed), the liquor was filtered (0.5 µm membrane) and evaporated to reach the iron concentration of about 12%, which was the usual for most of the ferric sulphate (FS) coagulants commercialized in Brazil.

**Chemical Characterization of the Produced Coagulants**

The ferric sulphate coagulants obtained from coal tailings (FS-B/CT), and the commercial PFS, were analysed in terms of pH, dissolved metals (Al, Ca, Cu, Cr, Fe, Mg, Mn, Pb, and Zn), and sulphate. Metal analyses were carried out by atomic absorption spectrometry. Sulphate concentrations were determined by the gravimetric method after ignition of the residue. All methods followed the “Standard Method for the Examination of Water and Wastewater” (Eaton et al., 2005).

**Results and Discussion**

The coal tailings used in this study were analyzed considering the following parameters: total sulphur, sulphate sulphur, pyritic sulphur, organic sulphur, carbon, hydrogen, and nitrogen (Table 1).

The results show that the main form of sulphur in the materials is pyrite. The coal tailings submitted to a pyrite concentration process presented a pyrite concentration of

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pyrite Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sulphur (%)</td>
<td>40.50</td>
</tr>
<tr>
<td>Pyritic Sulphur (%)</td>
<td>34.91</td>
</tr>
<tr>
<td>Sulphate Sulphur (%)</td>
<td>2.49</td>
</tr>
<tr>
<td>Organic Sulphur (%)</td>
<td>3.10</td>
</tr>
<tr>
<td>Pyrite Content (%)</td>
<td>65.37</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>6.05</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>0.77</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 1 Sulphur and CHN concentration in the pyrite concentrate.
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Table 2 Characteristics of the ferric sulphate coagulant produced by pyrite leaching process as well the composition of the commercial ferric sulphate

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ferric Sulphate from Pyrite</th>
<th>Ferric Sulphate Comercial</th>
<th>Specification of SABESP for Ferric Sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (g L⁻¹)</td>
<td>190.1</td>
<td>115.0</td>
<td>12 % (m/m)</td>
</tr>
<tr>
<td>Al (mg L⁻¹)</td>
<td>176.10</td>
<td>4419</td>
<td>&lt; 340 (mg kg⁻¹)</td>
</tr>
<tr>
<td>As (µg L⁻¹)</td>
<td>&lt;1.50</td>
<td>&lt;1.50</td>
<td>&lt; 50.0 (mg kg⁻¹)</td>
</tr>
<tr>
<td>Ca (mg L⁻¹)</td>
<td>586.70</td>
<td>56.70</td>
<td>–</td>
</tr>
<tr>
<td>Cd (mg L⁻¹)</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;5.0 (mg kg⁻¹)</td>
</tr>
<tr>
<td>Cr (mg L⁻¹)</td>
<td>6.04</td>
<td>305.00</td>
<td>&lt;50.0 (mg kg⁻¹)</td>
</tr>
<tr>
<td>Cu (mg L⁻¹)</td>
<td>10.06</td>
<td>11.50</td>
<td>–</td>
</tr>
<tr>
<td>Hg (mg L⁻¹)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;1.0 (mg kg⁻¹)</td>
</tr>
<tr>
<td>Mg (mg L⁻¹)</td>
<td>17.64</td>
<td>160</td>
<td>–</td>
</tr>
<tr>
<td>Mn (mg L⁻¹)</td>
<td>32.29</td>
<td>1585</td>
<td>&lt;1200 (mg kg⁻¹)</td>
</tr>
<tr>
<td>Pb (mg L⁻¹)</td>
<td>12.41</td>
<td>15.20</td>
<td>&lt;50 (mg kg⁻¹)</td>
</tr>
<tr>
<td>Zn (mg L⁻¹)</td>
<td>39.55</td>
<td>22.40</td>
<td>–</td>
</tr>
<tr>
<td>SO₄²⁻ (g L⁻¹)</td>
<td>415.6</td>
<td>330.0</td>
<td>–</td>
</tr>
<tr>
<td>Densidade (g.cm⁻³)</td>
<td>1.60</td>
<td>1.41</td>
<td>–</td>
</tr>
</tbody>
</table>

Note: SABESP is the most important sanity company of Brazil.

65% of pyrite in your composition.

Mineralogical analysis by x-ray diffraction was performed in order to determine the crystalline phases in the samples. The main minerals found were in the Pyrite concentrate from “Cambuí Mine”: Pyrite (FeS₂), Quartz (SiO₂), Magnetite (Fe₃O₄), Calcite (CaCO₃), Barite (BaSO₄), and Gibbsite (AlOH₃).

The coagulant produced presented an iron content of about 12% and presented a higher purity. For many metal contaminants, the levels are substantially lower, inclusively when compared to the commercial ferric sulphate coagulant produced from iron scraps (PFS).

**Water Treatment by Coagulation**

Studies involving water treatment were carried out with raw water from Guaiba Lake (Porto Alegre, RS, Brazil) using a conventional Jar Test apparatus. The coagulation procedure was carried out using a 1000 mL water sample. The samples of Ferric Sulphate produced by pyrite concentrate leaching and Ferric Sulphate, were added at the same molar concentration of 0.4 mM of the sum of Fe and Al. The pH was adjusted to 7.0 and the suspension was agitated at 100 rpm for 2 minutes, followed by slow stirring at a speed of 20 rpm for 3 minutes. Subsequently, the agitation was stopped and the samples were left undisturbed without any agitation for a period of 10 minutes, to allow the solids to settle. The treated water was analyzed for pH, turbidity, colour, metals (Fe, Al, Mn and Zn), hardness, and sulphate. All analyses followed the procedures described in the “Standard Method for the Examination of Water and Wastewater” (Eaton et al., 2005).

Table 3 presents the results obtained in the water treatment tests. All the coagulants were a good efficient in terms of residual amounts of suspended solids, turbidity, and colour. The residual amounts of potentially toxic metals in the treated water were very low and the lake water treated with all of the coagulants met the Brazilian standards for drinking water.

**Conclusions**

Through the process studied in this research, it was possible to obtain a coagulant rich in ferric sulphate from a pyrite concentrate. Among the contaminants found, there are the elements Al, Ca, Cu, Cr, Mg, Mn, Pb, and Zn. However, the higher the concentration of pyrite in the sample, higher is the purity of the coagulant, the pyrite concentrate can be used to produce a good quality ferric coagulant. The production of ferric sulphate coagulant could provide an economic income to the mining companies. Thus, in the Brazilian coal field areas, the concentration of pyrite should be encouraged.
**Acknowledgements**

The authors thank financial support extended by CAPES, CNPq and the Brazilian Coal Net for this research.

**References**


Eaton, A.D., Cresci, L.S., Rice, E.W., Greenberg,

---

**Table 3** Results obtained in the water treatment tests

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw water</th>
<th>Treated water with the produced coagulant</th>
<th>Treated water with the commercial coagulant</th>
<th>Brasilian Standards</th>
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</thead>
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<tr>
<td>pH</td>
<td>6.8</td>
<td>7.0</td>
<td>7.0</td>
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<tr>
<td>Suspended solids (mg L⁻¹)</td>
<td>23</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
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<tr>
<td>Dissolved solids (mg L⁻¹)</td>
<td>305</td>
<td>345</td>
<td>461</td>
<td>1000</td>
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<tr>
<td>Turbidity (NTU)</td>
<td>12</td>
<td>0.30</td>
<td>0.60</td>
<td>5</td>
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<td>Color (Hazen)</td>
<td>44</td>
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<td>2</td>
<td>15</td>
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<tr>
<td>Al (mg L⁻¹)</td>
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<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>0.2</td>
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<tr>
<td>Sb (mg L⁻¹)</td>
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<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
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<td>As (μg L⁻¹)</td>
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<td>&lt; 1.5</td>
<td>10</td>
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<td>Ba (mg L⁻¹)</td>
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<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>0.70</td>
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<tr>
<td>Cd (mg L⁻¹)</td>
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<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>0.005</td>
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<tr>
<td>Cu (mg L⁻¹)</td>
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<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
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<td>Cr (mg L⁻¹)</td>
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<td>&lt; 0.003</td>
<td>&lt; 0.003</td>
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<td>Fe (mg L⁻¹)</td>
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<td>&lt; 0.005</td>
<td>0.3</td>
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<tr>
<td>Hg (mg L⁻¹)</td>
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<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>0.001</td>
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<tr>
<td>Mn (mg L⁻¹)</td>
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<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.1</td>
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<td>Na (mg L⁻¹)</td>
<td>8.8</td>
<td>9.5</td>
<td>9.7</td>
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<tr>
<td>Pb (mg L⁻¹)</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>0.01</td>
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<tr>
<td>Se (μg L⁻¹)</td>
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<td>&lt; 2</td>
<td>&lt; 2</td>
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<tr>
<td>Zn (mg L⁻¹)</td>
<td>0.064</td>
<td>0.04</td>
<td>0.079</td>
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<tr>
<td>Cl⁻ (mg L⁻¹)</td>
<td>11.8</td>
<td>17.5</td>
<td>17.4</td>
<td>250</td>
</tr>
<tr>
<td>NO₂⁻ (mg L⁻¹)</td>
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<td>0.041</td>
<td>0.040</td>
<td>1</td>
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<tr>
<td>NO₃⁻ (mg L⁻¹)</td>
<td>0.75</td>
<td>0.92</td>
<td>1.00</td>
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<td>128.5</td>
<td>82.9</td>
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<td>CN⁻ (mg L⁻¹)</td>
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<td>&lt; 0.025</td>
<td>&lt; 0.025</td>
<td>0.07</td>
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<tr>
<td>F⁻ (mg L⁻¹)</td>
<td>0.08</td>
<td>0.06</td>
<td>0.06</td>
<td>1.5</td>
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<td>NH₃ (mg L⁻¹)</td>
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<td>&lt; 0.2</td>
<td>1.5</td>
</tr>
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<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Surfactants (mg L⁻¹)</td>
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<td>0.04</td>
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<tr>
<td>Hardness (mg CaCO₃ L⁻¹)</td>
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<td>49</td>
<td>134</td>
<td>500</td>
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<tr>
<td>Ethylbenzene (μg L⁻¹)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>200</td>
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<tr>
<td>Monochlorobenzene (μg L⁻¹)</td>
<td>&lt; 0.008</td>
<td>&lt; 0.008</td>
<td>&lt; 0.008</td>
<td>0.12</td>
</tr>
<tr>
<td>Toluene (μg L⁻¹)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>170</td>
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<tr>
<td>Xylene (μg L⁻¹)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>300</td>
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</tbody>
</table>


Abstract
We present experimental results on the recovery of valuable elements from wet magnetic separation tailings of EVRAZ KGOK. The plant annually generates 45 million tons of tailings. The problem of the generation of substantial amount of mining waste can be solved through tailings recycling. Of prime importance for the plant is utilization of multi-tonnage technologies of tailings recycling. Ore concentrate was obtained from the tailings by gravity separation (up to 4.5-7.5%). Titanium magnetite from concentrate is easily separated by magnetic separation and can be added to the main product of the plant. The recovery of scandium from pyroxenes is of high potential. Light silicate products of gravity separation are suitable as raw materials for the production of stone fiber. Experiments revealed a less pronounced effect of unwanted melt crystallization during cooling, which creates heterogeneities in stone fiber.

Keywords: tailings, recycling, ore concentrate, stone casting, basalt fiber, scandium

Introduction
The Kachkanar Ore Mining and Processing Plant is part of the EVRAZ industrial holding. In terms of its annual output, the plant is one of the top five largest ore mining enterprises in Russia. EVRAZ is located in the Sverdlovsk region and develops the Gusevogorskoe vanadium-titanium magnetite iron ore deposit. Because of its high content, vanadium is used as an alloy component for high-strength steel grades. The Kachkanar ore bodies associated with the ore massif of the same name are the only source of vanadium-bearing ores in Russia. The plant has been operated since 1956.

The plant’s annual output is approximately 55 million tons of iron ore. EVRAZ KGOK currently produces iron ore from three open pit mines, which are further processed in crushing, enrichment, sintering and pelletizing workshops. Tailings produced from wet magnetic separation in the volume of about 45 million tons per year are discharged to the tailings disposal site. Tailings slurries at about 10% solids are dumped at the tailings site, which currently stores 1.6 billion tons of tailings. The company is implementing a project to build a new tailings disposal site using advanced technology of tailings thickening, allowing the tailings to achieve solids concentrations of 65–70%, thus substantially reducing the area of tailings dump as well as the negative effect on rivers (Kuznetsov et al., 2013).

The problem related to the generation of substantial amount of mining waste can be solved through the use of waste processing technologies. The tailing dump can be considered as a technogenic mineral deposit. We studied the possibility of using tailings from the wet magnetic separation. Using individual samples, we analyzed the mineral and chemical composition of tailings. Artificial stone production can be regarded as a promising way of using large-tonnage tailings waste. Basalt fibers have recently come into the spotlight (Pisciotta et al., 2015) due to their superior physical and chemical properties, which rank above traditional glass fibers (Chen et al., 2016), which allow one to manufacture a wide range of different materials for construction and technical purposes (Reiterman et al., 2015).

Methods
In this study, we collected 76 kg of tailings from the EVRAZ KGOK tailing dump. Studies were performed at the Faculty of Mineralogy and Petrography of the Perm
State National Research University using a number of integrated methods. These included determination of mineralogy by optical microscopy and X-ray diffraction. The analysis was performed on a Bruker's 2D PHASER powder diffractometer using a copper anode, step time of 0.1 s over an angular range of 5 to 75°2θ from, the duration of one analysis was 15 minutes. The content of minerals was quantified using the TOPAS software. The chemical composition of the tailings was determined by X-ray fluorescence on a Bruker's S8 Tiger spectrometer using the Silicates software. The melting of the samples was simulated using a NETZSCH STA 409 PC Luxx synchronous thermal analyzer. The samples were heated to 1430 °C at a step of 10°C/min and then cooled. The chemical composition of minerals from tailings was determined using an OXFORD INSTRUMENTS INCA ENERGY 350 spectrometer Analytical conditions were 20 kV accelerating voltage, 10 mA beam current, and a 9 mm working distance.

**Results**

The particle size analysis of the tailings revealed the presence of a noticeable amount (more than 20%) of gravel-sized grains represented by rock intergrowths and fragments. In order to reliably determine the mineral composition of the tailings and in order to maximize the opening of the intergrowths and the recovery of useful components (titanomagnetite) as free particles, they were crushed to <0.2 mm particle size.

Optical mineralogical analysis showed that the crushed tailings are mostly diopside (42–74%), plagioclases (7–25%), epidote group minerals (5–15%), amphiboles hornblende and actinolite (2–15%), titanomagnetite (1–2%), olivine (1%), etc. Chlorites, sulfides, garnets, apatite, ilmenite, few biotite, and spinel are present as a few fractions of percent. The XRD data on individual samples substantially differ from those obtained by optical microscopy because of the presence of abundant intergrowths (e.g., pyroxenes and epidote with plagioclases and amphiboles) and mineral microinclusions. XRD analysis is capable of accurate quantification of the weight fraction of each mineral species and is designed for the accurate identification of intergrowths and microinclusions.

The chemical composition of the crushed tailings is heterogeneous from sample to sample despite the noticeable difference in their mineralogy. This is caused by similarities in the chemical composition of silicate minerals, which dominate in the crushed products (pyroxenes, amphiboles, epidote, plagioclases). The predominant components in the crushed tailings (wt.%) are silica (44.41–45.31), calcium oxides (20.12–22.51), magnesium (13.32–14.16), iron (9.49–10.40), and alumina (6.29–7.94), which account for more than 95% of the mineral mass.

X-ray fluorescence analysis data show that the chemical composition of tailings depends on the presence of the predominant minerals. In particular, the presence of silica and calcium and magnesium oxides is explained by the presence of the mineral species (diopside CaMg(Si₂O₆)) having the corresponding composition among pyroxene grains. Alumina is mainly present in plagioclase and epidote group minerals. Iron is found in epidote, amphibole, goethite, and pyrite. The most characteristic feature is the presence of trace elements, such as vanadium (in titanomagnetite) and scandium (in pyroxene). The presence of sulfur is associated with the presence of sulfides, which are also the main concentrators of non-ferrous metals (copper, arsenic, antimony, lead, zinc). Chromium is mainly present in chromiumspinsels.

The acidity index of tailings (SiO₂+Al₂O₃/CaO+MgO), the decisive criterion of the suitability of raw materials for manufacturing of all types of basalt products (basalt continuous fiber, basalt wool, cast basalt) was calculated to be 1.4–1.6. These values are clearly insufficient to recommend the original tailings as raw materials for production of high-quality basalt fiber.

Gravity separation is used to improve the quality of the original tails. The simulation of this process was carried out in the laboratory on a screw lock with a 160 mm gutter diameter. The original crushed tailings clasts
were beneficiated using a screw conveyor with the production of several products: concentrate (4.5–7.5%), final product (60–80%) and tailings.

Concentrate contains mainly titanomagnetite, ilmenite, and sulfides and small amounts of gold, tinstone, intermetallic compounds of Cu and Zn, native copper, and arsenic sulfides. Traces of gold (<0.25 mm) are found in a concentrate; they are present as Ag- or Cu-Ag-gold, usually with traces of mercury (Osovetsky, 2016). Titanomagnetite can be easily separated by magnetic separation and added to the main product of the enterprise. The final product is mainly composed of pyroxene, while the tailings generated by gravity separation are feldspars. An additional microprobe analysis of pyroxene grains revealed the permanent presence of scandium (0.1%). Stepanov et al. (2017) proposed the baseline data for designing a pilot plant with an annual processing capacity of up to 10,000 tons of tailings to produce high purity (99.5–99.95%) scandium oxide in the amount of 1000 kg per year.

The simulation of the melting process of the above-described crushed tailings produced by wet magnetic separation was carried out using a synchronous thermal analyzer. Experiments showed that the tailings products are characterized by a small weight loss during heating (<5%). The melting of the rock-forming minerals begins at 1200–1223°C with an endothermic effect being in the range between -479 and -731 J/g of rock.

Subsequent cooling of the resultant melt at a step of 10 °C/min was carried out to study its crystallization. Analysis of the cooling curves revealed the effect of unwanted nucleation and crystallization during cooling that produces heterogeneities in the products. This effect occurs at a temperature of 1150–1162°C.

Thermal testing of some products generated during gravity separation showed that they are more suitable raw materials for the production of basalt fiber. In particular, the melting of the tailings from gravity separation is accompanied by a lower endothermic effect (decreased by about 23%) and less pronounced crystallization during cooling compared with a similar process developed for the original product.

The quality of raw materials produced by gravity separation of the original tailings was improved due to removal of refractory components (e.g., titanomagnetite, chromite, ilmenite), a decrease in the content of iron, chromium, titanium and a number of other unwanted admixtures. At the same time, sulfides containing both harmful sulfur and toxic elements (e.g., arsenic) were removed from tailings.

Conclusions

Our study demonstrates the advances of the Perm University in the integrated use of raw materials, solving problems of tailings disposal and environmental protection. The price of the proposed technology should take into account the cost of tailings disposal. In the near future, EVRAZ KGOK plans to launch the development of a new ore deposit. In view of the long-term iron ore mining activity in this area, the company needs additional land plots for tailing dumping and disposal. It is planned to build a new tailings disposal site, but its area is limited by its proximity to the river. In connection with this, the application of relevant multi-tonnage and environmentally friendly technologies of tailings disposal are of prime interest.

References

Reiterman P., Holčapek O., Jogl M., Konvalinka P.

Formation of Industrial Gold-bearing Objects in the Development of placers on the Marakan River (Eastern Siberia)

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Abstract
The authors have studied technogenic and mineral formations that were arisen during the development of the Marakan gold placer (Eastern Siberia). Free gold is established in technogenic and mineral formations, which is due to technological and geological reasons. The mineral composition of man-made dumps includes a large amount of sulfides. During placers mining oxidation of sulfides occurs, with the release of gold in them. In acidic man-made waters, gold moves in dissolved form, precipitates and restores gold in the metallic phases. Based on the study of free gold and the theoretical prerequisites for the formation of chemogenically and biogenically deposited gold, the technogenic dumps of the Marakan deposit may have zones of increased concentration of newly formed free gold.

Keywords: man-mademineralformations, man-madewaters, freegold, boundgold

Introduction
The valley of the Marakan River is located in Russia in the north of the Irkutsk region, in the Bodaibo district. Loose formations of eluvial, alluvial, fluvio-glacial, deluvial origin are widespread in the valley of the Marakan River. The alluvial terraces of the gold-bearing placer of the Marakan River have a complex structure. They are represented by normal (interglacial) and fluvio-glacial alluvium. Placer gold occurrence is confined to zones of normal (interglacial) alluvium. It consists of a deep placer and placer of buried terraces of several levels. The bedrock is composed from carbonaceous slates with interspersed sulfides and thin interlayers of marbles. The deep part of the placer is composed by alluvium and is represented by a pebble-boulder-gravel material with clay (the eluvial-alluvial part). The main gold-bearing placer is associated with these deposits. The total thickness of the gold-bearing strata can reach 50 m. The placer is buried under glacial, upper Pleistocene and modern alluvial sediments (Mungalov et al. 1975).

Gold mining and production of primary concentrate is carried out by a gravitational method on an industrial instrument PPM-5 (deroker).

The objects of study were technogenic-mineral formations arising after the enrichment of the placer. Gold content is estimated from the material of boulder-pebble (+ 50mm) and gravel-sand (-50mm) precipitation after the devices of hydraulic washing. Boulder-pebble sediments are washed fragments of rock with the practical absence of clay-sandy aggregate. The composition of the detrital material can be judged on the geological structure of the raft. Sandy complexes are characterized by good sorting. Man-made dumps are well-washed and sorted formation (fig. 1). In the bulk, they are composed from rounded sandstone and shale fragments, as well as a large proportion of quartz and sulfides. The bulk sulfides are represented by oxidized and non-oxidized pyrite. The clay fraction is carried by the water stream from the instruments to the sumps, where the solid phase is gradually deposited on the bottom of the reservoir.
The mineral composition of the heavy fraction is represented by sulfides (pyrrhotite, pyrite, chalcopyrite), ore (ilmenite, hematite, magnetite) and hypergene (limonite) oxides, garnet. A small amount of rutile, zircon, epidote is found.

The placer gold of the Marakan River valley is represented by grains of small, medium and large classes (tab. 1). Gold is rolled over and semi-rolled, lamellar and tabular forms. The color of gold is golden yellow. There are particles of gold with yellowish films, and reddish-brown crusts of iron hydroxides (fig. 2).

According to previous studies, it was found that the distribution of free gold in sandy sediments is uneven. This is due to their gravitational differentiation. In places where pulp is discharged from sluices, the gold content in sandy sediments reaches tens of grams per ton. This material is transported by bulldozers to the general dump. Its location is relatively local and irregular.

**Methods**
The authors tested several sites of technogenic and mineral formations. 105 samples were collected and analyzed with a total volume of 1076 liters over a network of 2×2 m and 1×1 m. Sampling was performed near industrial devices in fresh technogenic deposits from the surface. A single sample with a volume of 20 liters was removed from the wells with a size of 0.3 × 0.3 m and a depth of about 0.2-0.3 m. The optimum volume of a schlich test, and the sampling step for man-made placers, are determined on the basis of previous methodological work. The sample was washed with a tray up to the “black” concentrate; the sample volume was 5–10 litres. After washing, the obtained black concentrate was dried. Visible gold was selected and weighed. The concentrate was reduced at the Perm State University, according to the following methodology: drying, separation of magnetic and electromagnetic fractions, sieving according to size classes, heavy-medium separation.

**Results**
According to the results of the mineralogical analysis, the average gold content on the PPM-5 device was 0.1 g/m³, the bulk of the gold loss is concentrated in the sand dumps.

<table>
<thead>
<tr>
<th>Size of fraction, mm</th>
<th>Weight of fraction, g</th>
<th>Yield of fraction, %</th>
<th>Accumulated output of fraction, %</th>
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<tbody>
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<td>− 0,125</td>
<td>0,005</td>
<td>0,2</td>
<td>0,2</td>
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<tr>
<td>+0,125-0,25</td>
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<td>2,4</td>
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<td>0,252</td>
<td>10,8</td>
<td>13,2</td>
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<td>+0,5-1,0</td>
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<td>23,6</td>
<td>36,8</td>
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<td>+1,0-2,0</td>
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<td>40,5</td>
<td>77,3</td>
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<tr>
<td>+0,2</td>
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<td></td>
<td>2,339</td>
<td>100,0</td>
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</tr>
</tbody>
</table>

**Table 1** Sieve analysis of gold according to exploration data.

**Figure 1** Man-made dumps of placer on the Marakan River.

**Figure 2** Gold particles from sand dumps.
Loss of gold during enrichment on the PPM-5 device is shown in the tab. 2.

**Discussion of results**

The study of man-made gold-bearing dumps revealed the presence of oxidized pyrite. This suggests that under the action of water and air sulfides begin to oxidize. Because of this, the aqueous medium in the man-made dumps becomes acidic (pH 2.0-4.0). The increase in the acidity of industrial waters occurs during the winter time when these processes are intensified due to the freezing of precipitation (Osovetsky et al. 2016).

In the investigation of gold particles from man-made dumps, the presence of grains coated with iron hydroxides in the form of a film was established (fig. 3). Gold particles are completely covered with iron hydroxides. The presence of iron hydroxide films on the surface of gold particles indicates the decomposition of primary sulfides by industrial waters and the further precipitation of iron hydroxides on the surface of gold particles. Gold nanoparticles precipitate along with iron hydroxides.

Gold, like iron, is released during the oxidation of sulfides, and enters into the technogenic water. The release of gold from sulfides is facilitated by frosty weathering, and the presence of microorganisms: iron-oxidizing and sulfate-reducing bacteria. Gold from technogenic waters is deposited on primary gold-bearing phases (gold particles) and forms small crusts on the surface of gold. As a result of this process, there is a “growth” of gold in man-made dumps. (Naumovetal. 2017).

**Conclusions**

Due to the undertaken research, it can be assumed that the process of “growth” of gold is taking place in man-made dumps. Over time, substantial consolidation of the gold-bearing phases may occur. The proof of this process is the presence of technogenic newly formed gold in the dumps. One of the main factors influencing this process is man-made water. It is necessary to study in detail the morphology, and the internal structure of the

<table>
<thead>
<tr>
<th>Size class, mm</th>
<th>Mass, g</th>
<th>Private output of fraction, %</th>
<th>Accumulated yield of fraction, %</th>
<th>Standard coefficient of extraction</th>
<th>Standard coefficient of loss</th>
<th>Extraction of gold, %</th>
<th>Loss of gold, %</th>
</tr>
</thead>
<tbody>
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<td>0.995</td>
<td>0.005</td>
<td>10.325</td>
<td>0.052</td>
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<tr>
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<td>10.85</td>
<td>21.23</td>
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<td>0.005</td>
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<td>0.200</td>
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<td>8.019</td>
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<tr>
<td>-0.1</td>
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<td>100.00</td>
<td>0.500</td>
<td>0.500</td>
<td>0.472</td>
<td>0.472</td>
</tr>
<tr>
<td>Total</td>
<td>21.2</td>
<td>100.00%</td>
<td></td>
<td></td>
<td></td>
<td>85.122</td>
<td>14.878</td>
</tr>
</tbody>
</table>
gold of man-made objects of the Marakan placer. In the future, it is possible to create areas of controlled accumulation of industrial gold.

Acknowledgements
The authors thank the Perm State University for providing the research laboratory. Also authors express gratitude to A.N. Bokarev for the possibility of conducting field research; V.A. Naumov and V.V. Goldyrev for criticism and help in writing the manuscript.

References
Naumov VA, Naumova OB (2017) Scientific bases of geology of technogenic-mineral formations; Perm. StateUn-ty - Perm
Abstract
The article presents the forming processes of technogenic and mineral formations (TMFs) – technogenesis and subsequent transformation of the composition and structure of TMFs – technogeogenesis. The authors studied technogeogenesis on the example of gold-bearing technogenic placers. The processes of TMFs conversion lead to the release, transfer, and accumulation of gold-bearing phases inside man-made dumps. Management of the processes of technogeogenesis leads to the creation of nature-like production technologies. Directions on the management of the formation of gold concentrations in TMFs were allocated. Experiments on the accumulation of gold on geochemical barriers were carried out.

Keywords: tailings, tecnogenesis, tecnogeogenesis, gold, accumulation, nature-like technologies, technogenic-mineral formations (TMFs).

Introduction
The present stage of civilization development is characterized by the fact that Humanity is beginning to understand and accept the limitations of its capabilities, the need to change behavior when using the bowels of the Earth. For the first time, this understanding in terms of quantitative indicators and development models was presented in 1972 in a report to the Rome Club “Limits to Growth”. Subsequent monitoring of data confirms the general trends of civilization.

Guide for the development of monomineral deposits remains at the present stage. Often, the main mineral is mined in the most accessible form of its location. Solid phases of minerals are preferred. We leave the future integrated development of resources to our descendants, storing by-products in dumps. Consequence of partial extraction of useful components brought environmental problems that arose at the place of mining. The problems are created precisely by those components, the extraction and use of which would bring an essential plus to the economics of field development.

The modern approach of geologists to the multipurpose development of the deposits and the reduction of environmental loads is implemented by the idea of TMFs re-developing. The solution of this problem is possible taking into account modern ideas about the TMFs as products of human geological activity. With this approach to the TMFs, we do not have the right to identify them with production waste. They should be considered as an intermediate product, technological reserve of the deposit, suitable for the further usage.

Methods
The structure and content of the TMFs have regular character of the substance distribution in accordance with the system for the formation of technogenic sediments (technogenesis). On the example of gold, we have traced the distribution of its particles that were not extracted for various reasons in the enrichment process; studied the patterns of behavior of gold particles on man-made objects with a wide geography (Ural, Siberia, Yakutia, the Far East, Canada (Yukon Territory, Klondike) ) (Kovlekov, 2002; Makarov, 2001; Mirzehanova, Mirzehanov, Debelaya, 2014; Naumov, 1994; Naumov, 2010; Perepelitsyn, Ryitvin, Koroteev, 2013; Naumov, LeBarge, Kovic, 2013).

Technogeogenesis, or processes of
transformation of the gold mineral phases in the composition of the TMFs is considered in detail by analyzing the series: Au - Hg - Cu; Au - Pt (Fe), Au - Pb. Gold technogeogenesis in technogenic formations (dissolution, transfer, accumulation) leads to mobilization and sedimentation, enlargement of gold particles (agglomeration, new formation, sticking of gold particles into a common aggregate) during the interaction of different gold particles (Au - Au).

Management of the formation of gold concentrations in industrial conditions was realized in the development and implementation of modular technologies in one of the placers of the Urals. According to the project Federal Program of the Ministry of Education and Science of the Russian Federation, 6% or 9.24 kg of chemically pure gold was additionally obtained for placers. Analysis of the finding gold forms in the sludge storages of gold ore facilities in the Urals and leaching dumps of the Muruntau deposit (Uzbekistan), facilities of the Yenisei ridge, Yakutia and Canada made it possible to prepare recommendations for increasing the degree of gold extraction in enterprises.

Gold is widely distributed in nature in different sediments, state of aggregation, different forms of finding. **In the solid phase:** free, bound in minerals, in intergrowths, “film” and sorbed on minerals. **In solutions:** mine and underwater waters, brines, oils. **In gases and sublimates,** it is often not seen, forms of finding are not know, therefore they are not removed. Technology of investigation and extraction is aimed on extracting of certain forms of gold finding. It does not take into account other forms. In mining gold (other forms of finding) comes into man-made dumps or man-made mineral formations (TMFs). The best studied is solid phase: free, bound in minerals, in intergrowths, “film” and sorbed on minerals.

The authors study the applied aspect of the physicochemical differentiation of gold within the framework of an international research group with Italian colleagues. The theoretical foundations of the mechanisms of dissolution and re-precipitation of gold have been developed. Gold is dissolved by cyanides of Na or K, acidic solutions of \( \text{FeCl}_2, \text{Cu}_2\text{O}_2, \text{NaCl}, \text{HCl}, \text{H}_2\text{SO}_4 \), etc. Gold transfer occurs by ore, waste and subsoil waters. Gold deposition takes place on geochemical barriers.

The experiments on gold accumulation at a number of geochemical barriers were carried out: 1) carbonate (Naumov, 1994) for acidic waters; the restoration of dissolved phases to clastogenic particles of native gold on the carbonate barrier in a concrete settling tank (Urals, Isovskiy mine) was established; 2) electrochemical (Naumov, 1994) on a metal grid; sedimentation of gold from technogenic waters on a copper wire by natural electrolysis was proved (the Urals, the Isov mine); 3) carbon (Naumov V.A., Osovetskii, 2010), the results of experiments were obtained, allowing to confirm the direction of the process of gold sorption, the mechanisms of its accumulation and the distribution of nanogold particles on the coal surface.

On the territory of Northern Italy and the Urals, the selected man-made model objects were used to study the composition and zonality of man-made and mine waters. One of the objects is a preserved skarn iron ore deposit with the presence of zones of arsenopyrite mineralization, located in the Southern Alps. Another is the dumps of the polymetallic object of the Eastern Urals. Samples of waste, bottom-waste and mine waters were taken in order to determine the magnitude of gold mineralization. Experiments on the formation of artificial carbonaceous barriers in the form of capsule modules are planned.

**Main results**

Among the geological processes associated with the TMFs are distinguished: 1) the processes of formation of the TMFs, or actually technogenesis; 2) geological processes of transformation of the composition and structure, occurring in the TMFs - technogeogenesis. Taking into account that the processes of technogenesis and technogeogenesis are manageable (depend on human activity), it is also possible to distinguish 3) the processes of technogenic ore genesis - the perceived formation of given characteristics of the structure and directions.
of change in the composition of the TMFs (Naumov, 2010; Naumov, Naumova 1997). Technogenic ore genesis has an applied value and is based on knowledge of the processes of technogenesis and technogeogenesis.

Technogenesis or formation of the TMFs occurs as a result of processes of mechanical differentiation and integration. The laws of distribution of substance and useful components in the dumps do not depend on the composition of the natural material (loose sediment deposits or crushing products of primary ores). At the same time, technogenic facies of three types are formed: alluvial, dump (bulk) and waste-alluvial (Naumov, 1994). Under the technogenic facies is accepted - the product of accumulation of the TMFs, formed during the technical activities of man in the process of deposits development.

Technogeogenesis appears in the processes of mineral new formations, the transformation of matter and useful components under the influence of internal and external factors of the geological environment. As a geological exogenous process - technogeogenesis is distinguished by the presence of destruction of rocks and mineral phases in the TMFs; transportation of material and transport of chemical elements in dissolved form; accumulation and formation of new mineral and petrographic differences.

The appearance of technogeogenesis in dumps is due to mechanical, physicochemical and biochemical differentiation and integration of the substance, including useful components. Here the role of surface, waste, ore, substernal, industrial waters developed within the limits of the TMFs is great. When saturated with useful components in the process of technogeogenesis, they can be considered as hydromineral raw materials of practical importance. Such waters are formed in the the TMFs formed during the mining of sulphide deposits containing copper, iron, arsenic, mercury, gold, silver, etc.

The concept of “technogenic ore genesis” represents the geological process of the creation by nature or man of new ore objects from technogenic sediments, as a result of the processes of technogenesis and following technogeogenesis (Naumov, 2010).

Gold technogeogenesis in technogenic formations, including the processes of dissolution and destruction, transfer and accumulation, leads to the redistribution of the metal and the formation of concentration zones.

Managing the processes of technogeogenesis has the following main aims:
- accumulation of useful components for the purpose of their subsequent extraction (nature-like production technologies);
- creation of nature-like environmental protection systems.

Conclusions
The processes of technogeogenesis in gold-bearing technogenic-mineral formations lead to the formation of “beneficiation plants in the subsoil”, where natural processes of redistribution of matter take place inside the technogenic objects. As a result of these processes, the release, dissolution, migration, regeneration and restoration (growth) of gold-bearing phases, including in the form of gravitationally recoverable gold, occurs.

Natural-like or technogenic processes of change in the geological environment are endogenous and exogenous geological processes activated by man. Today they appear everywhere as a new stage in the development of the noosphere, a technospheric stage. However, the study of these processes almost no attention. At the same time, these unconscious processes are controlled by us. The results of the geological activity of technogenic processes (the transformation of matter and space in technogenic formations that occur at the border of the interaction of litho-, bio-, hydro-, atmo- and sociosphere) are amazing. They lead to both negative and positive consequences for a person. Their controllability allows you to create cost-effective concentrations of useful components for mastering or use the laws of their transformation to produce substances with given characteristics of composition and properties. Mankind has launched the mechanisms of the “factories in the depths”. The task is to learn how to manage and create the necessary products.

Some ways to control the processes of technogeogenesis and increasing the degree of gold extraction can be outlined:
1) amplification of the technogeogenesis processes (ensuring circulation of industrial waters; activation of decomposition of sulphides, etc.);
2) formation of mechanical and chemical barriers inside man-made structures for the accumulation of useful components;
3) design of construction sites for the placement of the technogenic formations, taking into account the introduction of technologies for the extraction of man-made gold.

In general, the investigation of the generation of technogenic-mineral formations is of great theoretical and practical importance. The correct approach to the application of the TMFs allows one to develop a number of nature-like technologies that will be more efficient and environmentally friendly than the extensive way of developing new deposits.

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**References**


Useful Component Recovery from Saranovskaya Mine Rudnaya Wastes

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Abstract
This study presents experimental results on beneficiation of tailings from the Saranovskaya Mine Rudnaya (SMR) at the Main Saranovskoe deposit, Perm region. The goal of this study was to analyze the composition of tailings and to determine the degree of their suitability for upgrading using a spiral classifier. Laboratory studies show that the proposed upgrading flow chart was correct. The experiments yielded a chrome concentrate of economic importance. In addition, this study presents new quantitative data on the platinum-group elements (PGE) concentrations in the chrome ores from the central ore body (COB), microphotographs of mineral forms of platinum-group metals recovered from tailings and data on their chemical composition.

Keywords: chromite, tailings, beneficiation, platinum-group minerals, spiral classifier

Introduction
Chrome ores are the most important raw materials for iron and steel industry. Global chromite consumption is steadily increasing, amounting to 12 - 13 million tons per year. The main chrome ore deposits in Russia are Saranovskoe and Southern Saranovskoe (Perm Region), Aganozerskoe (Karelia), Sopcheozerskoe (Murmansk region). Of these deposits, only the Main Saranovskoe deposit with the estimated reserves of 4.7 million tons, which are about 11% of the above-mentioned deposits, is currently mined (State Report 2017). Nevertheless, Saranovskaya Mine Rudnaya is the largest and most important enterprise in Russia for chromite ore extraction and beneficiation. At present, the Main Saranovskoe deposit is currently mined. The thickest beds, containing ores with a similar chemical composition and known as the Western, Central and Eastern ore bodies are under exploitation. The mined ore is beneficiated at the beneficiation plant, which is located directly on the industrial site of the mine and is incorporated in a single process flow chart.

Many publications are devoted to the characteristics of the geological structure. The main Saranovskoe Deposit has attracted the attention of geo-log immediately after opening in the 30-ies of the XIX century (Zaitseva, 2009), thanks to the discovery of a new chromium-containing minerals: uvarovite (Hess, 1832). As the field of chrome ores it has begun to be developed since 1889 the Characteristics of its geological structure is the subject of numerous publications (Vakhromeev and others, 1936; Zimin, 1938; Volchenko and others, 1979). The monographic description of the Saranovsky magmatic complex with the detailed characteristic of its petrographic structure, and also the field is executed by O. K. Ivanov (1990). Later (2016) he compiled a description of the Mineralogy of the Deposit.

Description of the structure and composition of ore bodies of the Main Saranovskoye Deposit, the methods of their testing was made by V. F. Myagkov and V. L. Batalov in 1966. R. G. Iblaminov (2002) reconstructed the history of the formation of the Deposit.

The Deposit was studied in detail in the course of numerous geological exploration works, as well as various scientific and case studies. The most detailed information about the structure and composition of ore bodies was obtained as a result of geological surveying, which ensured the operation of the Deposit.
In view of the current trend of raw materials import dependence and the lack of domestically mined raw materials, the active use of beneficiation tailings of chromite ores appears to be of great importance.

We analyzed the composition of tailings generated at the Saranovskaya Mine Rudnaya (SMR) and performed experiments on tailings beneficiation to obtain an additional source of chromium, improve the ecological situation in the area and assess the possibility of the recovery of platinum-group metals.

**Object of Study and Analytical Methods**

The Main Saranovskoe deposit, located on the western slope of the Middle Ural Mountains in the Perm region (Russia), has been mined since the 1930s. Mining and beneficiation activities on the northern flank of the Main Saranovskoe deposit generated a large dump of solid wastes (tailings), 50 m in length, 8 m in width, and 6 m in height which are stored as a pile on the mine site (fig. 1).

Figure 1 shows sampling localities and Table 1 presents sampling data.

Shovels and 10 L metallic bins were used to collect samples. Samples were placed in plastic bags and labeled with a sample identification number and sample location. All of the samples were delivered to the laboratory for analysis, the <2 mm fraction was separated by sieving and the percentage of this fraction was determined along the pile contour. The 4 and 2 mm mesh hand sieves were used to obtain three fractions. The mineral composition of the >2 mm fractions not upgraded without using an additional preparation technique was studied using a Leica EZ4 stereomicroscope to determine the percentage of the ore component in the >2 mm fraction.

**Table 1 The weight of collected samples**

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sampling locality</th>
<th>Weight, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR-1</td>
<td>center</td>
<td>30</td>
</tr>
<tr>
<td>SR-2</td>
<td>base</td>
<td>30</td>
</tr>
<tr>
<td>SR-3</td>
<td>center</td>
<td>30</td>
</tr>
<tr>
<td>SR-4</td>
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<td>30</td>
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<tr>
<td>SR-5</td>
<td>base</td>
<td>30</td>
</tr>
<tr>
<td>SR-6</td>
<td>center</td>
<td>30</td>
</tr>
<tr>
<td>SR-7</td>
<td>top</td>
<td>30</td>
</tr>
<tr>
<td>SR-8</td>
<td>top</td>
<td>30</td>
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<td>base</td>
<td>30</td>
</tr>
<tr>
<td>SR-13</td>
<td>top</td>
<td>30</td>
</tr>
</tbody>
</table>

**Figure 1** Photo of tailings pile with sampling localities (Google Earth Pro).
Because of its high specific gravity (4.2-4.8), chromite can be easily upgraded using a spiral classifier (Polkin 1987). The <2 mm fraction was subjected to upgrading, because of the large volume of samples not requiring additional preparation. The next step was the selection of a spiral classifier, depending on its specifications. It was found practically that the SVM-250 spiral classifier is best suited for our purposes, but has substantial drawbacks, namely insufficient water flow inside a table. This disadvantage was overcome by using additional perforated hose.

Mineralogical and geochemical studies of samples were performed in the laboratories of the Nanomineralogy Sector and Department of Mineralogy and Petrography of the Perm State University. The chemical composition of rocks and ores was determined on Bruker’s S8 Tiger (Bruker, USA) X-ray fluorescence spectrometer. The total mineral composition was determined by X-ray powder diffraction using a D2 Phaser (Bruker, USA) diffractometer. The identification of mineral phases was based on the PDF-2 database (2010) The composition of the chromite grains was studied using a scanning electron microscope JSM-6390LV (Jeol, Japan) equipped with an EDS system (INCA 350 Oxford Instruments, UK). The contents of the platinum group elements (PGEs) were determined by ICP-MS with an ELAN-9000 instrument at the Institute of Geology and Geochemistry of the Ural Branch, Russian Academy of Sciences. The content of PGEs was analyzed in the <2 mm fraction concentrates in the laboratory of the Nanomineralogy Sector of the Perm State University using an AURORA M90 (Bruker, USA) inductively coupled plasma--mass spectrometer.

**Results**

The results of sieve analysis showed that the <2 mm particles prevail in the dump and account for two thirds of the dump tailings. The average value for all samples taken is 71% of the fraction less than 2 mm and 29% of the fraction greater than 2 mm. Table 2 shows the average mineral composition of the >2 mm fraction, which was not subjected to upgrading without preliminary preparation.

**Table 2** Mineral composition of the 2-4 mm and >4 mm fractions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight, g</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromite</td>
<td>145.7</td>
<td>33.5</td>
</tr>
<tr>
<td>Serpentine</td>
<td>277.7</td>
<td>64.7</td>
</tr>
<tr>
<td>Uvarovite + calcite</td>
<td>6.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Total</td>
<td>429.2</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2 shows that >2 mm fractions are not of particular interest due to the low proportion of this fraction in the dumped tailings. Second, nearly 65% of this fraction is represented by silicate rocks. The next step involves upgrading the <2 mm fraction to obtain two concentrates. Concentrate I is the lighter fraction represented by low density grains, while the concentrate II is the heavier fraction. The final concentrates were dried and weighed. The averaged data of gravimetric analysis for all samples were 67% of the heavy fraction concentrate and 33% of the light fraction concentrate. Both qualitative and quantitative analyses of the concentrates and the starting tailing samples were performed using various analytical techniques. Such methods as electron microscopy with a microprobe analyzer, X-ray structural analysis, X-ray fluorescence analysis, ICP-MS method, sieve analysis, mineralogical analysis under a microscope, which were discussed in the Methods Chapter. XRD analysis showed changes in the mineral composition of tailings, before and after upgrading (Table 3).

X-ray diffraction analysis confirmed that the upgrading resulted in the increase in the proportion of chromite and decrease in the proportion of impurities in the heavier fraction. XRF data also confirms the high-grade characteristics of the final product (Table 4).

The percentage of recovery of the useful component (chrome) was calculated for combined sample weighing 51 kg and is presented below in Table 5.

The mineralogical and geochemical data by Volchenko in 2011 were used to estimate the average content of PGEs in the western (WOB), central (COB) and eastern (EOB) ore bodies (mg/t, respectively): Os – 108, 110, 88; Ir – 140, 117, 50; Ru – 100, 110, 82; Rh – 8, 22, 10; Pt – 50, 70, 40; Pd – 6, 3, 10.
The study showed the presence of laurite RuS$_2$, erlichmanite OsS$_2$ series platinum-group minerals (PGM) in all ore bodies, which occur as idiomorphic grains, 5-50 micrometers in size, and the presence of braggit (Pt, Ni) S - vysotskite (Pd, Ni) S series occurring as small inclusions (1-10 micrometers in size) in the COB Cr-spinels. The authors revealed a trend of increasing concentrations of Os, Rh, and Pd upward the section (from west to east). Despite the complex nature of the ores, these authors showed that the recovery of precious metals is not economically feasible due to the lack of acceptable technology for PGM recovery and the use of chrome ores in refractory manufacturing. The form of occurrence and localization of PGM in the tailings was studied to identify the possibility of PGM recovery and ore upgrading. Since the PGMs are characterized by a small grain size (up to 50 μm), beneficiation tailings with a < 4 mm particle size, which are mostly Cr-spinel and serpentine in composition were collected. The <2 mm fraction was upgraded using a spiral classifier to obtain a high-grade Cr-spinel concentrate (95-100%). The 0.5-0.125 mm and <0.125 mm fractions were sieved out and upgraded with bromoform to ultra-fine concentrates and studied under the electron microscope. The 0.5-0.125 mm fraction was mounted into epoxy resin and polished twice to different depths of grains, and the <0.125 mm fraction was dusted as a thin layer directly onto a carbon tape. The study of these samples showed the presence of PGMs only in the <0.125 mm fraction. The PGMs (Fig. 2, table 6) are represented by laurite (8 grains) and erlichmanite (1 grain). Fragments of films of the irarsite composition (IrAsS) were found on two laurite grains. They are represented by isolated grains, while no intergrowths with other minerals or inclusions in Cr-spinel grains are found. The concentrations of PGE were determined by mass spectrometry in the chrome ore from the central ore body (Table 7).

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>TiO$_2$</th>
<th>Cr$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>MnO</th>
<th>SO$_3$</th>
<th>LOI***</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting tailings *</td>
<td>13.72</td>
<td>3.81</td>
<td>0.73</td>
<td>0.62</td>
<td>31.43</td>
<td>23.81</td>
<td>18.24</td>
<td>0.16</td>
<td>0.07</td>
<td>1.34</td>
<td>101.2</td>
</tr>
<tr>
<td>Heavy fraction</td>
<td>12.9</td>
<td>1.51</td>
<td>0.33</td>
<td>0.64</td>
<td>43.01</td>
<td>25.08</td>
<td>19.49</td>
<td>0.17</td>
<td>0.06</td>
<td>0.45</td>
<td>101.8</td>
</tr>
<tr>
<td>Light fraction</td>
<td>24.21</td>
<td>34.64</td>
<td>5.74</td>
<td>0.54</td>
<td>10.32</td>
<td>8.24</td>
<td>5.28</td>
<td>0.25</td>
<td>0.08</td>
<td>11.96</td>
<td>102.1</td>
</tr>
</tbody>
</table>

* - tailings from a dump

<p>| Table 3 The mineral composition of tailings before and after upgrading (average value for all samples, in %) |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Chromite</th>
<th>Serpentine</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Quartz</th>
<th>Albite</th>
<th>Magnetite</th>
<th>Actinolite</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting tailings*</td>
<td>51.4</td>
<td>28</td>
<td>3.8</td>
<td>3.6</td>
<td>2.1</td>
<td>2.8</td>
<td>1.8</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>Heavy fraction</td>
<td>100</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>Light fraction</td>
<td>31.1</td>
<td>32.8</td>
<td>6.8</td>
<td>6.8</td>
<td>8.6</td>
<td>4.6</td>
<td>6.2</td>
<td>3.1</td>
<td>100</td>
</tr>
</tbody>
</table>

* - tailings from a dump

<p>| Table 4 The results of x-ray fluorescence analysis (average value for all samples), wt.% |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr$_2$O$_3$, wt.%</th>
<th>Cr$_2$O$_3$, kg</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>heavier fraction</td>
<td>43.01</td>
<td>12.7</td>
<td>79.0</td>
</tr>
<tr>
<td>light fraction</td>
<td>10.3</td>
<td>2.1</td>
<td>21.0</td>
</tr>
</tbody>
</table>

<p>| Table 5 Percentage of recovery of the useful component Cr$_2$O$_3$, % |</p>
<table>
<thead>
<tr>
<th>Sample no. (tailings)</th>
<th>Weight of sample, kg</th>
<th>Cr$_2$O$_3$, wt.%</th>
<th>Cr$_2$O$_3$, kg</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>heavier fraction</td>
<td>30</td>
<td>43.01</td>
<td>12.7</td>
<td>79.0</td>
</tr>
<tr>
<td>light fraction</td>
<td>21</td>
<td>10.3</td>
<td>2.1</td>
<td>21.0</td>
</tr>
</tbody>
</table>
Table 6 The composition of platinum-group metals, wt. %

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>33.51</td>
<td>37.48</td>
<td>35.35</td>
<td>32.94</td>
<td>31.52</td>
<td>36.63</td>
<td>36.74</td>
<td>35.25</td>
<td>25.81</td>
<td>27.34</td>
<td>30.46</td>
</tr>
<tr>
<td>Ni</td>
<td>0.00</td>
<td>0.18</td>
<td>0.22</td>
<td>0.00</td>
<td>0.00</td>
<td>0.43</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.41</td>
</tr>
<tr>
<td>As</td>
<td>0.00</td>
<td>0.00</td>
<td>0.23</td>
<td>0.00</td>
<td>0.24</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>8.94</td>
<td>8.70</td>
</tr>
<tr>
<td>Ru</td>
<td>30.59</td>
<td>44.06</td>
<td>42.94</td>
<td>32.27</td>
<td>26.30</td>
<td>46.07</td>
<td>47.74</td>
<td>45.59</td>
<td>3.22</td>
<td>20.38</td>
<td>32.40</td>
</tr>
<tr>
<td>Ir</td>
<td>14.10</td>
<td>7.13</td>
<td>4.89</td>
<td>6.33</td>
<td>14.21</td>
<td>6.41</td>
<td>8.15</td>
<td>4.17</td>
<td>21.89</td>
<td>29.76</td>
<td>17.27</td>
</tr>
<tr>
<td>Σ</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Note. The columns show the average compositions (out of 2 analyses): 1-8 - laurite, 9 - erlichmanite, 10 and 11 - irarsite film on the laurite grains 1 and 3, respectively

Figure 2 Os-Ru sulfides (BSE): a, b - laurite crystals of various forms; c - a fragment of an irarsite film on laurite (b)

Table 7 Platinum-group elements (PGE) concentrations, ppm

<table>
<thead>
<tr>
<th>Element</th>
<th>Chromite</th>
<th>Chromite</th>
<th>Chromite</th>
<th>Chromite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>0.002</td>
<td>0.000</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>Ir</td>
<td>0.023</td>
<td>0.016</td>
<td>0.021</td>
<td>0.022</td>
</tr>
<tr>
<td>Pt</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>Ru</td>
<td>0.322</td>
<td>0.224</td>
<td>0.086</td>
<td>0.023</td>
</tr>
<tr>
<td>Rh</td>
<td>0.039</td>
<td>0.030</td>
<td>0.012</td>
<td>0.008</td>
</tr>
<tr>
<td>Pd</td>
<td>0.162</td>
<td>0.218</td>
<td>0.122</td>
<td>0.047</td>
</tr>
<tr>
<td>Au</td>
<td>0.000</td>
<td>0.000</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>Subtotal</td>
<td>0.551</td>
<td>0.491</td>
<td>0.249</td>
<td>0.103</td>
</tr>
<tr>
<td>Total</td>
<td>1.0415</td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8 PGE contents of tailings, ppm

<table>
<thead>
<tr>
<th></th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Au</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.30</td>
<td>0.00</td>
<td>0.77</td>
<td>0.42</td>
<td>0.09</td>
<td>0.06</td>
<td>0.23</td>
<td>1.87</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.00</td>
<td>0.73</td>
<td>0.06</td>
<td>0.03</td>
<td>0.08</td>
<td>0.14</td>
<td>1.10</td>
</tr>
</tbody>
</table>

1 – heavier fraction obtained from tailings upgrading using a spiral classifier, 2 – lighter fraction of obtained from tailings upgrading using a spiral classifier.
contents in the light and heavy fractions, obtained from beneficiation of tailings from the Saranovskoe chromite deposit using a spiral classifier.

The following conclusions can be made: although no economic concentrations were identified, the contents in Tables 7 and 8 are close to them. However, Volchenko Yu.A. reported that the PGE contents may reach economic concentrations, but he emphasized the impossibility of PGM recovery due to the need to crush lumpy chrome ore, which is the main industrial type in the enterprise. Also, there is an assumption that the PGMs might have migrated into tailings together with the associated silicate rocks. Moreover, additional upgrading tests using magnetic and electromagnetic separators proved to be ineffective. The results of this study allowed the enterprise to install an additional beneficiation line using spiral classifiers to obtain the final product in the form of the <2 mm chrome concentrate.

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The author thanks scientific secretary Stepanov Y.I., the head of sector of the technological mineralogy Smetannikov A.F. Academic Secretary of the Mining Institute of the Ural Branch, Russian Academy of Sciences, Blinov S.M., a former dean of the Geological Department of the Perm State University, Ivolovskiy Andrey, the mine surveyor of the Saranovskoe Mine Rudnaya and the chief geologist Babkin Sergey (2015-2017). Special thanks are also due to Osovetsky B. M., the head of the Nanomineralogy Sector and the head of the Department of Mineralogy and Petrography Iblaminova R.G. of the Perm State University.

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GEOTECHNICAL ISSUES RELATED TO MINE WATER
Numerical Simulation Investigation on Water-sand Mixture Flow through a Single Fracture

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Abstract
Quicksand is a hazard that water-sand mixture pours into underground space through a pathway and causes financial loss or even casualties. When the fractures connect sand aquifers and underground space, the water and sand will flow into underground space under hydraulic head and gravity. Numerical simulation of water-sand flow through one single straight fracture is conducted in this paper using DEM-CFD method. The results show that the sand mass flow rate has a positive linear relationship with fracture width and a 1.5 powder relationship with fracture aperture when water-sand mixture transport through a straight flat fracture is in the stable stage.

Keywords: fracture, quicksand, mass flow rate, numerical simulation

Introduction
Quicksand or sand inrush is a hazard which threatens the mining and tunneling. When sand aquifers are connected to underground space by a pathway, the water-sand mixture from the aquifers pours into the underground space through the pathway under the effects of gravity and hydraulic head. For the suddenness and rapidity of occurrence, quicksand is difficult to be predicted timely and is dangerous for production and construction in mining and tunneling. To avoid quicksand hazard, especially in mining, overburden failure were investigated to evaluate the risk of quicksand by scale modeling, empirical approach and numerical simulation (Zhang and Peng, 2005; Yang and Xia et al., 2011; Chen and Zhang et al., 2014). Flow rate of water-sand mixture in quicksand is widely focused in the precious investigations. Liu (2015) experimentally simulated the water-sand mixture flow across the broken zone of rocks. Sui (2017) investigated the speed of sand flow through a fixed porous bed and obtained an equation on calculation of mass flow rate. Zhang (2015) established a calculation model to explain the flow rate of water-sand mixture of quicksand occurring in the Longde coalmine. Liang and Sui (2011) analyzed the relationships among quicksand volume, particle size and diameter of the borehole. Yang et al. (2012) analyzed the relationship between velocity of water-sand mixture and width of fracture pathway, and the relationship between time and quicksand volume. Guo et al. (2013) experimentally studied sand flow through an orifice under variable hydraulic heads on soil-erosion problem. According to the quicksand accidents happened, the types of pathway is various. Drilling boreholes, faults and collapsed columns can all be the pathways. But the common pathway in the quicksand hazard is fractures, which always appears in the form of fracture network. Figure 1 is a diagrammatic sketch of quicksand through fractures. Therefore, the water-sand mixture flow through fractures is an important subject in the research of quicksand. Fracture network is composed by many single fractures and water-sand mixture flow through fracture network is a comprehensive result of water-sand mixture flow through each fracture. Hence, the investigation on water-sand mixture flow through a single fracture is the foundation of the investigation on the water-sand mixture flow through fracture network. Although the phenomenon of water-sand mixture flow through a single fracture is focused,
the relationship between mass flow rate of sand in water-sand mixture and the width and aperture of fracture is not investigated sufficiently. Therefore, this paper investigated the relationship between mass flow rate of sand in water-sand mixture and the width and aperture of fracture and the transport process of water-sand mixture through one single straight fracture by using DEM-CFD method.

**Methods**

DEM (Discrete Element Method) is an approach widely applied in the numerical simulation of granular materials. DEM is more suitable to realize the simulation of discontinuous material compared to the simulation methods based on the continuity hypothesis. EDM approach has an advantage on simulating sand as a kind of discontinuous materials. However, the DEM approach is not suitable for the fluid material. The common method to simulate fluid is calculational fluid dynamics (CFD) which is widely used in the numerical simulation investigation of fluid. But the CFD approach cannot realize the simulation of movement of sand particles. Water-sand mixture is a two-phase material containing solid and liquid phases. Neither DEM approach nor CFD approach can achieve the simulation of water-sand mixture. Therefore, a coupled DEM-CFD approach is carried out to complete the simulation of the movement of water-sand mixture. In coupled CFD-DEM, the movement of particles is obtained by DEM which applies Newton's laws of motion to every particle, while the flow of fluid is solved by CFD approach. The interactions between the fluid and solid phase is modeled by use of Newton's third law.

To investigate the water-sand mixture flow through a single fracture by numerical simulation, a numerical simulation model is established. The numerical simulation model for water-sand mixture transport through a single straight flat fracture is formed by a box and a slant fracture, as shown in Fig. 2. The box is a container of sand particles for modeling the watered sand layer and providing water-sand mixture. The size of the box is 14 cm long, 10 cm wide and 10 cm high. The bottom of the box is connected to the slant fracture. The joint is separated by a small wall which will be removed at the beginning of simulation. When the wall disappears, the sand particles move from the box into the fracture under hydraulic head and gravity. The fracture is a slant straight flat fracture with a 30°dip angle and the section of the fracture is a rectangle. After the sand particles leaving the box and entering the fracture, the sand particles move along the fracture until flowing out of the fracture. The sand particle is regard as a sphere. The diameter, density, Poisson's ratio and shear modulus of the sand sphere is 0.5 mm, 2600 kg/m\(^3\), 0.25 and 1×10\(^6\) Pa respectively. The models of interaction between particle and particle and interaction between particle and wall both are Hertz-Mindlin model. Moreover, the difference of hydraulic head between the top of box and the outlet of the fracture is set as 10 cm. The top of the box is the inlet of water and the outlet of the fracture is the outlet of water.

The factors influencing the water-sand mixture flow are various and complex. The fracture width and fracture aperture are two important factors in the water-sand mixture flow. To investigate the relationship between mass flow rate of sand in water-sand mixture and the width and aperture of fracture, the transport of water-sand mixture through a single straight flat fracture under different fracture apertures and fracture widths are simulated. Tab. 1 shows the numerical simulation scheme. There are 9 trials which
can be divided into two groups. One group contains No.1, 2, 3, 4 and 5 trials, which have different fracture apertures, the other contains No.6, 7, 8 and 9 trials, which have different fracture widths.

**Results**

Fig. 3 shows the process of numerical simulation of water-sand mixture transport through a single straight flat fracture. When the straight fracture is connected with the sand box, the sand particles fall into the fracture under water flow and gravity. The sand particles accelerate and flow along the fracture dip. After entering the fracture, the sand particles concentrate in the bottom of fracture and the stratification of sand particles strengthen with the increment of transport distance. The stratification is caused by the density difference of water and sand. The density of sand is higher than that of water, thus the sand particles sink and concentrate in the bottom of fracture. Transport distance, the velocity of sand, the velocity of water and density of sand particle all influences the degree of stratification. Generally, the long transport distance and high density of sand particles strengthen the degree of stratification while the high velocity of sand and water weaken the degree of stratification.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Fracture aperture (mm)</th>
<th>Fracture width (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>No.2</td>
<td>1.5</td>
<td>6</td>
</tr>
<tr>
<td>No.3</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>No.4</td>
<td>2.5</td>
<td>6</td>
</tr>
<tr>
<td>No.5</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>No.6</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>No.7</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>No.8</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>No.9</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

Fig. 4 shows the curve of accumulative mass of sand versus time. During the transport of water-sand mixture the sand flow comes into a stable state rapidly after a short initial state. The stable state maintains with a decrease of the height of sand layer. On the top of sand layer, a funnel forms and develops. When the height of sand layer is thin, the mass flow rate of sand begins to decrease gradually until the sand flow out entirely. Therefore, the transport process of water-sand mixture through a straight flat fracture can be divided into three stages: initial, stable and end stages. In the stable stage, the mass flow rate of sand keeps constant. The mass flow rate of the stable stage represents the maximum ability of the fracture to transport.
the sand in water-sand mixture under the same condition. Therefore, the mass flow rate of sand in water-sand mixture investigated in this paper is focused on that in the stable stage.

Fig. 5 shows the flow rates of sand in the stable stage under different fracture apertures. The mass flow rate of sand increases with the increment of fracture width. Data fit shows that the relationship between the sand mass flow rate and fracture width satisfies the positive linear correlation.

The mass flow rates of sand in the stable stage under different fracture apertures are represented in fig. 6. Similar to the relationship between the sand mass flow rate and fracture width, the fracture aperture also increases the sand mass flow rate. But the relationship between the sand mass flow rate and fracture aperture does not satisfy the linear relationship. Data fit shows that the relationship between the sand mass flow rate and fracture aperture is positive correlated by 1.5 power.

According to the results of data fit, the sand mass flow rate has a linear relationship with fracture width and a 1.5 powder relationship with fracture aperture when water-sand mixture transport through a straight flat fracture is in the stable stage.

Discussions and limitation

Water-sand mixture is a two-phase material containing sand and water. During the transport of water-sand mixture, the sand particles and water interact with each other. The transport of water-sand mixture is a comprehensive representation of interactions. The mass flow rate of sand in water-sand mixture is different with the mass flow rate of pure water flowing through a single straight fracture. The mass flow rate of water only fits for the cubic law. The sand mass flow rate of water-sand mixture has a linear relationship with fracture width and a 1.5 powder relationship with fracture aperture. The relationships with fracture width are both linear relationships. The difference of them is the relationship with fracture aperture. This means that the mechanism of sand in water-sand mixture transport is different with that of water only.

The transport of water-sand mixture through a single straight flat fracture is affected by many factors. However, this paper only investigates the effect of fracture width and fracture aperture on the mass flow rate of sand in water-sand mixture. The effects of other factors such as fracture dip angle, particle diameter and friction coefficient are not studied. Therefore, these factors are needed to be investigated in the future work. Furthermore, a straight flat fracture is a
simplified fracture and has a difference with the natural fracture. Therefore, the complex fracture should be investigated based on the investigation of one single straight fracture in the future.

**Conclusions**

This paper investigates transport of water-sand mixture through one single straight fracture and the relationship between mass flow rate of sand in water-sand mixture and the width and aperture of fracture by numerical simulation. By changing the fracture width and fracture aperture, the relationships between sand mass flow rate and fracture width and the relationships between sand mass flow rate and fracture aperture are observed and analyzed. The main conclusions are as follows:

1. The sand particles concentrate in the bottom of fracture and the stratification of sand particles strengthen with the increment of transport distance.
2. The transport process of water-sand mixture through a straight flat fracture can be divided into three stages: initial, stable and end stages.
3. The sand mass flow rate increases with the increment of the fracture width and fracture aperture. The sand mass flow rate has a positive linear relationship with fracture width and a 1.5 powder relationship with fracture aperture when water-sand mixture transport through a straight flat fracture is in the stable stage.

**Acknowledgements**

The authors thank.

**References**


The Software Development for Establishing Thermal-Hydraulic-Mechanical Coupling Models of Fractured Rocks

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College of Mining and Safety Engineering, Shandong University of Science and Technology, Qingdao 266590, China

Abstract
In order to provide a more convenient and efficient method to establish thermal-hydraulic-mechanical coupling models for fractured rocks, a software specialized was developed by the secondary development of COMSOL Multiphysics. The software can provide advanced settings for the geometry of pores and porosity distribution. The geometry of pores and porosity distribution can be defined as random distribution or Weibull distribution. A mechanical test was carried out to the rock specimen with a single pre-existing crack inclined at 45° using the MTS815.03 electrohydraulic servo controlled rock pressure testing machine. Then the experimental results was imported into the software to build the geometric model. Results indicate that fluid stress concentration occurred in the wring crack tip, which contributes to the crack propagation. The thermal stress mainly distributed in an area formed by connecting the wring crack tips. The permeability increases with increasing rock heterogeneity and the increase of rock heterogeneity contributes the crack growth.

Keywords: THM coupling, numerical model, fractured rock, porosity distribution, secondary development

Introduction
Water inrush frequently happens in China's coal mines, which has been a major threat to mine safety production. The complexity of geological systems in deep mines including high ground temperature, high groundwater pressure, and high ground stress, has motivated researchers to consider the temperature (T), hydraulic flow (H), and mechanical deformation (M) coupling model for fault water inrush. In particular, the framework of international projects like DECOVALEX has dramatically promoted the study of the THM coupling process (Bond et al. 2017; Jing et al. 1995; Rutqvist et al. 2002; Tsang et al. 2005). Sheng (2006) proposed a mechanical model of coupled THM processes for fault water inrush. In particular, the framework of international projects like DECOVALEX has dramatically promoted the study of the THM coupling process (Bond et al. 2017; Jing et al. 1995; Rutqvist et al. 2002; Tsang et al. 2005). Sheng (2006) proposed a mechanical model of coupled THM processes for saturated porous media, and this model was translated into a set of partial differential equations by using COMSOL. Zhu et al. (2009) proposed a THM coupling model considering rock damage. In the aspect of predicting fault water inrush, Sun et al. (2011) used high-precision microseismic monitoring techniques to monitor the continuous and dynamic failure characteristics of an inclined coal seam floor above a confined aquifer. Bai et al. (2015) established the identification criteria for monitoring and warning based on multiple field information monitoring and warning on delayed water bursting in a deep rock fault. Zhou et al. (2018) predicted the fault water inrush under the effect of mining depth, fluid pressure, fault dip, and fault length. Although a series of research on the THM coupling model have been carried out, most THM models were established by common software, instead of the software specialized for fractured rocks. In view of this, the major objective of this paper is to develop a software specialized for fractured rocks by the secondary development of COMSOL Multiphysics. The software can provide advanced settings for the geometry of pores and porosity distribution. The geometry of pores and porosity distribution can be defined as random distribution or Weibull distribution. A mechanical test was carried out to the rock specimen with a single pre-existing crack inclined at 45° using the
MTS815.03 electrohydraulic servo controlled rock pressure testing machine. Then the experimental results was imported into the software to build the geometric model.

**Governing Equations for the THM Coupling Model**

**Water flow equation**

According to previous work of the author (Liu et al. 2018), the water flow equation is the Darcy’s-Brinkman-Navier–Stokes equation

\[
\begin{align*}
\mathbf{u}_d &= -\frac{k}{\mu} (\nabla p_d - \rho g) \\
-\nabla \cdot \left( \frac{\mu}{\varepsilon} \left( \nabla \mathbf{u}_d + (\nabla \mathbf{u}_d)^\top \right) \right) - \frac{\mu}{k} \mathbf{u}_d + \nabla \mathbf{p}_d &= 0 \\
-\nabla \cdot (\mu \left( \nabla \mathbf{u}_h + (\nabla \mathbf{u}_h)^\top \right)) + \rho \mathbf{u}_n \cdot \nabla \mathbf{u}_n - \nabla \mathbf{p}_n &= 0
\end{align*}
\]

(1)

Where \( \mathbf{u}_d, \mathbf{u}_h, \) and \( \mathbf{u}_n \), are the velocity vector in the confined aquifer, the fault and the stope respectively; \( p_d, p_b, \) and \( p_n \), are the water pressure in the confined aquifer, the fault, and the stope respectively; \( \mu \) is the dynamic viscosity of water (N·s·m\(^{-2}\)); \( k \) is the permeability of porous rock (m\(^2\)); \( p_d \) is the water pressure (Pa); \( \rho \) is the water density (kg·m\(^{-3}\)); \( g \) is the gravitational acceleration (m·s\(^{-2}\)); \( \varepsilon \) is the porosity.

The energy conservation equation for porous media

According to Sheng et al. (2006), the energy conservation equation for solid skeleton is

\[
(1 - \phi) (\rho c_p) \frac{\partial T}{\partial t} = (1 - \phi) \nabla (K_s \nabla T) + (1 - \phi) q_s
\]

(2)

Where \( (\rho c_p) \) is specific heat capacity of solid skeleton (J/(kg·K)); \( K_s \) is thermal conductivity of solid skeleton (W/(m·K)); \( q_s \) is heat source intensity of solid skeleton.

The energy conservation equation for fluid is

\[
\phi (\rho c_p) \frac{\partial T}{\partial t} + (\rho c_v) (V' \cdot \nabla) T = \phi \nabla (K_f \nabla T) + \phi q_f
\]

(3)

Where \( (\rho c_p) \) is specific heat capacity of fluid (J/(kg·K)); \( K_f \) is thermal conductivity of fluid (W/(m·K)); \( q_f \) is heat source intensity of fluid.

Considering the compatibility of Eq. (2) and Eq. (3), the energy conservation equation for porous media is

\[
(\rho c_v) \frac{\partial T}{\partial t} + (1 - \phi) T_s \frac{\partial \phi}{\partial T} + (\rho c_p) (V' \cdot \nabla) T = \nabla \cdot (K_s \nabla T) + q_t
\]

(4)

\[
(\rho c_v) \cdot \phi (\rho c_p) + (1 - \phi) (\rho c_v) = \frac{\partial T}{\partial t} + q_t
\]

(5)

\[
q_t = \phi q_t + (1 - \phi) q_s
\]

(6)

\[
K_s = \phi K_s + (1 - \phi) K_f
\]

(7)

\[
\gamma = (2 \mu + 3 \lambda) \beta
\]

(8)

Where \( \mu \) and \( \lambda \) are Lame Constant; \( \beta \) is linear thermal expansion coefficient (1/K); \( T_s \) is absolute temperature under the application of stressless (K); \( q_t \) is heat source or sink for porous media; \( (\rho c_v) \) is specific heat capacity of porous media (J/(kg·K)); \( K_s \) is thermal conductivity of porous media (W/ (m·K)).

**Mechanical equation**

The mechanical equation is

\[
-\nabla \cdot \sigma = \rho g
\]

(9)

Where \( \sigma \) is total stress (Pa).

The compatibility of Eq. (1), Eq. (4), and Eq. (9) are the governing equations for THM coupling model.

**The software**

A model for establishing thermal–hydraulic–mechanical coupling models for fractured rocks is developed based on java language and Application builder of COMSOL, which can simplify the model building process, preserve the powerful multi-physical fields coupling function, and add the function of using ground temperature to predict water inrush. The running window of the software is shown in Figure 1. The available windows and user interface components consist of Menu toolbar, Quick access toolbar, Geometry toolbar, Multiphysics toolbar, Calculation toolbar, and Results toolbar. It is very convenient and simple for users to build a numerical model, instead of spending more time on studying the operation method of COMSOL. The numerical model settings can be easily set up, such as the geometric model and material parameters.
Figure 1 The running window of the software

Figure 2 The running window of the Geometry toolbar
The running window of the Geometry toolbar is shown in Figure 1. The Geometry toolbar can provide two building geometry methods consisting of Geometry builder and import. The Geometry builder consists of basic parameter settings and advanced settings. The advanced settings connect the MATLAB functions, which can provide pore settings.

The running window of the Multiphysics toolbar is shown in Figure 2. The Multiphysics toolbar can provide the settings of thermal-hydraulic-mechanical coupling parameters.

The Calculation toolbar is shown in Figure 3. The Calculation toolbar can provide the boundary condition setting, mesh building function, mesh precision selection, etc.
function, study setting function (including stationary study, time dependent study and parametric sweep function), and calculation starting button.

The Results toolbar can output ground temperature calculation results. The running window of the Results toolbar is shown in Figure 4. The results can be saved and displayed in the form of picture, text, and video. The results of stress, seepage velocity, pressure, and et al. can be also output in the Results toolbar. In addition, the Results toolbar can provide the settings of the data set, such as the cut line and cut point.

**THM coupling model**

In order to study the effect of thermal-hydraulic-mechanical coupling environments on the fracturing characteristics of fractured rock, based on the previous triaxial experimental results of the author (Liu and Shen 2016), the fracture of specimen is processed to document format supported by the software. Then the document is imported into the software to build the geometric model. The porosity distribution has great influence on rock permeability. Therefore, the seepage toolbar can provide the advanced setting for the porosity distribution. The porosity distribution can be defined as random distribution or Weibull distribution. When the distribution type is Weibull distribution. As shown in Figure 5, the scale parameter $\lambda$ is 0.1, which reflects the average porosity. The shape parameter $k$ reflects the discrete degree of the porosity. The discrete degree decreases with decreasing shape parameter.

Figure 6 shows the fluid stress and thermal stress. The fluid stress concentration occurred in the wring crack tip, which contributes to
the crack propagation. The thermal stress mainly distributed in an area formed by connecting the wring crack tips.

Figure 7 shows the fluid velocity distribution at different shape parameters. When the shape parameter is 50, the rock porosity can be considered homogeneous. In this figure, the fluid flows out of the wring crack into the complete area. The area expands with decreasing shape parameters, especially around the wring crack tip, which indicates that the permeability increases with increasing rock heterogeneity and the increase of rock heterogeneity contributes the crack growth.

**Conclusions**

The software can provide a more convenient and efficient method to establish thermal-hydraulic-mechanical coupling models for fractured rocks. The discrete degree of real pore distribution can be well simulated by the random distribution or Weibull distribution. The discrete degree decreases with decreasing shape parameter. According to the THM coupling, the fluid stress concentration occurred in the wring crack tip, which contributes to the crack propagation. The thermal stress mainly distributed in an area formed by connecting the wring crack tips. The permeability increases with increasing rock heterogeneity and the increase of rock heterogeneity contributes the crack growth.

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**References**


Use of the permeability test of Carboniferous rocks in the underground coal mines located in the Upper Silesian Coal Basin

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Abstract

Carboniferous rock permeability tests can be used both for documenting hydrogeological and gas conditions, as well as for predicting the possibility of pre-exploitation demethanation of seams and rock mass surrounding mining excavations. The article describes the research process of rarely performed non-destructive profiling of permeability of hard rocks in different directions (x, y, z) using a PDPK-400 permeameter created by Micrometrics. The solution can be applied in mining hydrogeology, and in particular in the assessment of the water hazard in mines located close to reservoirs in flooded mine, evaluation of water filtration through safety pillars and in determining zones with increased permeability, among others for the migration of mine gases to demethanize the deposits, e.g. through holes from the surface.

Keywords: permeability, hydrogeological properties, USCB, rock mass, rocks

Introduction

Extraction of hard coal generates various interdependent hydrogeological phenomena. The restructuring of hard coal mining conducted since 1990 in USCB have led to the abandoning of some mines and coexistence of active and flooded mines. Mining activity negatively affects on water environment and results in drainage of aquifers and discharge of large amounts of contaminated minewater to surface watercourses. Lack of activities aimed at dewatering of mine workings of decommissioned mines causes them to be filled by the water from the natural inflow. The water level in the flooded excavations increases gradually until a hydrodynamic equilibrium is obtained with the aquifers in the surrounding Carboniferous rock mass. Conditions for the formation of hydrodynamic equilibrium may occur in border regions with active mines as a result of filtration of water that leaks or escapes from the decommissioned mine's reservoirs to the workings of an active mine. In the area between the flooded and active mines, there are conditions for hazards related to the flow and accumulation of water and gases in the rock mass. This may determine the possibility of a water hazard (disruption of the safety and effect pillars) and methane hazard in active mines and surfaces (pushing methane out of flooded excavations). Mining exploitation carried out at ever greater depths records lower values of water inflow to mine workings, but increases methane emission from coal seams, which is associated with known regularities in the geological structure of USCB and variability of porosity. The methane capture in the CBM, CMM and AMM process is increasingly difficult to plan due to the constantly decreasing porosity and permeability of rocks in the vertical profile. The difficulty in determining the conditions of water and gas circulation in mining excavations and rock mass and the difficulty in establishing plans for draining the rock mass and its demethanation is often caused by the lack of knowledge of the variability of the rock and rock mass permeability distribution in the vertical profile.

The permeability of rocks is relatively rarely investigated in mining hydrogeology in the areas of hard coal mines. The tests are carried out on rock material taken from mine workings as solid samples or on cores from holes made at the bottom of the mine. Commonly used methods of researching hard rocks include specially prepared rock samples, tested in one direction, generally in a direction parallel to the axis of the core sample and perpendicular to the stratification. Such
standard tests allow obtaining the test result at least by an order of magnitude smaller than in the case of a test made perpendicular to the core axis and parallel to the bedding of rocks. The test result is obtained in a time-consuming manner and after preparation of the core and selection of test samples. In addition, it replicates the filtration process, which is closer to the inter-layer filtration process. The research process of profiling the filtration coefficient in the direction perpendicular to the axis of the core sample, i.e. parallel to the stratification using the PDPK-400 device created by Micrometric, is described below.

**Characteristics of the test method with the application of PDPK-400 permeameter**

The PDPK-400 permeameter is used for non-destructive drill core permeability profiling. This device gives the possibility of precise measurement of the permeability of one-meter rock samples cut from the core perpendicular to its axis, in two planes, in the XY system (photo 1A). The markings are carried out using gases, mainly nitrogen class 5.0 or 6.0. The device allows to determine the heterogeneity of samples thanks to the tested filtration properties, in order to identify the ranges of high and low permeability of the examined rock layers. The device is equipped with a built-in sensor that indicates the exact location of the measurement sites, and also has the option of selecting any interval of the core to be tested and planning frequency of measurements. The test is carried out with a wide measurement range from 0.001 mD to 30 D. The time of determination of the permeability at one measuring point varies from 2 to 35 seconds. The permeameter enables testing of drill cores of various diameters, but not less than 2.5 cm, and of any length of the drill core tested in measuring cycles from 2.5 cm to 3 m in one measuring cycle. It conducts measurements in an extremely precise, fast and efficient manner, giving the possibility of non-destructive profiling of permeability of drilling cores in the direction of parallel flow to the stagnation. The device also allows to conduct tests of permeability on individual samples (2.5-20 cm) cut out from the core or on rectangular cube samples used in geomechanical studies with height or thickness below 20 cm. Then the measurements are made in three planes, perpendicular to the axis of the sample in the XY system and parallel to the axis in the Z-system (photo 1B), i.e. in a parallel and perpendicular direction to the strangulation.

The device is fully integrated with the control unit equipped with the PROPERM software, giving the possibility of the current registration of the test. Based on the obtained data, it is possible to create graphs of variability of permeability as a function of depth, taking into account the entire lithostratigraphic profile of drilled layers and determination of fragments with increased and reduced permeability.

The principle of measuring permeability is to determine the time curve of nitrogen pressure drop in the main tank, which is connected to the probe injecting the
medium into the sample under test. The permeameter allows measurements of sample permeability including corrections for the gas slip effect (Klinkenberg correction), so that even at low speeds, the gas flowing through the porous rock behaves in accordance with Darcy’s law.

In the case of samples where intense gas flows occur in fissures with high permeability and small width, linear flow velocities are characterized by high values. Under these conditions, the flow becomes turbulent and there is additional flow resistance due to inertia effects. Permeability measurements performed by the PDPK 400 can therefore also be carried out under conditions of high inertia of the sample, even with relatively low differences in applied pressures. Hence, the analysis includes the Forchheimer correction. The inertial resistance virtually disappears for samples with a permeability <0.1 mD for initial pressures <10 psig.

Possibilities of application of permeability in mining

Permeability is an important parameter describing fluid filtration processes (gas, water). In the area of USCB, the inflow intensity and chemical composition of water entering active and abandoned mines depend on the degree of the Carboniferous hydrogeological structure “opening” and lithology of the Carboniferous series in which the mine is located. Due to the conditions of supplying the Carboniferous region, the USCB area is divided into an exposed and covered hydrogeological subregion. In contrast, a different lithological formation differentiates hydrogeological properties in particular lithostratigraphic series. In the productive carbon, four lithostratigraphic series were separated, differing essentially in permeability and the ability to store and release free water. Starting from the oldest, these are: the parallel series (PS), the Upper Silesian Sandstone Series (USSS), the mudstone series (MS) and the Cracow Sandstone Series (CSS). For individual lithostratigraphic series, the permeability, in field studies, expressed by the filtration coefficient shows a high variability (Różkowski, ed. 2004) for:

- CSS from 5.0 · 10⁻⁹ m/s to 3.3 · 10⁻⁴ m/s,
- MS from 9.6 · 10⁻¹⁰ m/s to 5.0 · 10⁻⁴ m/s,
- USSS from 4.0 · 10⁻¹¹ m/s to 2.5 · 10⁻⁵ m/s,
- PS from 8.5 · 10⁻⁹ m/s to 8.4 · 10⁻⁶ m/s.

In the north-eastern part of the USCB, permeability studies give the opportunity to assess the inflows, flows and filtration of water (the course of the study should reflect the flow directions perpendicular to the core axis, i.e. parallel to the rock stratification). For gas, these studies are of less importance. The permeability of rocks examined in the direction perpendicular to the stratification becomes more important in the case of assessing the vulnerability of groundwater to contaminants (Bukowski, Bromek, Augustyniak 2006). It can also be a relevant element in the assessment of the common hazard associated with the accumulation and pushing of mine gases from mining excavations of abandoned mines, as a result of flooding. This part of the basin is located in the hydrogeologically exposed subregion, where the Carboniferous rock mass is not effectively isolated, and thus it is easily recharged into the infiltration water from the surface and shallow deposits of aquifers that build the deposit overburden. The flooding of Carboniferous forms is mainly related to the occurrence of the complex of the Cracow and Upper Silesian Sandstone Series, in which permeable compositions predominate (Figure 1).

However, in the south-western part of the USCB, the main problem in mines is not so much related to the flow and filtration of water as to the migration of mine gases, mainly methane. It is recommended here to perform permeability tests in each direction in relation to the stratification of rocks, i.e. parallel and perpendicular to the axis of the drill cores. The filtration coefficient determined for water in this region is more important only locally for safety and boundary pillars from water reservoirs in mining excavations. In this part of the basin there is a hydrogeologically covered subregion, which is characterized by the presence of deep impermeable formation isolating Carboniferous deposits. Mines located in this part of the USCB conduct coal exploitation mostly within the mudstone and parallel series, in which there are less
favourable conditions for recharging the rock mass with water, and the coal seams are characterized by high methane capacity.

Below are exemplary tests using the PDPK-400 permeameter made on the core of the Carboniferous rock from the USCB. The tests included 33 m of the rock core with a diameter of 8.0 cm that was profiled. The studied core fragment included works of the Upper Silesian Sandstone Series from the depth interval of 355.00 ÷ 388.00 m. The measurements were carried out in the XY plane with a stage of approximately 5 cm. An exemplary graph of permeability variability of these formations as a function of depth is presented in Fig. 2.

Conclusions
The PDPK-400 permeameter allows quick identification of high and low permeability ranges of the rock layers. It allows to obtain an accurate profile of changes in rock mass permeability with a depth and to a relatively accurate separation of zones or layers with features characteristic for privileged water flow paths, migration of gases and contaminants and insulating zones, etc. The tests in the parallel lining to lamination indicate the conditions of filtration of the fluid in the layer, and in the perpendicular direction show the possibility of its percolation. Therefore, the PDPK 400 device gives complete data on the basis of which the conditions of filtration and percolation of water in any tasks of mining hydrogeology and general hydrogeology can be determined. The obtained results can be a solid base for studying model filtration processes and in rock mass composed of compact rocks. They can also be a tool for assessing the rock mass permeability in methane prevention prior to commencing mining exploitation.

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References


Figure 2. Variability of permeability within the borehole profile
Integrating Hydrogeology with Geotechnical Engineering

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Abstract
Integrating physical hydrogeology with geotechnical engineering is a valuable part of slope design in mines and can be a critical safety aspect, particularly in underground mining.

This integration is not always carried out adequately. Designs are being made with assumptions about drained conditions or with simplistic assumptions about hydrostatic pressure distributions within saturated rock masses below a “phreatic line”.

For new projects, perhaps the first aspect to consider is whether the highest water pressure likely to occur would affect stability. Designs for mines with strong and poorly-fractured rock masses may be essentially independent of groundwater pressures. Weak, layered sedimentary rocks may be extremely sensitive to groundwater pressures. This consideration is the first point of integration of hydrogeology with geotechnical engineering.

Slope design and underground design and support can be optimised without compromising safety with a proper understanding of the magnitude and distribution of groundwater pressures around mines.

Understanding the distribution of groundwater pressures requires adequate hydrogeological investigation and conceptualisation. Measurements of groundwater pressures are essential. Numerical modelling may be important to predict groundwater behaviour as a mine is developed and after closure.

Integration of the disciplines requires good communication.

Keywords: geotechnical engineering, hydrogeology, mining, slope failure, inrushes

Introduction
Integrating physical hydrogeology with geotechnical engineering is a valuable part of slope design in open pit mines. In underground mining hydrogeology can be important in designing access drives, mine workings and roof support. Groundwater conditions may be a critical safety aspect regarding inrushes of water.

In the past and perhaps now, this integration is not always carried out adequately. Designs are still being made with assumptions about drained conditions. Simplistic assumptions are made about hydrostatic pressure distributions within saturated rock masses or soils below a “phreatic line” or “phreatic surface”.

For many years, some hydrogeologists like me have worked to provide stronger integration of hydrogeology and geotechnical engineering in the mining area.

Why do I think this is important? What are the key issues and how should we think about hydrogeology in association with slope stability?

The first aspect to consider with any new mining proposal is whether the highest water pressure judged likely to occur would affect stability. Estimating the highest likely water pressure may be a matter of hydrogeological judgement, given the setting within which the mine will be developed or into which it will be extended.

Which rock mass conditions will be independent of the probable groundwater pressure conditions? This question is a geotechnical matter, providing the first point of integration of hydrogeology and geotechnical engineering in a mining project.

Designs for some mines with strong and poorly-fractured rock masses such as fresh, metamorphic and plutonic rocks will
be essentially independent of groundwater pressures. Others, for example in weak, layered sedimentary rocks, may be extremely sensitive to groundwater pressures. This consideration is the first point of integration of hydrogeology with geotechnical engineering.

Safety is a key issue. Water pressures that exceed those included in design calculations can cause failures which, if sudden, can kill people. Every effort must be made to avoid sudden failures and catastrophic water inrushes in underground and surface mines.

Apart from safety, slope design and underground design and support can be optimised with a proper understanding of the magnitude and distribution of groundwater pressures around mines. Such optimisation may be a key economic aspect of a mine, making the difference between a feasible project and one that fails economically.

In some situations, numerical modelling is essential to predict groundwater behaviour as a mine is developed and after closure. However, most mines are not managed with models but by observation and measurement. The value of a good numerical model can be in focussing attention on areas of potentially high groundwater pressures, where piezometers are most needed.

Integration of the disciplines requires good communication. In the author’s experience, this must often be driven from the hydrogeological side to the engineering team. Perhaps the best, most recent publication on the subject of groundwater and mining, at least for open pit mines, is that of Beale and Read (2014). This comprehensive book is readily available from the publishers.

This paper provides a few examples, hoping to stimulate further action to improve communication of hydrogeological information into design of open pit slopes and underground mines.

**Example 1: A shallow, groundwater-related slope failure**

The photograph shows the complete loss of a small, shallow gold mine, where ground movements destroyed the only economically-viable design. The failures occurred in saturated clays, themselves in-situ, completely weathered metamorphic rock. So why did the slope fail?

The cause of the failure was groundwater pressures in weak material. Those pressures were accurately predictable by knowledge only of

1. the depth of the mine below the local water table
2. recognition that the low relief terrain with low hydraulic gradients would allow hydrostatic assumptions to be used to predict pressure with depth below the water table.

In this instance, the groundwater pressures that caused the slope failures probably did not exceed 300 kPa (about 30 metres depth below the water table. The failures were
attributable to mining downwards faster than groundwater pressures could dissipate.

**Example 2: A deeper groundwater-related slope failure**

Photograph 2 and Figure 1 show another complete loss of a small gold mine as a result of mining below the water table in weathered to fresh metamorphic rock. The cause of the failure was an incorrect assumption that the water table was deeper than the bottom of the slope and that, therefore, there were no groundwater pressures to consider in the slope design.

In this instance, the water table elevation was easily predictable by a consideration of the regional hydrogeological setting, even without drilling. There was a nearby salt lake and its bed elevation would have been similar to the water table elevation at the mine. The bed elevation of the lake was tens of metres higher than the bottom of the slope.

**Photograph 2: Structural failure in weathered to fresh Archaean rock**

**Figure 1: Diagrammatic section showing slope failure and groundwater assumptions**
Example 3: Catastrophic inrush to underground mine

Figure 2 shows the location of a catastrophic inrush to an underground mine. In this instance, there were progressive signs of instability in a stope roof (a geotechnical matter) several hundred metres below the water table. Earlier mining of shallower parts of the deposit had not intersected any cavities in the rocks that formed the roof of the mine. However, the final part of the deposit to be mined was faulted laterally and located directly beneath the cavernous limestone.

The consequential risk of the hydrogeological setting was that any roof instability had a risk of a catastrophic inrush of groundwater. Maybe this recognition would have led to a more focussed geotechnical study?

The failure occurred suddenly, with a very high rate of groundwater inflow (maybe 50 m$^3$/s over the first hour). Fortunately the inrush happened overnight when no-one was working underground. The mine flooded completely and was lost.

Example 4: Pore pressure distributions

The simplest conceptual model relates groundwater pressure to the depth of mining below the water table using the simple equation $P = \rho gh$. This condition can apply well in low relief terrain where equipotentials are vertical and groundwater movement is horizontal.

As soon as a mining void is created below the water table, flowlines towards the mine perturb the flow field and reduce the pore pressures to some extent, at least near the mine.

In high relief terrain, the vertical component of natural groundwater movement also means that the equation $P = \rho gh$ is invalid, typically over-estimating pore pressures. In these cases, numerical modelling has a place in making estimates of the distribution of pore pressures with time and with mine development. Figure 3 gives an example of a modelled head distribution at a mine in high relief terrain, with steep gradients. Near the modelled position of the

![Figure 2: Diagrammatic location of the inrush to the underground mine](image-url)
water table the steep head gradients mean that the pressures below the water table are in places lower than given by the relationship P = ρgh.

One consequence of over-estimating pore pressures can be over-conservative slope design, leading to excessive mining costs. Equally, good numerical modelling with an appropriate distribution of calibration data from piezometers located behind areas of active mining, can point to areas of stability risk. It is those areas which deserve priority in measuring groundwater pressures.

**Discussion**

The paper’s examples present two open pit slope failures caused by groundwater pressure and one catastrophic groundwater inrush. All three mines were lost at great cost to the owners and the loss of contractors’ or employees’ jobs. There were no injuries or fatal accidents in these cases.

All were caused by hydrogeological factors.

In most situations where rock strengths are moderate to low or when structurally-controlled failures are possible, groundwater pressures in walls and floors of open pit mines and in the rock mass around an underground mine should be understood and measured. This information needs to be communicated to the geotechnical engineers who design these aspects of a mine.

The fourth example illustrates that there are circumstances where numerical modelling is important in providing a distribution of estimated pore pressures for input to stability analyses. This hydrogeological information, expressed as pore pressure distributions, leads to optimised slopes that still can have acceptably low risks of failure.

One underlying message from this paper is about communication. Hydrogeologists need to understand how to communicate effectively to engineers, who have a different background and culture to many people with science backgrounds. Effective communication of good information and of

![Figure 3: Example of pore pressure modelling in high relief terrain](image-url)
uncertainty can bring respect and good teamwork.

A parallel issue is discontinuities in the distribution of ages through our ranks.

**Time distribution of professional experience**

Groundwater-related issues in slope stability are not a new topic. Relevant papers can be found decades ago in the literature. However, the lessons seem to need repeating by older practitioners and re-learning by younger practitioners year after year.

In areas of mining where professional employment is affected by fluctuating demand and prices (industrial metals such as iron, copper, nickel etc and precious metals such as gold), there are time bands of missing experience in our professional groups. For many years I have had 15-20 years more experience than practically all of my colleagues. Mining engineers with whom I work report the same gap in years of experience in younger professionals. This fluctuating demand for professional skills may not apply in long-term mining situations such as decades-long contracts to supply coal for power stations. However, in the commercial world of mining commodities for which demand fluctuates, professional employment fluctuates too.

**To conclude….**

I urge all of us in the physical hydrogeology area to continue to work hard to bridge the gap between science and engineering. We must communicate effectively with geotechnical engineers, in their language, if they are to respect hydrogeological advice and we are all to achieve the best compromises between mine stability, safety and economics.

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**References**

Implementation of slope drainage system for optimal slope design at Anfisa open pit, Khabarovsk Territory, Russian Federation

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Abstract
Open pits’ slope angles determine company profit and work safety. Steep slope and benches angles increase company’s profit as well as increase risks of landslides occurrence. Thus, slopes design should be optimal – profitable and safe. Groundwater negatively influence slope stability. Implementation of slope depressurization program greatly influence slope stabilization and reduce negative risks of pit wall deformation.

The object of the study is Anfisa open pit at gold mineral deposit “Albazino”, situated in Khabarovsk Territory, Russian Federation. Complicated geology conditions along with low hydraulic permeability of rocks are the reasons of high groundwater level in the South and South-East walls of Anfisa open pit which substantially influences open pits slope stability.

The main goal of the investigations is optimization and construction of depressurization system at South and South – East walls of Anfisa open pit to achieve slopes stabilization.

Introduction
Open pits’ walls angles along with other mining aspects determine company profitability and safety. Steep walls increase company’s profit as well as increase risks of landslides occurrence. Thus, slopes design should be optimal – profitable and safe. High pore-water pressure negatively influence slope stability. Therefore, implementation of slope depressurization programs can greatly influence slope stabilization and reduce risks of pit wall failure.

The payback of a slope depressurization program in terms of an increased walls angle and/or improved slope performance is dependent on many factors, including the geomechanical properties of the rock massif and the height of the wall. Every $10 million invested in slope depressurization activities can save $50-100 million realised in mining costs (Geoff Beale, 2013).

The object of the study is Anfisa open pit at gold mineral deposit “Albazino”, situated in Khabarovsk Territory, Russian Federation (Figure 1). Reserves (JORC) of the deposit are estimated at 2.3 Moz GE, resources (JORC) are 1.6 Moz GE. At the deposit there are two open pits and one underground mine in operation. In addition, two open pits and two underground mines will start soon. The largest of the quarries is named Anfisa. Complex geological conditions along with low hydraulic permeability of rocks are the reasons of high groundwater level in the South and South-East walls of Anfisa open pit which substantially influences open pits slope stability.

The main goal of the investigations presented in the article is optimization and implementation of a depressurization program at the South and South-East slopes of Anfisa open pit. Initial configuration of the open pit was unstable without depressurization system implementation. Instability confirmed by rock mass movement at South and South-East walls. Preliminary cost estimate of slope flattening accepted by the mine as the main scenario assessed.
around 50 million USD. Considering high costs of pit wall flattering development few alternative scenarios were assessed. All scenarios considered development of depressurization system at the pit walls where instabilities took place.

The following tasks were solved to assess the efficiency of the proposed depressurization systems:

- Interpretation of geotechnical core logging documentation to determine hydraulic characteristics of rocks. This innovatory approach is based on relationship of the Q – classification system and hydraulic properties of rocks used.
- Development of 3d numerical model of groundwater flow.
- Slope stability assessment considering effect of different options of depressurization systems.
- Detailed description of the tasks is presented further.

**Interpretation of geotechnical core logging documentation**

Geotechnical core logging documentation was conducted in accordance with the standard of International Society of Rock Mechanics (ISRM). Documentation result contains rock characteristics according to Rock mass classification – Q-system (Barton et al. 1974).

Based on core logging documentation hydraulic conductivity for every drill run interval was calculated using the following formula:

$$K \approx 0.002/(Q_{H2O}D^{5/3}) \text{, m/s}$$

(1)

Where $D$ is a depth of top of drill run interval relatively to ground surface, in m, $Q_{H2O}$ – permeability rock quality (Barton, N. 2006, Barton, N. 2007),

$$Q_{H2O} = \frac{RQD}{J_{n}} \times \frac{J_{a}}{J_{r}} \times \frac{J_{w}}{SRF},$$

(2) dimensionless value

Where $RQD$ - Rock Quality Designation, $J_{n}$ - Joint set number, $J_{r}$ - Joint roughness number, $J_{a}$ - Joint alteration number, $J_{w}$ - Joint water reduction factor, $SRF$ - Stress Reduction Factor (Using the Q-system, 2015).

$$Q_{c} = 10^{7} K(\text{m/s}) = 0,00864 \text{ (m/day)}$$

(3)

Where $Q_{c}$ - Gives a description of the rock mass stability in jointed rock masses. High $Q_{c}$-values indicates good stability and low values means poor stability

$$Q_{c} = \frac{RQD}{J_{n}} \times \left( \frac{J_{r}}{J_{a}} \times \frac{J_{w}}{SRF} \right) ,$$

(4) dimensionless value

Where $\frac{RQD}{J_{n}}$ - Degree of jointing (or block size)

$\frac{J_{r}}{J_{a}}$ - Joint friction (inter-block shear strength)

$\frac{J_{w}}{SRF}$ - Active stress.

Hydraulic conductivities for every interval with geotechnical core logging documentation were calculated using...
both approaches. Calculated parameters varied substantially. The reason is that used approaches do not take into account specific conditions of current deposit. That is why calculated parameters require calibration to the real hydrogeological conditions of the deposit. The next step was calibration.

Calibration of hydraulic properties
Hydrogeological investigation report contains information on packer pumping tests. In terms of calibration, results of core interpretations for both approaches and pumping tests results were compared. Best results of calculated parameters are presented for the second approach by equation (4).

The comparison of results is showed in table 1. Calculated hydraulic conductivity is used for hydrogeology schematization and creation of numerical model.

### Table 1 Comparison of conductivity coefficients by geotechnical core logging interpretation and packer tests.

<table>
<thead>
<tr>
<th>Interval, m</th>
<th>Arithmetic mean value of the hydraulic conductivity, m/d (geotechnical core logging interpretation)</th>
<th>Hydraulic conductivity, m/d (packer tests)</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>To</td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>100</td>
<td>0.0425</td>
</tr>
<tr>
<td>100</td>
<td>202.7</td>
<td>0.0183</td>
</tr>
<tr>
<td>202.7</td>
<td>280</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

The comparison of results is showed in table 1. Calculated hydraulic conductivity is used for hydrogeology schematization and creation of numerical model.

**Numerical model of the groundwater flow**
Considering results of hydraulic conductivity calculations schematization of hydrogeological conditions were conducted. Table 2 presents results of hydrogeological conditions were conducted.

**Table 2**

<table>
<thead>
<tr>
<th>Hydraulic conductivity, m/d (packer tests)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

**Figure 2**
Principal schematization of Horizontal (a) and vertical (b) boreholes used for drainage (Beale, G. and Read J., 2013)
on the quarry’s slope. Boundary conditions were changed during calibration to reach the best convergence between the monitoring data and calculated seepage levels parameters.

The following scenarios were considered and simulated on the groundwater model:

- Base case: no depressurization,
- Depressurization scenarios using:
  - horizontal depressurization wells,
  - vertical depressurization wells, and
  - drainage drift with raising boreholes.

10 horizontal wells on berm with elevation +360 m. simulated. Number of horizontal wells limited by pit design, space limitations for installation works, water removal form the pit benches and the short length of pit walls where groundwater discharges.

The groundwater model allowed estimating inflow into drainage systems for each scenario. The results were then used for slope stability calculation.

**Slope stability**

Calculations of slope stability executed in program Rocscience Slide. The method of calculation based on search weak landslide surface with the lowest factor of safety (FOS). Most critical sliding surfaces presented on figure 3. Mechanical properties used in calculations determined at laboratory and during fields tests. Mechanical properties characterized every rock type.

Results of slope stability estimation of South and South-East walls as well as schematic geological cross sections are presented in figures below (Figure 3).

**Discussion**

Table 3 presents parameters of the 4 different scenarios (base case without depressurization and 3 options of drainage systems). It includes basic characteristics (slope safety factor and groundwater inflow) and preliminary cost estimate for each scenario. Table 4 shows pros and cons of different drainage systems scenarios.

Increasing of well quantity does not effect on safety factor because groundwater flow in rock massif associated with highly fracturing zones. In that case, for the dewatering purpose most effective way is to drill horizontal wells exactly through these zones. It may be solved by accurate identification of those zones using information from pit wall mapping and exploration drilling.

Three-dimensional model of drainage drift with rising boreholes is presented in figure 4.

---

**Table 2: Schematization of hydrogeology conditions**

<table>
<thead>
<tr>
<th>Rock / Color of rocks on cross-sections</th>
<th>Hydrogeology schematization</th>
<th>Accept hydraulic conductivity coefficient in the hydrogeology model, m/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual soil</td>
<td>Aquitard</td>
<td>0.5</td>
</tr>
<tr>
<td>Silt stone with sandstones layers</td>
<td>Aquitard</td>
<td>0.016</td>
</tr>
<tr>
<td>Granodiorite</td>
<td>Aquitard</td>
<td>0.016</td>
</tr>
<tr>
<td>Siltstone</td>
<td>Aquitard</td>
<td>0.016</td>
</tr>
<tr>
<td>Siliceous - carbon shale</td>
<td>Aquitard</td>
<td>0.016</td>
</tr>
<tr>
<td>Microdiorite</td>
<td>Aquitard</td>
<td>0.016</td>
</tr>
<tr>
<td>Sandstone with silt stones layers</td>
<td>Aquitard</td>
<td>0.016</td>
</tr>
<tr>
<td>Granite-porphyry</td>
<td>Aquiclude (confining bed)</td>
<td>0.0019</td>
</tr>
<tr>
<td>Spilite</td>
<td>Aquiclude (confining bed)</td>
<td>0.0019</td>
</tr>
<tr>
<td>Rocks confined to tectonic fault</td>
<td>Aquiclude (confining bed)</td>
<td>0.0019</td>
</tr>
</tbody>
</table>
Figure 3 Safety factors of South and South-East walls using different drainage systems
a) Slope without drainage system. Slope is unstable.
b) Slope is stable, but safety factor less than regulation value.
c) Slope is stable, but safety factor less than regulation value.
d) Slope is stable and safety factor above than regulation value.

Table 3 Comparative table of the drainage systems scenarios

<table>
<thead>
<tr>
<th>Type of drainage system</th>
<th>Safety factor</th>
<th>Short characteristics of drainage system</th>
<th>Discharge of groundwater</th>
<th>Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal wells</td>
<td>1.09</td>
<td>Number of wells: 10; Drilling meters drilled: 1,600 m.</td>
<td>16 m³/h</td>
<td>$ 240 thousand</td>
</tr>
<tr>
<td>Vertical wells</td>
<td>1.12</td>
<td>Number of wells: 5; Drilling meters drilled: 1,600 m. Drift’s length: 572 m; Number of wells cluster: 6; Number of boreholes: 24; Drilling meters: 24,000 m.</td>
<td>27 m³/h</td>
<td>$ 400 thousand</td>
</tr>
<tr>
<td>Drainage drift and rising boreholes</td>
<td>1.29</td>
<td>Number of wells cluster: 6; Number of boreholes: 24; Drilling meters: 2,400 m.</td>
<td>46 m³/h</td>
<td>$ 1.2 million</td>
</tr>
<tr>
<td>No drainage systems</td>
<td>1.2</td>
<td>Additional stripping to flatten pit wall. 50 m³/h groundwater discharge</td>
<td></td>
<td>$ 50 million (the cost of stripping to flatten pit wall: drilling and blasting, haulage)</td>
</tr>
</tbody>
</table>
Conclusion

Result of this work is based on innovative method of hydraulic conductivity determination using geotechnical core logging. Based on risks and effectiveness analyses drainage drift with rising boreholes is recommended. The second option is stripping to pit wall flatten and construction of vertical dewatering wells. Nevertheless, disadvantages of this option are higher cost of additional stripping; drainage system should be equipped with warmth-keeping facilities and difficulties with wells service.

References


Table 4 Pros and cons of drainage systems scenarios

<table>
<thead>
<tr>
<th>Type of drainage system</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal wells</td>
<td>Lower cost. Accessibility on berms. Fast implementation (2-3 months).</td>
<td>1. Limited effectiveness. Safety factor less than regulation value. 2. To avoid water freezing in pipes, drainage system should be equipped with warmth-keeping facilities (heating cable and other).</td>
</tr>
<tr>
<td>Vertical wells</td>
<td>Lower cost. Fast implementation (2-3 months).</td>
<td>1. Limited effectiveness. Safety factor less than regulation value, but higher performance than horizontal wells. 2. Difficult access to wells location. 3. Wells drill can be implemented after geophysical investigations for high fractured rocks' zones identification. 4. To avoid water freezing in pipes, drainage system should be equipped with warmth-keeping facilities (heating cable and other).</td>
</tr>
<tr>
<td>Drainage drift with rising boreholes</td>
<td>Most effective drainage method. Safety factor above than regulation value.</td>
<td>1. Higher cost of mining workings. 2. Longer implementation period (about 2 years).</td>
</tr>
</tbody>
</table>

Figure 4 3d model of the drainage drift with rising boreholes


HYDROGEOLOGICAL AND HYDROGEOCHEMICAL MODELING
Active Dewatering Of Limestone Quarry And Drinking Water Production – Feasibility Assessment Using A Groundwater Model

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Abstract

Lhoist Industries Ltd. plan to deepen the Boverie Quarry (Rochefort, Belgium), in which two Frasnian limestone reefs are exploited. If this project is allowed, the dewatering will dry up the Tridaine gallery that provides drinking water for the city and Saint-Remy’s Abbey of Rochefort. Therefore, the project of deepening has to conciliate both quarry dewatering and drinking water production. The solution found by the quarry owner is to achieve the dewatering using three wells, for technical safety or water quality reasons, located in the periphery of the quarry and to distribute the pumped water to both the city and abbey. Hydrogeological characterization and a model using the SUFT3D research code tend to show that quarry dewatering and drinking water production could be achieved during and after the quarry operation, even by using a single well.

Keywords: Belgium, Quarry dewatering, Peripheral well, Drinking water supply, Groundwater modeling

Introduction

In Belgium, as in many other states having a small surface and a high population density, mineral industry and drinking water production are closely tied together. Indeed, as lateral expansion of quarries is therefore extremely limited, most of them have to be deepened. In such a case, the bottom of the extraction pit could reach the water table and a dewatering system has to be established to continue the extraction operations. Most often, quarries dewatering is carried out by means of a sump, which is by far the least expensive solution. Like any other kind of dewatering systems, sumps affect the regional hydrogeology and, occasionally, the productivity of nearby groundwater catchments by, for example, drying up the wells or increasing the pumping costs (Younger et al. 2002). In order to mitigate the effect of quarry dewatering on groundwater catchments, mine water could be used for drinking water production. However, water that is also collected in the sumps could not be of sufficient quality to be used as drinking water without a heavy and very expensive treatment. In those cases, a viable option to reconcile both dewatering and drinking water supply is by means of drilling one or more peripheral wells.

Lhoist Industries Ltd. have chosen this alternative with regard to their project of deepening the Boverie limestone quarry in Rochefort (Belgium). At the site, the mining company operates two Devonian limestone reefs for high-grade lime production. Actually, groundwater contained in these formations is drained by the Tridaine gallery, an old artificial drainage gallery, which will dry up if the deepening project comes true. This drainage gallery provides drinking water for the majority of the 12,500 inhabitants of the city of Rochefort as well as for Saint-Remy’s Abbey of Rochefort, for beer brewing.

Even if the quarry owner has already decided to drill three wells, a groundwater...
flow model has been developed to assess the feasibility of (1) dewatering the quarry with a single well located in its periphery and (2) providing enough water to fulfill the water demand of both the city and abbey.

**Context and Project Description**

The Boverie Quarry is located in the southern part of Belgium, in the Famenne-Ardenne UNESCO Global Geopark. The quarry lies on a topographic ridge called “Calestienne”, which marks the limit between the Fagne-Famennium depression to the north and the Ardenne plateau to the south (fig. 1).

The “Calestienne” is made of Givetian and Frasnian limestone and shale formations. Concerning the Frasnian stage (fig. 2), in which the quarry is located, the sedimentary sequence begins with the shale of the Nismes Formation. It continues with the limestone reef of the Arche Member, which changes laterally into the shaly Ermitage Member. The Arche Member is topped by the clayey limestone of the Bieumont Member, which precedes the second limestone reef of the Lion Member. The upper part of this limestone reef is crossed longitudinally by a major fault zone (fig. 2). The Frasnian sedimentary sequence ends with the shale of the Boussu Member, which overlaps the Lion Member.

The Arche and Lion Members are hydraulically connected together in the quarry zone and represent a single aquifer formation. It contains the water table drained by the Tridaine gallery. Due to their lithologies, the surrounding geological formations are relatively impervious and tend to isolate the aquifer. Consequently, the aquifer may be compared to “a big bathtub” with limited inflow from the surrounding geological formations. The main inputs are the recharge (410 mm/year on average) and the infiltration of the Entre-Deux-Falleux (E2F) stream in the Lion Member to the northeast (fig. 2), and the output being the Tridaine gallery (765,000 m³/year on average). As highlighted by several pumping tests, the major fault zone in the upper part of the Lion Member induces a higher hydraulic conductivity of the aquifer in this area. Despite this fault zone, no other preferential flow paths, such as karstic phenomena, have been encountered following geophysical investigations or during the quarry operation.

Currently, the bottom of the extraction pit is limited to the altitude of 220 m.a.s.l., nine meters above the elevation of the Tridaine gallery. This drain has a catchment capacity of 50 m³/h, from which 10 m³/h are permanently attributed to the abbey for beer brewing while the other 40 m³/h are used by the city of Rochefort for public drinking water supply. During high water periods, the gallery discharge can increase up to 300 m³/h and the excess water overflows in surface water. However, during low water periods, the gallery discharge can decrease to 10 m³/h, jeopardizing the water supply of the city, which needs to buy water from the regional water company, which in turn is not always able to provide the required volumes. The project of Lhoist Industries Ltd. consists in the deepening of the Boverie Quarry to the altitude of 160 m.a.s.l., drying up the Tridaine gallery as a consequence. To ensure the continuous supply of drinking water, the quarry owner proposed to achieve the dewatering using three peripheral wells. In this way, the water loss during high water periods can be decreased and, last but not least, the city of Rochefort will not suffer of water scarcity during low water periods.

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The main pumping well (Lion-1) has been drilled in the high hydraulic conductivity zone located in the upper part of the Lion Member, 100 meters northwest from the nearest mining face (fig. 2). The borehole is 156 meters deep (bottom at the altitude of 91 m.a.s.l.), 440 mm wide and equipped with 305 mm wide stainless steel screened tubing. As expected, fractures have been intersected during the drilling operations as well as important water inflows, showing the potential high productivity of the well. It will be used as a single pumping well in the model. In the event of technical failure or water quality issue of this well, two backup wells were drilled around the quarry pit (fig. 2).
Figure 1 Location of the Boverie Quarry (star) within the “Calestienne” (after Poulain 2017)

Figure 2 Frasnian geological map with the location of the Boverie Quarry, Tridaine gallery (triangle), Lion-1 pumping well (diamond), backup wells (stars) and piezometers (circles) (DEM Hillshade from SPW)
Groundwater modeling: Conceptual model and calibration

A groundwater flow model has been developed with the SUFT3D (Saturated and Unsaturated Flow and Transport in 3D) research code, which has already demonstrated its effectiveness in a number of previous studies (e.g. Brouyère et al. 2009; Orban et al. 2010). This code uses the finite elements method to solve flow problems in variably saturated conditions. The greatest strength of the code is its ability to subdivide the model into sub-domains to perform different water budgets in the model. Those sub-domains communicate with each other by means of internal boundary conditions to simulate groundwater flow between the different sub-domains.

The model extends over the Arche and Lion Members as well as the part of the Bieumont Member located in the extraction area. A finite element mesh of 27,000 prismatic elements (mean side length of 20 m) and 19,500 nodes, vertically divided in five layers, characterizes the model. The top of the mesh coincides with the topographic surface retrieved from a digital elevation model and the bottom has been arbitrarily set to the altitude of 50 m.a.s.l. in order to represent the future deepening of the quarry (pit bottom at 160 m.a.s.l.) as well as the whole height of the pumping well. The dip of the geological layers is also taken into account.

The conditions prescribed at the boundary of the model domain are Fourier external boundary conditions with the exception of the contact between Nismes Formation and Arche Member, which is a no-flow Neumann external boundary condition. The choice of Fourier boundary conditions has been made to represent the probable groundwater lateral inflows that may enter the model as a consequence of the decrease of the piezometric head during the quarry dewatering. A Fourier external boundary condition has also been prescribed for the Tridaine gallery.

In order to estimate the water budget for the Arche and Lion Members separately and to assess the quantity of groundwater flowing from the Arche Member to the Lion Member, four sub-domains have been introduced. One subdomain corresponds to each limestone reef, one to the more permeable zone of the Ermitage and Bieumont Members in the middle of the extraction pit and one to the rest of these two members. Groundwater exchanges between the different sub-domains are described by Fourier internal boundary conditions.

As explained previously, the only solicitations of the model are the recharge and the infiltration of the E2F stream. The recharge is represented by a Neumann external boundary condition prescribed on the top face of each element composing the top layer of the model domain. The recharge calculation takes into account the lack of soil and vegetation in the mined area. The infiltration of the E2F stream in the Lion Member is also represented by a Neumann external boundary condition, prescribed on the top face of each element crossed by the stream. As the downstream part of the E2F stream drains the groundwater table during high water periods, a Fourier external boundary condition has been prescribed in this zone. This boundary condition is deactivated during low water periods to avoid water inflow.

The model has been divided in ten zones to describe the spatial heterogeneity. Within each of these zones, hydrogeological parameters such as hydraulic conductivity and effective porosity are constant. Three zones correspond to the Arche Member, three more to the Bieumont Member, one to the Lion Member and the last three zones are located along the fault, in the upper part of the Lion Member.

Model calibration has been performed over a whole year (May 2010 to May 2011) based on observed data collected in five piezometers spread out in the Arche and Lion Members (fig. 2), and with the discharge of the Tridaine gallery. The simulation has been run in transient conditions, with a time step of one day and weekly solicitations. The choice of such a short time step has been made to reproduce the fast response of the aquifer to the recharge, as good as possible. The calibration has been done by trial and error approach, by changing the hydrogeological parameters of the different zones as well as
the exchange coefficients of both internal and external boundary conditions.

The analysis of residuals (fig. 3) shows that the model is well calibrated but tends to overestimate the piezometric head when it is low. This trend may be explained by the better calibration during high water periods, which has been done voluntarily to improve the model accuracy during high recharge events. In this way, the dewatering discharge could be ascertained precisely to avoid flooding of the extraction pit.

**Groundwater modeling: Dewatering simulation**

According to the blueprint of Lhoist Industries Ltd., the deepening of the Boverie Quarry would take place in four phases (tab. 1), each one corresponding to the creation and operation of a new extraction level. During each of these four phases, the bottom of the extraction pit will be lowered by 15 meters. In order to mitigate any potential groundwater contamination and to avoid any risk of flooding, the water table must be kept always at least ten meters below the bottom of the extraction pit. Giving the project specifications, the dewatering of each level should be achieved in one year and the water table should stabilize during the whole levels operation, i.e. 6.5 years.

Dewatering simulation has been performed in transient conditions for a period of 30 years, with a monthly time step and monthly solicitations. The mean monthly recharge applied to the model has been calculated from the data collected between 2008 and 2017. The same recharge is applied to the model every year until the end of the simulation. Due to a lack of data, the infiltration of the E2F stream is the same one as for the model calibration. As for the recharge, the same solicitation is also applied every year. To represent the drying up of the Tridaine gallery and to avoid water inflow in the model, the corresponding Fourier boundary condition has been deactivated at the beginning of the simulation. As the downstream part of the E2F stream will not drain the groundwater table anymore during the quarry dewatering, the corresponding Fourier boundary condition has been deactivated for the whole simulation.

Modeling results (fig. 4) show that floor dewatering is achieved in one year with a constant pumping rate of 132 m$^3$/h, except for phase 1 where the pumping rate is 145 m$^3$/h. This higher value required for the first floor dewatering might be explained by the higher drawdown (23 m) needed for the operation of this level, compared to the drawdown of phases 2 to 4 (15 m) (fig. 4a).

On the other hand, the pumping well discharge required for the water table stabilization is constant from phase to phase, with a value of 113 m$^3$/h (fig. 4b). The stability of the pumping rate required during levels operation indicates that groundwater lateral inflows coming from the surrounding geological formations should be limited.

In the light of these results, the use of one single peripheral well should be enough to lower the groundwater table everywhere under the Boverie Quarry pit (fig. 4a). It is quite clear that the possibility to achieve the dewatering in such conditions mainly relies on the high hydraulic conductivity of the aquifer formation as well as on the exchange coefficients of both internal and external boundary conditions.

![Figure 3](residuals.png)

**Figure 3** Residuals of the model calibration, data from five piezometers

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pit bottom (m.a.s.l.)</th>
<th>Water table max. altitude (m.a.s.l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>205</td>
<td>195</td>
</tr>
<tr>
<td>2</td>
<td>190</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>175</td>
<td>165</td>
</tr>
<tr>
<td>4</td>
<td>160</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 1 Operation schedule of the Boverie Quarry deepening
limited lateral inflows from the surrounding geological formations. The model shows that the dewatering of the Boverie Quarry could be achieved while ensuring the drinking water supply of 50 m$^3$/h required for the city and Saint-Remy’s Abbey of Rochefort. Finally, a dynamic management of the well pumping rate could be done according to the hydrogeological conditions: when the local water supply rate and minimum piezometric level are respected, the well discharge could be adjusted to minimize groundwater wastage to surface water, avoiding over pumping of the aquifer.

**Conclusions**

The model developed with the SUFT3D research code seems to prove that the deepening project of the Boverie Quarry using one single peripheral well is feasible, owing to the high hydraulic conductivity of the aquifer as well as to the limited lateral inflows. The model has been calibrated, especially for high water periods. It shows that the discharge of the pumping well should be sufficient to guarantee the drinking water supply of both the city and abbey. However, Lhoist Industries Ltd. have already drilled two more wells, for security or water quality reasons. The modeling results still require to be validated by a long-term pumping test.

**Acknowledgements**

The authors would like to thank Lhoist Industries Ltd. for letting them access freely the Boverie Quarry and for sharing all the hydrogeological data they have gathered over time. The authors also thank the reviewers and Walter Verhaert who helped to improve the quality of this manuscript. Last but not least, they thank Isabelle Bonniver (UNamur) for the comprehensive hydrogeological synthesis of the site and Gaëtan Rochez (UNamur) for his unconditional help during the plentiful fieldworks.

**References**


**Figure 4** (A) Dewatering simulation results for pumping well Lion-1 and piezometers located in the quarry; (B) pumping well Lion-1 discharge during the different operation phases (X axis of both graphs are purely indicative)
**Abstract**

Since 2016, Somaïr has been operating in northern Niger an open-pit mine to extract uranium from a sandstone reservoir hosting a regional groundwater aquifer. The first part of this article relates the geological and hydrogeological studies carried out to design the dewatering system. In the second part, we compare dewatering plans to the encountered settings during mining operation and describe actions carried out inside and outside the pit as operations progressed in order to keep the pit toe dry for mining.

**Keywords:** Open-pit dewatering, Groundwater modelling, Water management, Uranium mining

**Introduction**

Geological exploration work carried out in the 1950s in northern Niger, led to the development of a uranium mining industry operated by two companies, Somair and Cominak, subsidiaries of the Orano Group. The main mineralized reservoirs are located in the Arlit region, on the edge of the Tim Mersoi sedimentary basin, with an underground mining operation for Cominak and open-pit mining for Somaïr.

In 2012, Somaïr launched the project to operate the Artois pit, known to be the deepest open-pit of its portfolio. To ensure dry operations while mining a dewatering system needed to be engineered in a collaboration between Somaïr’s operation engineers and Orano Mining technical experts. Mining operations started in 2016 and will reach in 2019-2020 the ultimate expansion of the forecasted open-pit.

This article presents how the dewatering system was designed prior to mining operation and how operators were able to adapt the system during the recent exploitation.

**Regional Setting**

The Somaïr mine site is located in the Arlit region of northern Niger. It lies in a plain relief, 80 km west of the Aïr granitic massif with an average elevation of 430 m. The landscape is monotonous (regs with small pebbles and sandy areas) and uniformly flat. Climate is arid with an average annual rainfall around 40 mm/yr, annual average temperature around 28°C and pan evaporation ranging from 10 to 15 mm/day.

Geological formations of the Arlit region consist of sedimentary deposits of the Tim Mersoi basin, dated from Lower Paleozoic to the Cretaceous. This sedimentary basin presents a succession of marine and continental sedimentation environments, lying unconformably on the Air Massif Precambrian basement (see fig. 1). Sedimentary sequences alternate layers of sandstone and shale, regionally dipping to the west. The structural setting is characterized by North to South regional trending structures (Arlit flexure-fault) and East-North-East to West-South-West secondary faults (Autruche, Izerataguen flexure-faults).

Groundwater is hosted by three sandstone layers (Izegouande, Tarat and Guezouman) separated by shale layers but interconnected through major faults (Boko 2017). Prior to the commencement of mining operations, groundwater flow was from recharge area on the edge of the basin towards Arlit flexure-fault (Dodo 1992 and Le Beux 2013b).
flexure-fault acted as a semi-permeable barrier, flattening the groundwater gradient to the East and allowing groundwater connections between aquifers on either side of the flexure-fault. In the present conditions, groundwater east of the Arlit flexure-fault regionally converges towards the Cominak underground mine. Locally, the Tarat and Izegouande aquifers are dried out due to dewatering activities at the Somaïr mine.

**Artois Open Pit Project**

*Geology and Hydrogeology*

Somaïr operates a number of open-pits to extract uranium from a Tarat sandstone reservoir. These open pits are located between two major structures, Arlit flexure-fault to the west and Autruche flexure-fault to the east, creating two anticlines. The depth of the each open pit depends on its location with respect to the resulting syncline varying from 50 m to more than 100 m in the deepest areas of the syncline.

The mineralized horizon hosts an aquifer with an average thickness of 30 m. The groundwater flow direction (see fig. 2) is mainly influenced by the water supplied from the pit lake of a former open-pit (average abstraction of 35,000 m$^3$/month). Prior to Artois operation, the groundwater level in the Artois syncline ranged from 385 m in the northern side where the Tarat sandstone outcrops, to an average of 350 m in the vicinity of the forecasted Artois pit.

Groundwater flow in the Artois syncline is partly disconnected from the regional groundwater flow (Le Beux 2013a), with the Arlit and Autruche faults acting as compartmentalizing barriers. The recharge is considered very low, most probably limited to the northern side of the syncline, where a prominent wadi system intersects an outcropping Tarat sandstone formation. It is a productive aquifer (wells specific capacity of exceeding 5 m$^3$/h per m) and has been used for production of industrial water supply since the mid 2000s. Well abstraction rose to 150,000 m$^3$/month in the mid 2010s with an overall depletion in the syncline of the aquifer of about 2 m/year.
Artois open pit operation and dewatering strategy

Mining operation of Artois open pit started in 2016 and production is forecasted until 2022. It is expected to reach the level of 300 m in 2019-2020, the deepest section Somair’s mine portfolio. At it’s ultimate limits the open pit will be 1,660 m from north to south and 700 m from east to west. Although it was expected that the southern and eastern edges of the pit would be dry (Autruche flexure-fault, see fig. 2), most of the open pit extension to the north would require dewatering to lower the water table below the pit floor (up to 50 m depressurization).

Mining operation progresses from south to north with two work faces, one dedicated to advancement of the overburden stripping and the other one for ore mining. The northern open pit wall will therefore always be about 300 m ahead compared to the open pit ore toe. In order to induce a rapid depressurization of the starter pit, it was decided to set up an evolutive ring of perimeter dewatering wells intersecting inflows on the western and northern open pit wall (see fig. 3). The location of the first ring to the north was set to intersect the deepest section of the syncline where the dewatering wells were expected to provide the best specific capacity.

The dewatering scheme was approached with a model simulating groundwater flow in the Tarat sandstone reservoir. It was calibrated based on 10 years of groundwater monitoring in the Artois syncline. The objective of the simulation was to define (i) how many dewatering wells would be required to lower the water table, (ii) how much water would be abstracted from the dewatering wells, (iii) what depressurization could be achieved and (iv) how much water would have to be managed by the in-pit dewatering systems.

The simulations (Le Beux 2015) were run to forecast the first 3 years of Artois operation (2016-2018, see fig. 4). The results indicated that 14 to 16 dewatering wells, at a distance of 80 to 120 m from each other, would be required to lower the water table to approximately 325 m. The total abstraction rate was estimated at 180,000 m$^3$/month at the start, then dropping to 110,000 m$^3$/month after one year of operation. Individual wells would be operated at flow rates of 7,300 to 13,000 m$^3$/month (10 to 18 m$^3$/h) which is respectively in the range of 40 to 70% of the critical flow rates of historical wells currently in operation in the Artois syncline.

In-pit water abstraction was estimated to be in the order of 25,000 m$^3$/month after 2018. Water was planned to be managed from...
mobile pumps, with a standard flowrate of 55,000 m³/month (or 80 m³/h) with a lifting capacity of 40 m, and installed in sumps dug ahead of the ore excavation. Water abstracted from all sumps would then be pumped out of the open pit from a primary pond equipped with a fixed pumping system (flowrate of 100 m³/h with a lifting capacity of 120 m). The installed abstraction capacity will exceed the estimated water inflow and will be operated at less than 40% of its availability.

**Water Management during Operation**

**Perimeter dewatering system**

A total number of 19 dewatering wells were put into production in 2016. Individual flowrates ranged from 9 to 15 m³/h with specific capacities of 0.4 to 5 m³/h per m (monthly water abstraction of 100,000 to 130,000 m³, see fig. 5).

In early 2017, a review of the dewatering strategy based on 6 months return of experience was organized (Beal 2017). The data collected during this period indicated that the aquifer depressurization was consistent with the model simulation, however, the specific capacity of the wells tended to decrease faster than expected. It was therefore decided to set a monthly target of 120,000 m³ of abstracted water as a performance indicator for the dewatering wells, but, in order to keep pumping at target abstraction rate, the number of wells needed to be increased.

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**Figure 3** Artois open pit design and dewatering strategy. The location of the open pit can be seen in fig. 2B.

**Figure 4** Groundwater simulation results 2016-2018 (from Visual Modflow)
Additional wells were drilled between existing dewatering wells of higher specific capacity and in areas where the syncline was the deepest. Individual flowrates were expected to range from 5 to 10 m³/h. Target costs were optimized by changing the design to smaller diameter wells and installing lighter equipment for the temporary wells.

**In-pit dewatering system**

The first in-pit water seepages were observed in 2017 when the pit floor reached the elevation of 325 m in accordance with the depressurization targets forecasted by the hydrodynamic modeling (see fig. 4). Two sumps were blasted at elevation 320 m (to the west) and 308 m (to the east), below the mined ore horizon (see fig. 6). The location of the dewatering sumps was set in low ore grade area, in order to minimize ore dilution in excavated material. Until early 2019, water abstraction from the in-pit sumps remains lower than forecasted (in the order of 20,000 m³ abstracted) most probably because the open pit floor acts as a large evaporation zone and water inflows were largely
intercepted by the dewatering ring of wells. Light submersible pumps are used to divert abstracted water from in-pit sumps towards a primary pond set along the haul road above the mineralized level. From there water is pumped out of the open pit with a fixed system and used for ore processing in the plant (see fig. 6).

In-pit dewatering was augmented by abstraction from open-holes drilled in the western edge of the open pit floor where the ore reservoir was the thickest and deepest. Wells were drilled 30 m deep and equipped with 4-inch submersible pumps protected by a cooling skirt. Although their abstraction rate has never exceeded 2.5 m³/h, these wells have a very low capital investment cost compared to dewatering wells.

To improve the specific capacity of these in-pit dewatering wells, it was suggested to fracture the reservoir along a blast line located on the northern wall, between the two dewatering sumps. Holes were drilled every 5 m to an average of 20 m below the open pit floor. Open-hole wells were then positioned between blasted holes to intersect fractures. It is expected that these new wells will be able to abstract more water and dry out the current in-pit sumps. These wells are planned to be put to production in the second quarter of 2019.

**Conclusions**

The Artois open pit operation is currently Somaïr’s largest mine and the main area requiring a groundwater management plan. Operations were prepared in 2015 with the first geological and hydrogeological studies targeting to model the reservoir geometry and hydrodynamic behavior. The dewatering strategy first consisted of setting up a ring of dewatering wells around the pit to mitigate the inflow from the regional groundwater system. Residual water from the anticlinal bottom had to be managed by in-pit sumps.

Two keys to success of the Artois open pit operation can be highlighted. The first one relies on operator agility to modify the dewatering system with a continuous objective to intercept as much water as possible with an increasing number of wells of lower specific yield. The second one consists in testing and implementing in-pit dewatering methods which combine in-pit sumps and wells with reservoir fracturing techniques.

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**References**


Abstract
The paper addresses the mechanism of floodwater inrush from a ground sinkhole into underground excavation. As demonstrated by computed simulation, a natural hydrofracture of the rock mass may develop from the sinkhole into the mine opening under the effect of low stresses in the rock mass and water hydrostatic pressure. On approaching the mine opening the fracture may stop growing due to local rock compression near the mine opening. A strong infiltration water flow may occur from the fracture into the opening that may lead to water erosion of roof and dynamical water inrush into the opening.

Keywords: underground mining, ground surface, sinkhole, floodwater, technogenic rock stresses, natural hydrofracture, filtration, water inrush

Introduction
Emergency situations caused by spontaneous hydrological events show a continuous trend towards increasing frequency and scale of consequences (Guidelines 2000). Major economic damage from floods due to snow melting is inflicted to engineering constructions on the earth surface. However, under certain conditions meltwater may affect safety of underground mining. There are a variety of mechanisms of this effect. As a rule, they are associated with general increase in the rock mass water saturation and intensification of infiltration.

Underground mining of solid mineral resources at small depth is sometimes accompanied by local sinking of the earth surface with rupture of rock continuity referred to as technogenic ground fall-through. The fall-through is caused by a shift of the undermined rock into the opening. In Russia design and construction of buildings in such cases are done in accordance with appropriate codes of practice to avoid adverse effects (The Building Codes 2011).

The surface sinkholes are often filled with water. In this case, besides the dangerous geomechanical effect on mining safety, the sinkhole becomes a source of hydrogeological hazard as a reservoir of water that can breakthrough into the underground mine opening. The water breakthrough into the underground opening may proceed by various mechanisms depending upon rock mass geological structure, features of its stress state and water pressure. Water inflow into the underground opening from a surface reservoir in a homogeneous and well-penetrable rock mass may proceed by a water infiltration mechanism (Mironenko & Strelsky 1993, Luckner & Shestakov 1991). Another mechanism of water penetration into the underground opening may take place in the rock mass with horizontal layers. In this case rock undermining is associated with generation of vertical rock mass tension, bending and disclosing of layer contacts, water filling of the layer contacts, rupture of some layers due to critical bending deformation, which results in water penetration into the opening (Iophis & Maltseva 2002, Baryakh & Samodelkina 2012, Liu et al. 2014).

If vertical pressure of the overlying rock is about twice as high as natural horizontal stress (this situation is characteristic of sedimentary rock in regions with rather calm geodynamical environment), fields of tensile horizontal technogenic stress may be generated in the undermined rock. Tensile cracks may develop and become filled with water in such regions. This water as a factor of force may play an active role in the crack
development due to pressure on the crack sides. Such fracture cracks may become major canals for water breakthrough into openings both from surface and underground reservoirs (Odintsev and Miletenko 2015).

In subarctic regions water breakthrough may also be caused by generation of so called frost cracks due to extremely low negative temperature. The generation of the frost cracks descending into depth up to ten meters is characteristic of subarctic regions and is not associated with mining activities. These cracks may be considered natural objects affecting subsequent tecnogenic geomechanical and hydrogeological processes in the rock (Grechishchev et al. 1984).

Another mechanism for water breakthrough from the sinkhole to the opening related to both to crack generation and infiltration flow is considered below on the example of the Yun-Yaga coal mine. As known, study of practical experience is the best way to understand the specific mechanism of an event and to develop adequate methods for prediction of similar cases in future.

**Water breakthrough from a sinkhole into a ventilation gallery at the Yun-Yaga mine**

The now closed Yun-Yaga mine was used to extract coal from the Yun-Yaga coal deposit located in the north-eastern part of the Pechora coal basin (Gorbachevskij 2007). The climate of this region is subarctic with sharp temperature and pressure variations. Average temperature for a many-year period of observation is minus 6.3°C with absolute minimums of -42 to -52°C and maximums of +30 to +32°C.

The Yun-Yaga deposit is located in a region involving a zone of permafrost. The zone is 50-60% of the whole area, and there are multiple through taliks in the remaining portion, the zone maximum thickness is 180-200 m (average 50-70 m, predominant values up to 20-30 m), temperature ranges from -0.5 to -3.0°C. The through many-year taliks are as a rule located under large undrained lakes, the Yun-Yaga river, some streams and in a region of sinkholes.

The mine field geological structure has several water bearing sandstone layers located in roofs of coal seams under operation. The deposit natural hydrogeological conditions are impaired due to mine construction. The mine construction was accompanied by large water inflow (reaching 720m³/h). The underground water state underwent considerable change by the end of the construction. A large drawdown cone was generated that reached and even went beyond the deposit outline involving the Yun-Yaga river-valley. The total decrease in the underground water level in main water-bearing horizons was 65 to 130 m.

A water breakthrough occurred from a rather small surface sinkhole into the ventilation gallery located at about 30m below the sinkhole. The sinkhole was formed in the area of influence of the excavation. However, the sinkhole had no hydrological connection with the ventilation gallery, which was explained by sufficiently plastic properties of the overlying rocks and rapid closing of induced cracks (Kostarev & Mitishova 2000).

Water from the ventilation gallery penetrated further into the lava and the conveyor drift. The water-resistant doors did not give effect due to water infiltration through the surrounding rock mass and concrete partitions. Lack of power and flooding of the pumping stations led to flooding of the coal mine (Miletenko 2007).

The breakthrough occurred during the period of high level of melt water (above 0.5 m) due to complete thawing of the overlying rock strata after their partial freezing in winter. The causes of the flood included limited water runoff and insufficient conveyance capacity of the hydrotechnical construction (bridge). The water breakthrough into the ventilation gallery began with weak dripping of water from the roof of the gallery, which turned into strong dripping with erosion and fall of loose roof rock and intense flow of water from the roof.

The coal seam thickness was 1.9 m and inclination was 10° (fig.1). The immediate roof was a 1 m siltstone layer of 40M Pa strength; the main roof was a sandstone layer about 14 m thick and 70-90 MPa strong. The overlying rock mass in the weathering area was weakened by oxidation process and individual frost cracks.
Check-up at the mine reported the following main geomechanical cause of the event – development of a frost crack. But this conclusion was not supported by any calculations. Frost cracks cannot be deeper than ten meters. The season-associated temperature variance has no effect at such a depth due to the talik effect. Development of the major crack should occur in another manner. Therefore, this event was considered abnormal and requiring a special examination.

**Modeling of water breakthrough**

An attempt was made to model the geomechanical and hydrogeological situation using the approach described in (Odintsev and Miletenko 2015). This approach is based on the assumption that the occurrence of a large water-supply crack is associated with the combined effect of technogenic pressure reduction of rocks and hydrostatic effect of water in the crack. The growing crack is actually a hydrofracture of the rock.

Since the initial geometric and geomechanical situation was not known in detail, different calculation schemes existed for the formulation of modeling problems. Each of the patterns included a rock mass up to 100 m deep and a 50-meter part of the excavations. On the part of the excavated seam (50 m in length) the resistance of the support to the movement of the overlying rocks was set by back pressure of 0.5 MPa. There was no back pressure in a small part of the excavation, including the ventilation gallery.

In the calculation the sinkhole was assumed to be an ellipsoid earth surface depression of about 3m in depth, water pressure near the sinkhole bottom was 0.03 MPa. Since the sinkhole had no hydraulic connection with the mine opening and permafrost was absent in the considered area, the rock mass was assumed to be homogeneous elastic solid medium with 103 MПа modulus of elasticity and Poisson's ratio of 0.3.

Rock pressure in the virgin rock mass was specified by the academician A.N.Dinnik hypothesis that vertical stresses were determined by weight of overlying rock (about 0.6 MPa at a 30 m depth), while side stresses depended upon Poisson's ratio of the rock. They were 0.25 MPa in the case considered.

The conditions of the absence of permafrost in the considered area of rock mass were considered. It was due to technogenic influence of mining and the influence of sinkhole. For this reason, the rock mass was considered an elastic medium without internal stress sources.

A variety of situations with initial crack starting from the sinkhole were considered including a small vertical frost crack beginning from the sinkhole bottom and a crack coming out from the sinkhole at an angle (fig.2). As concerns crack growth two factors were considered, i.e. technogenic stress state of the rock mass and water pressure in the crack changing with depth by hydrostatics law.
Calculation of crack development was made by sequential steps according to the finite element method. Possibility of rock destruction at the crack end was assessed at each step by the Griffiths-Irwin criterion as described in (Odintsev and Miletenko 2015). The vertical coordinate reflects the change in depth from the earth surface. The horizontal coordinate defines the changes along the coal seam. If the criterion was met, a small length increment was specified along the direction of the highest tensile pressure of the rock. As a result of a sequence of calculation steps a trajectory was found for crack development from the sinkhole to the ventilation gallery due to rock natural hydrofracure.

Figure 2 shows some results of stress calculation for a situation when a water-conducting crack approached the ventilation gallery (the distance from the crack end to the gallery was 2 m with a crack of 24 m in length). Figure 2a shows isolines of main stress which is the highest tensile stress leading to rock fracture. Figure 2b shows isolines of von Mises stress that allows assessment of the rock area of pre-destruction. Rock permeability is known to increase rapidly in this area (Stavrogin & Protosenya 1985).

The analysis of the stress-strain state of the rock mass near the end of the crack and the ventilation gallery shows that the crack can reach the roof of the gallery under some conditions or stop in its development under other conditions (due to the features of the geometry of the opening and the local compression of the rock). The first case is the situation with dynamic break of water into the crack at once, the second case reflects the possibility of water infiltration into the opening.

The problem of infiltration theory is solved to analyze the features of the flow into the ventilation gallery, including the water infiltration directly from the surface and sinkhole together with the water infiltration from the water-conducting crack. The hydraulic conductivity of siltstone 0.001 m/s was used in the calculation.

As follows from the calculations, for a crack less than 20 m in length the infiltration water flow from the surface and from the crack to the rock mass is extremely low. The situation changes when the crack approaches the mine opening. In this case interaction between the crack and the opening begins. Figure 3a shows the situation for a 24 m long crack. In the figure the isolines of values of the infiltration rate (m/s) are shown. These values must be multiplied by a correction factor of 10-3. As seen, the infiltration flow of water is strongly limited by the end of the crack. Figure 3b shows isolines in the immediate vicinity of the opening. These isolines are constructed on a different scale for a different finite element mesh to verify the correct calculation and to more accurately estimate the amount of possible water flow into the hole.

The assessment showed that the water flow through the free surface of 15 m² can reach about 50 m³ per hour. Such an intense water flow may really cause washout of weak
rock in the roof of the ventilation gallery and partial roof fall into the opening with the major crack start and water breakthrough in the opening to follow, which was the actual case.

Discussion of results

The modeling has demonstrated that the actual picture of the catastrophic water inflow into the ventilation gallery cannot be explained by infiltration mechanism only. The catastrophic water breakthrough may be caused by development of a major water-conducting crack growing from natural frost crack in the bottom of the sinkhole towards the mine opening.

It follows from the modeling that the major water-conducting crack may be considered as natural hydrofracture of the rock mass in the area of low technogenic stress. Hydrostatic pressure in the crack increases during water flood and the crack may grow to a considerable depth. This factor is of much importance for a case when the sinkhole occurs near the border of projection of the undermined seam portion to earth surface.

It should be noted however that under real conditions of block structure of the rock mass the induced deformations can form a more complex picture as established in (Iophis et al. 2007). Here we used the idea of the rock mass in which the induced water-free cracks were closing over time.

As follows from our modeling, the major rapidly growing crack may stop to develop near the mine opening. In this case a heavy local infiltration inflow into the opening may occur. In practice such a local water inflow in loose rock often leads to washout and fall of the rock from the roof of the opening. In the case considered the rock mass failure area reached the end of the water-conducting crack, which resulted in a powerful stream of water into the opening.

The conclusion may be made that if water penetration into mine openings proceeds by the crack-and-infiltration mechanism, heavy dripping from the opening wall and roof should occur before the catastrophic breakthrough. Therefore, one may predict the critical situation with breakthrough of the major portion of water into the mine opening and take preventive measures beforehand to reduce hazardous consequences of the water breakthrough.

Assessment of the possibility of water breakthrough into underground openings in subarctic regions should involve assessment of possible effect of permafrost, which in general prevents water penetration into underground mine openings. However, one has to take into consideration that taliks may be generated in the rock mass under the effect of mining at small depth. In addition, the presence of natural and artificial water reservoirs on the surface further contributes to the generation of taliks. In this case the poorest conditions for water breakthrough into underground openings at small depth are formed due to spring thawing of subsurface rock.
Conclusion
The meltwater-filled sinkhole changes dramatically rock geomechanical state and makes conditions for generation of a hydrofracture crack to mine opening. Hazardous water inflow into underground mine opening may be associated both with direct hydrofracture crack egress into the opening and with preliminary intense infiltration water inflow from the crack into the opening if the crack development slows down. In loose rock, an intense infiltration inflow of water, which manifests itself by a very intense dripping of water from the roof of the mine, can be an indicator of the approaching washout of the rock and the flood of water from the water-conducting crack. Timely modeling of possible situations with due consideration of geomechanical and hydrogeological factors could help to predict hazardous situations and to prevent water breakthrough in the mine opening.

References
Disruptive Technologies in Mine Water Management – The Future

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Abstract
This paper outlines the development of a mine water management system using “smart” technology. It will provide the mining industry with many advantages in mine water treatment and management, as it integrates the fourth industrial revolution in its system, such as nano-electric sensors being installed almost everywhere in the mine to monitor real time data and quantum computing for faster data processing that is being administered in the blockchain. This will enable a collection of all possible mine water treatment parameters and eventually the development of a “smart” mine water treatment plant.

Keywords: Nano-electric Sensors, Quantum Computing, Blockchain, Mine Water Management

Introduction
Current mine water management usually consists of “blindly” end-of-the-pipe treatment. This treatment does not take into consideration water chemistry or volume changes prior to arriving at the plant. Neither does it take into consideration the effects of the weather or operational procedures. Yet, all these parameters can be monitored and processes regularly and potential changes in volume or the water chemistry can be identified hours or weeks in advance, allowing the mine water management (e.g. pumping rates) and treatment adjust to the predictable, future changes. In addition, this allows optimizing the work flow at the mine water management site and ordering consumables or scheduling electricity needs before they are necessary.

As the world is adjusting to the fourth industrial revolution, usage of disruptive technologies in mine water management is advantageous. This will help to treat and manage polluted mine water more effectively by improving the currently existing mine water management technologies. This will be achieved without disturbing the industry, by: improving (e.g. technological age of the mine), implementing existing (e.g. electrocoagulation, integrated membrane technologies) and researching new technologies (e.g. new sensors, valorisation of mine water).

This paper describes a step by step approach in developing a system that uses disruptive technologies to treat and manage mine water. The system uses industry 4.0 technology such as nanotechnology in electronics by e.g. developing RFID-based mine water sampling (Cheng et al. 2008; Yu and Meyyappan 2006). The use of GoldSim (Nalecki and Gowan 2008; Usher et al. 2010; Wolkersdorfer 2008) together with quantum computing (Tabakin 2017) will help to visualise and dynamically simulate the large amount of data to be collected during the study. Mine water treatment in almost all current mine water treatment plants is not effective enough as it does not take advantage of all the potential residing in modern technology. Current mine water treatment plants normally react instantly when the volumes or chemistry changes (Wolkersdorfer 2008), therefore, there is usually no interaction between precipitation, water inflow into the mine, technological changes within the mine, water analysis of the plant and the outflow or storage of the treated water.

This proposed, new technology will help with accurate continuous data collection and monitoring as opposed to scheduled, discontinuous monitoring. In consequence,
this will lead to better decision making. It will also help in detecting any changes in the mine water quality trend before it occurs, i.e. early detection of changes in the mine water chemistry and volumes. Inflow and outflow monitoring will allow for an accurate water balance and therefore take precautions if there is a risk of overflow in the plant. More advantages include reduced uncertainty in determining the potential risks posed by the mine on the environment, e.g. flooding will be detected before it occurs. Costs of treating mine water will be reduced as there might be no necessity for regular chemical monitoring, and all necessary steps can be done using the system discussed in this context. The technology will also help in improvement of mine water models, i.e. chemical and water balance models.

Parameters to be measured and processed include online monitoring of flow and physio-chemical parameters, results of sampling campaigns, RFID controlled sample management, results of chemical analyses of the mine water and data processing, e.g. statistics of various scales. Due to the large volumes of data that will be collected, techniques used in the process will include blockchain technology for data tracing (e.g. Ikeda 2018), quantum computing (e.g. Tabakin 2017), expert systems, fuzzy based decision mechanisms (e.g. Golestanifar and Ahangari 2012) or neural networks (e.g. Diamantopoulou 2005; Singh et al. 2009) and an overall control of the quantity and quality of mine water using the above techniques in artificial intelligence.

**Methods**

In most cases, an underground mine is likely to have polluted mine water; therefore, this proposed technology will be best implemented and tested in a mine with mine water problems. The mine water management in this mine will be converted stepwise and disruptive technologies will be integrated accordingly. This will include setting up quantum computing (in the long run), installing RFID tagged devices (e.g. pumps, sensors), setting up a digital object management scheme based on existing name conventions and teaching the employees how to use this technology to provide them with the best available option to manage the water in the mine. A project plan will be set up in conjunction with the mine and all the relevant water pathways and users that are pertinent for the water treatment and technology advanced water treatment process. In this concept, all water pathways into, through and out of the mine will be monitored and used to feed the developed system with relevant data (fig. 1). The system will give a clearer picture of the mine water management in the mine, i.e. how much water flows into, leaves and flows through the mine (“mine water make”).

To avoid unauthorised access, a digital rights management is imperative, which includes managing different access levels of various users. Because of the problems related to wireless devices in a real situation environment (e.g. Chen et al. 2015), not all sensors might become wireless sensors. Yet, current technology development might be able to provide innovative sensor technology which is able to overcome those problems and other problems encountered in water related sensor technology (e.g. Zhuiykov 2012). However, new sensors or technologies will not be developed; rather existing sensors and technologies will be adapted into the developed system. Yet, there will be development of a concept and software application to include all necessary concepts into a working system at a real mine with the need of more sophisticated water management.

Methods to be included are data processing, statistical methods, simulation (e.g. GoldSim; Nalecki and Gowan 2008; Usher et al. 2010) into an expert system or artificial intelligence-based decision process, depending on the complexity of the data. Due to blockchain technology that will be applied in this system, data will be accessed anywhere, anytime, and users shall be able to trace the source of data.

After a clearer approach to introducing disruptive technologies and developing the system (fig. 2), the following will then be achieved:

- Concept and software to run the developed system on an existing mine,
- Use smart technology to manage mine water underground, during transportation and in the process,
- Investigate sensor technology for mine water,
Figure 1 Water treatment operation in a mine with new technology

- Describe the geothermal energy in the mine water within the process, and
- Provide a technological concept for managing mine water in the view of "smart" technology.

This will then lead to a fully functioning system, which includes all aspects of mine water management from sampling to data processing to process control (fig. 3). In addition, there will be a need to identify and describe methods of separating the water streams in a mine so that the amount of polluted water that needs treatment can be minimised. Techniques to separate different water streams in surface or underground mines are known (e.g. Birk et al. 1964) but usually not used because practical and cost reasons might interfere with the management of various water streams. This study will identify methods that are currently used and how they could be implemented in the mine of the future.

Conclusions

Integrated control of all relevant water related processes within the mine and the plant to optimise mine water management and treatment is an important part in future mining operations. This will enhance the technology age of mining, bringing mine water management to the next stage and possibly be relevant in the fourth industrial revolution concept. The study will provide the mining industry with many advantages, e.g. instead of purifying a waste during the mine water management process, a resource can
Figure 2 Relevant steps and their connection in the system to be developed with introduction of disruptive technologies.

Figure 3 Comparison of past and current mine water treatment plant (left) with the future mine water treatment plant (right).
then be produced, it also helps us to get rid of old habits such as intensive liming and enables the mining industry to produce at lower costs and more environmentally friendly.

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References
Assessing Different Coal Combustion Residue Scenarios in Opencast Coal Mines, Mpumalanga, South Africa

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Abstract

This study assesses the flow and transport characteristics of backfilling opencast coal mines with coal combustion residues (CCR’s), in order to assess its feasibility. Generic models were constructed to simulate six backfilling scenarios, which include: (1) No CCR's, (2) CCR's above water table, (3) CCR's below water table, (4) CCR's in middle of pit, (5) CCR's down gradient, and (6) CCR's below weathered zone. Results indicate that all scenarios have the potential to contribute to a less negative environmental impact. This paper demonstrates the model setup and approach using Scenario 5 where a rise in water levels in the pit was achieved, reducing acid mine water generation and re-directing plume migration.

Keywords: Fly ash, coal ash, backfill, opencast coal mines, feasibility, flow and transport, effect

Introduction

South Africa relies heavily on coal to generate electricity and meet the countries energy demands (National Electricity Regulator 2004). The result of coal mining are numerous abandoned coal mines within the region of Mpumalanga, South Africa (McCarty 2011). Several of the shallow underground mines have collapsed and most are discharging acid mine water (AMW), causing elevated contaminant concentrations in nearby surface and ground water bodies (McCarty 2011). Additionally, the burning of coal for power generation produces large amounts of coal combustion residues (CCR’s) annually (Reynolds-Clausen and Singh 2016), which are disposed of in holding ponds or landfill sites, with limited space. Therefore, there is a need to prevent AMD generation from abandoned mines, whilst consequently disposing of coal ash.

A proposed solution is to backfill opencast coal mines with CCR monoliths. Therefore, it is important to understand the hydraulic behaviour of CCR monoliths when disposed of in an opencast coal mining environment. However, limited studies have focussed on understanding this applications behaviour in order to assess its feasibility and determine whether this activity will have a positive, negligible or negative effect on groundwater quality. This study aims to address this gap by assessing the flow and transport characteristics of CCR’s under numerous backfilling scenarios by achieving the following objectives: (1) To develop conceptual models of backfilling scenarios, (2) to determine the changes in the hydrogeological flow regimes, and (3) to identify changes in contaminant concentrations and plume migrations.

Methods

Generic transport models were constructed to represent the following CCR backfill scenarios in Mpumalanga, South Africa: (1) mine spoils only / no CCR’s, (2) CCR’s above the water table, (3) CCR’s below the water table, (4) CCR’s in middle of pit to the surface, (5) CCR’s down gradient to the surface, and (6) CCR’s below the weathered zone.

A three-dimensional MODFLOW USG control volume finite-difference grid was set up, consisting of 8 layers (10 meter thickness), 100 × 100 cells in each, with a 10 m cell size. All layers are flat, whereby the upper second and third layers (20 – 30 meters below ground
level) attain a north and south general head boundary introducing a 10m flow difference. Drain boundaries are temporarily placed in the pit during the active mining phase to simulate mine dewatering. Additionally, drains were placed at the lower portion of the pit (discharge zone) to simulate mine water discharge. The mining pit is square in shape with a length / breadth of 300 m and a depth of 30 m. The total size of the square model spans an area of 80 000 000 m$^2$, with the opencast mine placed in the centre spanning an area of 90 000 m$^2$.

**Hydrogeological properties**
All hydrogeological properties are representative of the Witbank Coalfield in Mpumalanga (Hodgson and Krantz 1998; Bart and Sci 2008; Steyl 2011). The Witbank Coalfields comprise of four main hydrogeological units; the weathered, the primary unconfined, semi-confined and confined aquifers. The area receives 688 mm/annum with a recharge rate of 21 mm/a (3 %) (Kirchner 1991). A summary of the study site input parameters are presented in Table 1 on the next page.

**Coal ash properties**
The hydraulic conductivity of coal ash is known to decrease over time as it is exposed to moisture and oxygen (USEPA 1994). Two main local studies, conducted by October (2011) and co-researcher Johnson (2019), have formed the basis on which hydraulic conductivity values of coal ash in Mpumalanga are derived (Table 2). These hydraulic changes are accounted for in the model by using the function of 'time variant materials' within the MODFLOW-USG code. A summary of the coal ash numerical input parameters are presented in Table 3 on the next page.

**Mine spoil properties**
Mine spoils are extremely heterogeneous, varying in hydraulic conductivity over several orders of magnitude. Despite their heterogeneity, a general approximation of mine spoil hydraulic conductivity is 10-1 m/d (Hodgson and Krantz 1998). As the mine spoils age, levelled mine spoils become less permeable due to the decomposition of material, compaction and silting up of channels (Rehm et al. 1980). This is accounted for in the model by varying recharge rates throughout the mining cycle. Additionally, mine spoils contain pyrite minerals, forming acid mine water (AMW) when exposed to sufficient amounts of air and water (USEPA 1994). As AMW is the source of contamination in the model, it is simulated as a non-reactive SO4 concentration when mine spoils are recharged in conjunction to their respective mining phases (Table. 5). A summary of the mine spoils numerical input parameters are presented in Table 5 on the next page.

**Results and Discussion**
The conceptualization of practical CCR backfilling scenarios were made on the basis of preventing AMD formation, by either limiting the oxygenation or saturation of mine spoils. Resulting in the development of six backfill scenarios, which include backfilling with: (1) mine spoils only / no CCR's, (2) CCR's above the water table, (3) CCR's below the water table, (4) CCR's in middle of pit to the surface, (5) CCR's down gradient to the surface, and (6) CCR's below the weathered zone. All the simulated results were compared against backfilling with mine spoils only (baseline scenario) to evaluate the effect that CCR backfilling will have on opencast coal mines. This paper primarily focusses on scenario 5, which is presented in Figure 1.

Flow model results simulated water levels of 11.00 meters below ground level (mbgl) upon entering the pit and 14.00 mbgl when exiting the pit, creating a hydraulic flow difference of 3.00 m (Figure 2). Groundwater entering the pit experiences a 12.05 % rise in water levels in the upper portion of the pit. Groundwater flow is limited by the ash monolith, which due to its low permeability, forces water to flow around the ash monolith. Groundwater recharge over the ash monolith induces a perched water table of 4.28 mbgl and 10.06 mbgl for layers 1 and 2 respectively.

Solute transport results indicate that scenario 5 did not exhibit a southwards extending contaminant plume, but instead displayed a minor 50 m horizontal eastwards and westwards plume (Figure.
### Table 1 Hydrogeological numerical input parameters

<table>
<thead>
<tr>
<th>Hydrogeological Zone / Aquifer</th>
<th>Layer</th>
<th>Thickness (m)</th>
<th>Hydraulic Conductivity (m/day)</th>
<th>Specific Storage</th>
<th>Specific Yield</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weathered</td>
<td>1</td>
<td>10</td>
<td>0.12</td>
<td>0.002</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Unconfined</td>
<td>2 - 4</td>
<td>30</td>
<td>0.07</td>
<td>0.001</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Semi-confined</td>
<td>5 - 6</td>
<td>20</td>
<td>0.05</td>
<td>0.001</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Confined</td>
<td>7 - 8</td>
<td>20</td>
<td>0.004</td>
<td>0.001</td>
<td>0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Table 2 Coal ash variable input parameters

<table>
<thead>
<tr>
<th>Mining stage</th>
<th>Hydraulic conductivity (m/day)</th>
<th>Recharge (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Backfill</td>
<td>0.8</td>
<td>10</td>
</tr>
<tr>
<td>10 years post-backfill</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>15 years post-backfill</td>
<td>0.01</td>
<td>8</td>
</tr>
<tr>
<td>100 years post-backfill</td>
<td>0.001</td>
<td>5</td>
</tr>
</tbody>
</table>

### Table 3 Coal ash numerical input parameters

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (m)</th>
<th>Hydraulic Conductivity (m/day)</th>
<th>Specific Storage (1/m)</th>
<th>Specific Yield (m³/m³)</th>
<th>Porosity (m³/m³)</th>
<th>Recharge (m³/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 3</td>
<td>30</td>
<td>0.001 – 0.1</td>
<td>0.008</td>
<td>0.08</td>
<td>0.05</td>
<td>0.01 – 0.0002</td>
</tr>
</tbody>
</table>

### Table 4 Mine spoil variable input parameters

<table>
<thead>
<tr>
<th>Mining stage</th>
<th>Recharge (%)</th>
<th>SO4 Concentration (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Backfill</td>
<td>10</td>
<td>3500</td>
</tr>
<tr>
<td>10 years post-backfill</td>
<td>10</td>
<td>3500</td>
</tr>
<tr>
<td>15 years post-backfill</td>
<td>8</td>
<td>2000</td>
</tr>
<tr>
<td>100 years post-backfill</td>
<td>5</td>
<td>2000</td>
</tr>
</tbody>
</table>

### Table 5 Mine spoil numerical input parameters

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (m)</th>
<th>Hydraulic Conductivity (m/day)</th>
<th>Specific Storage (1/m)</th>
<th>Specific Yield (m³/m³)</th>
<th>Porosity (m³/m³)</th>
<th>Recharge (m³/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 3</td>
<td>30</td>
<td>1.1</td>
<td>0.02</td>
<td>0.2</td>
<td>0.25</td>
<td>0.01 – 0.0002</td>
</tr>
</tbody>
</table>

3). Consequently, reducing down gradient plume concentrations by 90.33%, providing an improvement to the direct down gradient water quality, with an additional lateral spreading of the plume into the adjacent aquifers.

**Conclusions**

It has been concluded that all modelled CCR backfilling scenarios provide a less negative environmental impact, improving groundwater quality discharging from opencast coal mines. The benefits provided by the more favourable scenarios include: 1) increase in pit water levels keeping larger volumes of mine spoils saturated, thus reducing the formation of AMD; and 2) management of water levels to retain and direct the contaminant plume within the pit, thus directing plume migration to increase management options, and 3) reducing recharge in areas where CCRs are exposed to the surface, thus reducing total volume of water in the system.

**References**


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Figure 1 Conceptual model of scenario 5

Figure 2 Simulated water levels of scenario 5

Figure 3 Comparative contaminant plume results of the baseline scenario (left) and scenario 5 (right)
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Hodgson FDI, Krantz R. (1998) Groundwater Quality Deterioration in the Olifants River Catchment Above the Loskop Dam With Specialised Investigation in the Witbank
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MINE WATER AND ISOTOPES
Aspects Of The Organization Of Regulated Assignment Of Excessive Brines In Superficial Water Objects Of The Entities Of The Potash Industry (on the example of the Verkhnekamsky field of potash and magnesian salts)

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Abstract
One of the world’s largest the Verkhnekamsky field of potash and magnesian ores (VKFPMO) is actively developed. The main industrial complexes on development of this field are located within the Solikamsk-Berezniki industrial hub. Large volumes of production will inevitably make substantial effects on the environment, her separate components. The volume of formation of excess brines at the enterprises of the potash industry of VKFPMO is \( \approx 10^7 \text{ m}^3/\text{year} \). Naturally, the problem of minimization of influence of such large amount of the polluted sewage is one of main ecological problem of Perm Krai.

Keywords: Verkhnekamsky field of potash salts, excess brines, hydrodynamic modeling, removal of sewage, potash salts, enrichment of potash ore, Kama River (Kama Reservoir).

Introduction
Until recently only PJSC Uralkali was engaged in development of the Verkhnekamsky field of potassium and magnesian salts, however now other large companies are actively connected to its development. LLC EuroChem-Usolye Potash Plant plans to start the large Usolye mine in the nearest future, production objects of PJSC ACRON are under construction. At the same time total production of finished goods can reach over 20 million tons/year. Such large volumes of production will inevitably make substantial environmental impact, its separate components. The superficial water objects are subject to the greatest loading that is caused by specifics of the accepted productions of both extraction of ore, and extraction from it the useful components.

Assignment of the considerable volumes of excess brines led to increase in content of chlorides in the Kama River (The Votkinsk reservoir) even around Perm more than by 10 times in comparison with the period before the fissile development of VKFPMO. In the foreseeable future at expansion of production capacity on PJSC Uralkali, start of production of LLC EuroChem-Usolye Potash Plant and PJSC Acron it is necessary to expect increase in volume of excess brines \( \approx 20 \text{ million m}^3/\text{year} \).

Several solutions of a problem are possible
1. Technological path. Creation of waste-free schemes of productions of finished goods, introduction of the combined schemes of enrichment allowing to reduce substantially specific volumes of formation of excess brines, transfer of technological processes of the bound to enrichment of ore in the developed space of mines.
2. Use of excess brines in the national economy. Transfer to their “beneficiary”, accepting at the same time that he undertakes all subsequent scratches from effect of these brines on a surrounding medium.

Possible directions of use of excess brines:
- downloading in oil wells for maintaining of intra reservoir pressure;
- in quality:
  - tools for fight against frosting of roads;
  - liquid mineral fertilizers;
  - raw materials of chemical productions.

If to consider excess brines as raw materials for chemical production, then considering volumes their education, it owes
very large-capacity chemical production. To the most meeting these requirements production of soda is. So by production of 1 million soda 1-1.5 million m$^3$ of brines can be used, it is necessary for consumption of 20 million m$^3$/year productions of at least 13 million tons per year of soda. Now annual production of soda in our country is 3 million, respectively utilization of the considered volume of excess brines requires increase in the output of at least 4 times. Upon transition to the combined schemes of enrichment and decrease in specific indicators of formation of excess brines in to 3 times, it is required smaller increase in production of soda is substantial.


Key characteristic for assessment of possible scales of these actions is the effective jointing (porosity) containing breeds ($\xi$). In approximate estimates as an estimated value we accept $\xi = 0.018$.

In view of that in the long term $= 20 \times 10^6$ tons/year the potash enterprises will work with annual production rate at least $= 10$ years, in this case burial of the accompanying volume of the formed excess brines will require existence of the containing breeds by W volume $= 1 \times 10^{10}$ m$^3$, at the characteristic power of the containing thickness of HW$ = 100$ m, its area has to be F$ = 10^6$ m$^2 = 10$ km$ \times 10$ km. At the combined scheme of enrichment according to W$ = 0.3 \times 10^{10}$ m$^3$.

4. Dilution to ecologically acceptable levels, by their assignment in the superficial water objects.

Now has experience of realization of assignment of excess brines in the main water object within the Solikamsk and Berezniki industrial hub of the Kama River (Kama Reservoir).

We calculated assimilative ability of the main water intake of sewage of this area – the Kama River (Kama Reservoir) around Berezniki. The assimilative ability of a water object is understood as ability of a water object to accept a particular mass of pollutants (also particular amount of heat) in unit of time without violation of standards of water quality in the checkpoint or point of water use.

In work potential volumes of pollutants which the considered water objects can assimilate within a year were calculated. Calculations were executed for the long-term period covering years of various water content. The analysis of results of calculation of potential containment of pollutants, the Kama River within the Solikamsk and Berezniki industrial hub showed that this water intake can successfully assimilate chloride (up to 4 million tons/year), a magnesium (up to 800 thousand tons/year), sulfate (up to 1.5 million tons/year) and calcium (up to 3 million tons/year) even in the most shallow years. However it is necessary to consider that very essential intra annual nonuniformity of a drain therefore in work the possibility of the organization of adjustable dumping of sewage is considered is characteristic of the Kama River.

Formally in the presence of the adjustable capacity capable to accumulate thrown off drains during rather long time term, it is possible to allocate two limit types of the adjustable (operated) dumping:

1) tough regulation depending on the hydrological and hydrochemical mode of a waterway receiver in strict accordance with condition: concentration of pollution/ the allowed concentration$\leq 1$;

2) the dumping with some constant expense during the particular period of T focused on minimum monthly flow with security of 95% for the considered T period. At the same time the single adjustable parameter is a priori established duration of dumping of T during passing of high water discharges.

In case of the organization of adjustable dumping also potential containment a water object of pollutants is of great interest if to dump them only in the period of a spring high water.

For this purpose like regulation potential volumes of pollutants which the considered water objects can take for the period of a spring high water were also calculated. At the same time, concentration paid as averages according to the measured hydrochemical tests in the period of a spring high water for the entire period of observations.

Thus, the Kama River (Kama Reservoir) within the Solikamsk and Bereznikosky industrial hub can accept without deterioration in the water management.
indicators = 4 million m$^3$ of excess brines, with orientation to the minimum monthly flow of 95% of security. At realization of adjustable assignment of brines, depending on the hydrological and hydrochemical mode, with accumulation during the low-flow period and the fissile dumping into the period of passing of a flood, removal of sewage there can be at least = 4.5 times more, i.e. dumping = 18 million m$^3$/year is possible (Lepihin 2017). Considering that specific volumes of formation of excess brines make 1 m$^3$ on 1 t of finished goods, the assimilative capacity of the Kama River (Kama Reservoir) quite could will cope not only with the modern volumes, but their possible body height in the short term.

However it is necessary to emphasize that these estimates are received at the following very serious assumptions:

- the full is provided of a dilution of the taken-away drains more narrow to alignments of an initial dilution;
- not operated, poorly controllable dispersed, diffuse polluters caused by filtrational unloadings from sludge collectors and pedigree dumps will completely be excluded.

The idiosyncrasy of excess brines is the their raised mineralization, and respectively and high density, in these conditions achievement efficient a dilution is very the difficult and expensive task. Also very the difficult task is decrease in their filtrational unloadings from sludge storage.

In too time removal of sewage in water objects, has such important advantage to ensuring environmental safety, in comparison with burial in the underground horizons as a minimum inertance of the considered processes. If in a control alignment in the automatic mode it is recorded excesses of acceptable level of pollution of water, then almost instantly this violation can be eliminated by change of the mode of dumping.

The main scratches at assignment of excess brines in the superficial water objects leading to decrease in reliability of the Kama River (Kama Reservoir) as main source of technical water supply for all Solikamsk and Berezniki industrial hub.

Assignment of data exuberant brines, without effective initial dilution, owing to the very high density results in the considerable vertical inhomogeneity of content of pollutants on depth of the Kama Reservoir. On certain sites of the Kama Reservoir the content of pollutants in benthonic area more than much exceeds their contents in the superficial horizons. Water intakes are located, as a rule, at the considerable depth owing to need of ensuring its work during a deep winter periods, the threat to their operational stability is created.

The brines which are taken away without preliminary initial dilution can extend to the considerable distance in benthonic area, creating very essential load of a biota.

At working off of technology and constructional solutions carrying out natural experiments is almost not possible because of their bulkiness, need of keeping of the water legislation regarding protection of waters, and laboratory researches are very not correct because of complexity of simultaneous ensuring similarity on a complex dynamic (Reynolds numbers of Re, Froude Fr) and also density criteria (Richardson’s number of Ri). Therefore as the main tool of the solution of an objective computing experiments on the modern supercomputer were used (a cluster of the Uranus of IMM UB RAS). The computing experiment was realized on the basis of interface of hydrodynamic models in 1-, 2-and 3-dimensional statements.

The technology of such calculations was repeatedly discussed in domestic and foreign editions (Lubimova 2016, Miguel Cañedo-Argüelles 2017).

The analysis of the presented design and technology solutions of the organization of the disseminating release for assignment of excess brines showed that for conditions of the Kama Reservoir (Kama River) near the Solikamsk and Berezniki industrial hub the option can reckon with benthonic assignment of drains as priority. It, first of all, is caused by features of the hydrological mode of the considered water intake: considerable intra annual fluctuations of level of water and ice mode. In this case when dumping excess brines it is necessary to use the selection of the taken-away drains from a sludge storage that considerably will increase overall performance of this waste device.
Realization of adjustable dumping is possible only on condition of correlation of volumes of dumpings of sewage with real water discharges in the water intake. In this work the results of numerical model operation characterizing distribution of concentration on depth and on the water area as a result of dumping of sewage into the water intake were used. These data allow to choose with deep arguments an optimum design and the scheme of assignment of excess brines.

Adjustable dumping of excess brines depending on the hydrological and hydrochemical mode of water currents receivers allows to use much more fully their assimilative potential and without holding any other additional water preserving actions is capable to lower substantially the maximum peaks of concentration of pollutants which are observed at minimum flows of water currents receivers.

References
Acid rock drainage prediction of metalliferous soils from O’Kiep, Namaqualand, South Africa: A Humidity Cell Test assessment

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²Bioresource Engineering Research Group (BioERG) and Chemical Engineering Department, Cape Peninsula University of Technology, Cape Town, South Africa
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Abstract

Samples of metalliferous soils (MS) from the O’Kiep area in South Africa were evaluated for their potential to form acid rock drainage (ARD). Metalliferous soil leachates (MSL) were measured weekly for their pH, electrical conductivity, total dissolved solid, alkalinity, sulfate and Potential Toxic Elements (PTEs). Characterisation of the MS showed that the soils are rich in major oxides, i.e. SiO₂ > Al₂O₃ > FeO₃ with PTEs being S > Cu > F. ABA tests indicated that the MS exhibited a slightly acidic trend with a paste pH of 3.9. Furthermore, the acidity potential (28 kg CaCO₃/t) indicated that the MS had an acid rock drainage potential (ARDP).

Keywords: Acid Base Accounting, acid rock drainage, humidity cell tests, metalliferous soils, O’Kiep

Introduction

Metalliferous mining usually causes environmental contamination challenges due to mine waste and tailings affecting the hydrology, topography including, local vegetation; culminating in the destruction of natural habitats and degradation of soils, which essentially results in the subsequent collapse of the environment in which the mining is taking place (Moncho et al. 2017). As a result, metalliferous soils (MS) are exposed to environmental conditions in these metalliferous mining areas, culminating in a variety of biological, chemical and physical activities which could facilitate the formation of a high concentration of potentially toxic elements (PTEs) (Erdogan et al. 2018). PTEs such as; As, Ba, Cu, Pb, Se and Zn may pose potential human health risks, especially in areas with mining activities. Earlier studies showed that MS from the O’Kiep have higher concentrations of PTEs, as geochemically characterised by Moncho et al. (2017) and Erdogan et al. (2018). PTEs are usually present in MS; albeit, in concentrations that maybe high in mining overburden and tailings than in soils, a risk which has to be investigated to minimise environmental and human health implications (Portales et al. 2015). According to Erdogan et al. (2018) and Fey (2010), the soil texture and type in arid regions, consist of a different principle of soils with special sub-soil characteristics comprising of calcic and silicic constituents.

O’Kiep is a former Cu mining area with ore mineralisation being dominated by Cu-rich sulphidic ores, i.e. chalcopyrite and bornite, which are the most abundant copper bearing minerals in the area. Some of these constituents undergo oxidation, e.g. pyrite oxidation, which initiates ARD, one of the biggest environmental challenges in the mining industry. ARD enhances the dissolution of rocks, acidifies aquifers, processes which mobilises PTEs (Egiebor and Oni 2007). If the rate of acid generation due to sulphide oxidation, is in excess of
acid neutralising minerals, then progression into the formation of low pH mine water may ensue. In addition to the acidity produced, the consequent mobilisation and solubilisation of mineral containing ore would result in PTEs dissolution into liquid phase, particularly at low pH, leading further into ARD thus severely affect to the receiving environment. Therefore, the ultimate goal of the research reported herein was to use ARD prediction tests in conjunction with other relevant data to assist with development of strategies for the management of mine wastes including the MS of O’Kiep. By predicting acid rock drainage potential (ARDP), environmental impacts and assessment of soils in O’Kiep especially post mining, could be done. Characterisation of the metalliferous soils and to determine weathering rates using the humidity cell tests (HCTs) and the variation in leachate quality, was conducted.

Methods
Sample collection and MS analyses
Sandy-silt-clay MS samples (n = 10, 5 kg each) with limited agricultural potential were collected in August 2017 from O’Kiep, Namaqualand, South Africa. Each MS sample was collected using polypropylene buckets washed with dilute 0.5 M HCL and sterile distilled water to minimise environmental and physical alteration. Sampling locations were cleared of litter and surface rocks prior to sample collection. These sub-soil samples were collected based on field examination to account for physical weathering and surface conditions. All sample buckets were labelled and transported to the laboratory. Figure 1 enlists sampling locations (marked using a GPS), i.e. highland (OCM1, OCM2, OCM3); midland (OCM4, OCM5, OCM6) and lowland (OCM7, OCM8, OCM9, OCM10), with each sample being collected at a depth of 1 to 1.5m from the surface, using a Draper

![Figure 1](image_url)
After each week cycle, metalliferous soil leachates (MSLs), i.e. 750 mL were collected in to flasks. Subsequent to filtration (45 μm filter into polyethylene bottles of 500 mL capacity; the MSLs produced were analysed for quality characteristics to account for alkalinity, electrical conductivity (EC), pH, total dissolved solids (TDS), sulphate (SO₄) and for PTEs using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) as per 6020B method described in EPA (2014).

Results and Discussion

Mineralogical composition and Acid base accounting (ABA) of the metalliferous soils

In the O’Kiep region, several secondary minerals have been observed at the surface. These minerals occur as extremely fine-grained particles described as efflorescent salts (Fosso-Kankeu et al. 2017). The presence of these minerals in large quantities is indicative of rapid acidification potential, particularly if ARD formation processes are initiated. Therefore, PTEs generated by dissolution and oxidation of the primary minerals, may lead to the incorporation of secondary minerals into the local environment by either adsorption and/or ion exchange. There was a variation among the MS mineralogical composition based on the XRD results obtained. However, the dominant mineralogical constituents (Table 1), were quartz and albite while the major elements included S and Cu. Quartz (80.1%) is reported to be less reactive in oxidising conditions and has minimal acid neutralising potential. The presence of albite (2.92 %) and Muscovite-IM (0.19%), is indicative of an ore body bearing granite and gneisses (Singh 2005), a characteristic attributed to the geology of the study area.

Furthermore, the presence of Halloysite-10A, also known as kaolinite (0.26%), was indicative of constituents that normally occur in arid soils (Ziegler et al. 2003). The MS samples were characterised by a high SiO₂ (67.6%) and Al (12.4% as Al₂O₃), Fe (7.3% as Fe₂O₃), K (4.0% as K₂O), Na (1.9% as Na₂O) and Ca (1.6% as CaO). The major PTEs (mg/kg) were S (2437) > Cu (1192) > F (1079) > Ba (674) > Mn (457) > Cl (131).

The paste averaged pH of 3.9 indicated that the MS of O’Kiep are slightly acidic, which
is an indication of the presence of sulphides that could react to form acid. This was also confirmed by the total sulphur content of up to 0.89% for samples tested, with a further lowly (0.14) NPR value. This suggested a considerable percentage of sulphur and a greater potential of ARD production. The total acidity was attributed to dissolved PTEs, which are generally dominant in ARD. The AP was approximated to be high (28 kg CaCO$_3$/t), which corresponded to a negative NNP average of -32 kg CaCO$_3$/t. By using a criteria as described in Miller et al. (1991) in combination with the NP to AP ratio criteria of Adam et al. (1997), the MS of O’Kiep can therefore be classified as having an ARDP.

Weathering of metalliferous soils
HCTs are long-term (20 to >300 weeks) leach tests considered to be among the most reliable geochemical characterisation methods for ARDP (Maest and Nordstrom 2017). Similarly, the ABA test can be used to determine the ARD chemistry, PTEs release rates and generic MS behaviour when exposed to environmental conditions suited for ARD formation. The geochemical analyses of the MSL using ABA tests, exhibited slightly acidic leachates characterised by AP of ≈3.9; results which were similar to those obtained using the paste pH. There was no clear indication as to the influences of pH changes, as this parameter can be affected by several environmental mechanisms including specie retention in the solid phase of the MS which can culminated in MSL characteristic variation during HCTs.

As such, the MSL generation and its quality characteristics could be directly associated with factors such as simultaneous oxidation of sulphide species and the dissolution of major oxides and calcite, which would in turn minimise the acidification of the MS. The slightly acidic values observed

Table 1 Averaged mineralogical composition and XRF analysis of metalliferous soil samples

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>(% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>80.1</td>
</tr>
<tr>
<td>Albite, ordered</td>
<td>NaAlSi$_2$O$_6$</td>
<td>2.92</td>
</tr>
<tr>
<td>Muscovite-IM, syn</td>
<td>KAl$_2$<a href="OH">AlSi$<em>4$O$</em>{10}$</a>$_2$</td>
<td>0.19</td>
</tr>
<tr>
<td>Halloysite-10A</td>
<td>Al$_2$Si$_3$O$_4$(OH)$_2$H$_2$O.</td>
<td>0.26</td>
</tr>
<tr>
<td>Illite</td>
<td>(K,H$_3$O)(Al,Mg,Fe)$_2$[Si(Al)$<em>2$O$</em>{10}$][OH]$_2$H$_2$O)</td>
<td>0.13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Major Oxide (wt. %)</th>
<th>PTEs</th>
<th>mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ (12.4)</td>
<td>Ba</td>
<td>674</td>
</tr>
<tr>
<td>CaO (1.6)</td>
<td>Cl</td>
<td>131</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (7.3)</td>
<td>Co</td>
<td>25.6</td>
</tr>
<tr>
<td>K$_2$O (4.0)</td>
<td>Cr</td>
<td>83.9</td>
</tr>
<tr>
<td>MgO (1.0)</td>
<td>Cu</td>
<td>1192</td>
</tr>
<tr>
<td>MnO (0.1)</td>
<td>F</td>
<td>1079</td>
</tr>
<tr>
<td>Na$_2$O (1.9)</td>
<td>Mn</td>
<td>457</td>
</tr>
<tr>
<td>P$_2$O$_5$ (0.2)</td>
<td>Mo</td>
<td>5.9</td>
</tr>
<tr>
<td>SiO$_2$ (67.6)</td>
<td>Nb</td>
<td>15.0</td>
</tr>
<tr>
<td>SO$_2$ (0.3)</td>
<td>Ni</td>
<td>39.9</td>
</tr>
<tr>
<td>TiO$_2$ (0.8)</td>
<td>Pb</td>
<td>61.5</td>
</tr>
<tr>
<td>LOI (1.7)</td>
<td>Rb</td>
<td>197</td>
</tr>
<tr>
<td>Totality (99.3)</td>
<td>S</td>
<td>2437</td>
</tr>
<tr>
<td>H$_2$O (0.4)</td>
<td>Sc</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>Sr</td>
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</tr>
<tr>
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<tr>
<td></td>
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<td>5.5</td>
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<tr>
<td></td>
<td>V</td>
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</tr>
<tr>
<td></td>
<td>Y</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>97.7</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>279</td>
</tr>
</tbody>
</table>
for MS samples of O’Kiep, indicated that the generated H+ ions were to some extent, being consumed by the dissolution of the identified aluminosilicate minerals. This was evidenced by the total alkalinity of the MSL, determined to be <5 mg/kg CaCO3. Furthermore, the EC and TDS values of the MSL were initially averaged at 376 mS/m and 5046 mg/kg, respectively, with a sequential steady decline of up to 109 mS/m and 964 mg/kg, being observed. Similarly, the SO42- concentration of the MSL declined from 2682 to 574 mg/kg. Therefore, the variation in EC and TDS profiles was analogous to the observed SO42- trend, indicating that the EC and TDS are predominantly associated with SO42- concentration and MS sample decomposition thus weathering, which was an indication of ARD formation. Additionally, PTEs presence in the MSLs, indicated dissolution in the liquid phase; an observation supported by the increase of Si in the MSL from 5.9 to 11.5 mg/kg; albeit, with minimal decrease of Ca from 204 to 186 mg/kg – a phenomena associated with complexation of the Ca with other oxide species to form a precipitate.

The principal carbonates observed in MS were calcite and quicklime at 1.6%. The rate of PTEs release was initially rapid during the initial stages of the HCTs with subsequent decreases thereafter. The highest average of the major PTEs in the MSL were observed during the first week of the test at the following concentrations (mg/kg): Ca (167) > Mg (46.9) > Al (26.1) > Cu (17.5) > Cl (12.3) > Si (10.6) > Na (7.83) > Mn (4.73) > K (1.02) > Ni (0.5) > Zn (0.92) > Fe (0.42). Other PTEs occurred at low concentrations, e.g. F < 2 mg/kg, in the MSL. The highest decline in the release of PTEs was observed over time (mg/kg): Al (8.1), Cu (5.9) and Mg (5.1) followed by Na (2.02), Mn (0.6) Fe (0.02), K (0.54), Pb (0.1), Co (0.02), Ni (0.14) and Zn (0.3). Although slight variations were observed in the MSL for some PTEs, a steady decline over the period of experimentation (n = 3 weeks) was observed. The MSL contained higher sulphur content and was rich in PTEs. The Na in the MSL is related to albite while K is associated with muscovite in the MSL as the sulphides were assumed to have been partly altered due to oxidation to secondary minerals (i.e. goethite and hematite). Primary minerals, such as chlorite and quartz grains, might be covered in iron sulphate, with the Fe leaching being low in the MSL due to reduced oxidation rates. After the first week of the experiment, the concentrations of the Fe in the MSL started to decrease. However, lowly dissolved Fe in the leachate does not indicate the absence of pyrite oxidation (Gleisner and Herbert Jr 2002). Additionally, the reduction of Ca, Mg and Mn was likely due to the products of neutralisation reactions in the MS. Therefore, the dissolution and leaching of these elements is caused by acid generation related to pyrite oxidation (Mákitalo et al. 2016). The observed leaching of Al, K and Na is most likely due to aluminosilicate dissolution of MS constituents such as albite, which was also observed in the MS.

Conclusion
In the present study, ABA tests suggested that the MS had a high acid producing potential. This was confirmed by the results of ongoing HCTs, which revealed a potential of acid rock drainage formation. Low CaCO3 in the MS, contributed to the decline in the neutralising potential of the metalliferous soil studied. Monitoring of the leachate quality showed that the MS sample started producing acid very early in the test, i.e. in the first week of experimentation. The results suggested that there is a risk for ARD formation in the metalliferous soils of O’Kiep under pyrite oxidation conditions. Results of this study also suggested that there was accelerated PTEs leaching from the metalliferous soils which would result in uninhibited formation of PTEs thus contamination of the surrounding groundwater bodies. PTEs contamination in MS in O’Kiep may pose health and environmental risks. The acidic nature of MS of O’Kiep would thus be unsuitable for growth of agricultural commodities.

Acknowledgements
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References


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Abstract

Literature review indicates multiple North American sedimentary basins hosting deep subsurface mines contain three component fluids based on age (Modern, Pleistocene, pre-Pleistocene or “ancient”). Pleistocene cool climate recharge apparently occurs regardless of basin position relative to limits of Laurentide glaciation. Three component mixing models are proposed to monitor for potentially troublesome vertical migration of shallow subsurface fluids to leaks in deep mine shafts and workings. Component fluids in mixtures can be differentiated using stable isotopes of hydrogen and oxygen, in combination with tritium, major metals (Ca, Na, Mg, K), select anions (Cl, SO₄, Alkalinity, Br), and total dissolved solids.

Keywords: sedimentary basins, isotopes, mixing models, mine leaks

Introduction

Many wet, deep underground mines have operated successfully in North America relying upon life of mine pumping and/or grouting programs to manage inflows. Costs of protracted pumping and associated effects on the physical and geochemical hydrogeological environment are weighed against costs and potential efficacy of grouting. Decision-making on water control approaches also factors in the life span of shafts and other components of mine infrastructure that require continuous use and, hence, durability.

Pumping to depress the water table around shafts and mine workings is one preferred method of water ingress control for gold, zinc and copper mines (Straskraba and Effner, 1998). In multiple cases, base metal and precious metals mines appear to have relatively short operational lives (perhaps a decade). Pumped water is relatively low in dissolved solids and can be discharged safely, and wetness in the mine workings does not adversely affect the integrity of the ore and country rock. Consequently, mine water is merely a geotechnical nuisance with an associated cost to manage. After shaft sinking, grouting is often done to supplement other water control measures, but grouting is not critical to the survival of these “hard rock” mines.

In contrast to “hard rock” mines that have relatively short lives, mines extracting strata-bound and diapiric ores, such as evaporites, can operate for decades. For example, multiple salt mines in North America have remained active for more than a century without substantial disruption (e.g. Avery Island, Cayuga and Detroit). Potash has been mined from deep shafts in the Williston Basin of Saskatchewan starting 61 years ago (Patience Lake – 1958). Eight of the ten still-active operations have produced for nearly 50 years or longer (Saskatchewan Mining Association 2014). For mines with such long operational lives that are surrounded by saline or otherwise poor quality groundwater, grouting has an environmental and mine sustainability advantage over pumping for water control.

Risk of Substantial Water Influx

Differences in the way “hard rock” and “soft rock” mines approach water control also leads to a practical understanding that the risk of substantial water influx varies according to the transmissivity of the...
rock type(s) hosting and overlying the ore bodies. In the absence of direct connection to surface water bodies, mines in crystalline rock may be less vulnerable to catastrophic flooding events because of the typically low transmissivity and storativity of most igneous and metamorphic rocks (Fetter 2001; Freeze and Cherry 1979), as well as their resistance to natural erosion, dissolution and to mine damage (blasting and subsidence). Water control for mines in crystalline rock may, therefore, be hydrogeologically more accommodative to life of mine pumping than grouting because water is more of a nuisance than a geotechnical hazard.

Conversely, underground mines in sedimentary basins are more vulnerable to catastrophic inflows because of potential connections to multiple regional aquifers in the stratigraphic sequence, the vulnerability of some sedimentary rocks to slake/weaken when wetted, evaporite dissolution and greater potential for damage from mining. Mines in sedimentary basins that operate over many decades may be at higher risk, particularly if they expand beyond the limits of adequately dense characterization data collection. Strata-bound ore bodies may maintain regularity over vast distances, but an unexpected geological anomaly that cross-cuts stratigraphy and transmits water can terminate mine life.

Grouting serves an important role in water management for many mines situated at depth in North American sedimentary basins. In fact, grouting is essential to the survivability of wet evaporite mines, because the ores are highly water-soluble. Mine stability can be lost quickly if inflows are not controlled to minimize pillar dissolution and loss of support. The Retsof Mine in western New York, the first Belle Isle Mine in Louisiana, and the Patience Lake Mine in Saskatchewan were all lost because of uncontrolled flooding (Van Sambeek et al. 2000; Goodman and Hocking 2016; Genzwill and Martin 1996).

**Potential for Mixing of Waters from Multiple Hydrostratigraphic Units**

Many underground mines in North American sedimentary basins operate at depths between 250 and 1000 meters. Consequently, there is a large hydrostratigraphic section penetrated by shafts. The stratigraphy above the mines often includes more than one regional-scale aquifer. Each aquifer in the local, vertical sequence often has its own unique water quality and stable isotopic signature in an undisturbed state. So, there is commonly a layered geochemistry within the layered physical hydrostratigraphy. The subsurface formation waters can range from very modern to millions of years old. The geochemical facies and isotopic signatures in the hydrostratigraphic section can vary with depth. Typically, but not always, there is normal superposition of waters of different ages, with youngest near surface and oldest at depth. A notable exception where waters of different ages are stratified in unpredictable sequences is the Williston Basin in Saskatchewan (Rostron and Holmden 2003).

When water seepage into mine workings begins, an immediate question arises as to which water-bearing formation is serving as the source aquifer. Often, the lowest aquifer (i.e. the one closest to the mine ceiling) is initially the culprit, but if the water influx is not stopped in a short period of time, or if the inflow rate increases over time, a second question arises as to whether or not more than one aquifer has connected to the mine inflow. The purpose of this paper is to advocate use of major ion and stable isotope geochemistry, in combination with other tools (e.g., pressure/flow monitoring, microseismic and subsidence surveys), to detect undesired subsurface changes that promote vertical mixing of deep and shallow formation waters around mines.

**Monitoring Programs and Analyses Useful for Detecting Vertical Fluid Migration in Advance of Mine Inflow**

Because the field laboratories for mine hydrogeological studies are so large (often more than 25 km$^3$), well and piezometer networks to monitor potential source water aquifers can be quite expensive. Furthermore, installing and testing wells after a mine inflow starts, in some cases, is too slow a process to provide timely answers to hydrogeological questions on which to base water control decisions, particularly when answers are needed under duress. Hence, installation and
sampling of wells/piezometers before and during both mine development and operation can provide critical baseline information for evaluation in the event of a substantial mine leak breakout, particularly when integrated with shaft water databases, mine subsidence and closure surveys, and microseismic monitoring.

Exploratory holes drilled during the early mine planning and characterization phase of development can be instrumented with wells and piezometers to monitor for changes over the operational life that may span decades. Routine, vertical profiling of water seepage in mine shafts is recommended to catalogue isotopic and major ion water signatures in each major and minor water-bearing zone penetrated, starting at the time of pilot hole drilling, continuing through sinking and then periodically over the life of the mine.

Stable isotopes of hydrogen (δD) and oxygen (δ18O), in combination with tritium (3H with enrichment), major metals (Ca, Na, Mg, K), select anions (Cl, SO4, Alkalinity, Br), total dissolved solids (TDS) and specific gravity are useful for hydrostratigraphic characterization in most basins. Alkalinity can be broken down into specific carbon dioxide species by the analytical laboratory or by reference to Figure 19 in Hem (1985) if pH and temperature are documented (often measured in the field at the top of sampling). Sulfur isotopes may also be useful when formation waters are high in sulfate (Matheson et al. 2018), and strontium isotopes may also be useful in carbonate-dominated systems. Chloride-bromide ratios are a powerful tool in evaporite basins to differentiate between saline connate formation waters with a complex evolutionary history and simpler salt-contact brines (Richter and Kreitler 1993).

Baseline Information from the Literature

Existing, published geochemical and isotopic data for several North American sedimentary basins can be analyzed to determine representative signatures for key hydrostratigraphic units. For purposes of this paper, we focus not on the particular geologic formations comprising basin-specific aquifers, but stratification of water types and their interpreted ages in each basin sequence. Our literature review included isotopic and geochemical studies of formation waters in the U.S. Gulf Coast, the Permian Basins of New Mexico, Texas and Kansas, the New York State and Ohio portions of the Appalachian Basin, the Michigan Basin and the Findlay-Algonquin Arch region of Ontario, Canada that separates the Michigan and Appalachian Basins.

Published data provide baseline information for mines to compare against their own databases. In many North American basins, there are at least three end-member fluids to consider. In the northern basins these are: modern meteoric recharge, Pleistocene glacially-enhanced recharge, and highly evolved ancient basinal fluids (often brines). To the south, a similar tripartite hydrostratigraphy is apparent. Even beyond the limits of Laurentide glaciation, Neogene or Pleistocene-aged water is commonly reported that appears to record enhanced recharge under wetter, cooler climate conditions.

To take practical advantage of these patterns, mixing models are proposed to monitor for potentially troublesome vertical migration of shallow subsurface fluids to leaks in deep mine shafts and workings. Mixing models are important, because water control engineers/scientists must be able to interpret subtle changes in water geochemistry and isotopic signatures as they relate to potential source aquifers for mine leaks and assess those connections for their associated flooding risk to the mine.

Mixing models in Figure 1 assume sampling of wells/piezometers before and during both mine development and operation can provide critical baseline information for evaluation in the event of a substantial mine leak breakout, particularly when integrated with shaft water databases, mine subsidence and closure surveys, and microseismic monitoring.

Mixing models for two basins, the Appalachian Basin (New York State portion) and the U.S. Gulf Coast are presented in Figure 1. Both basins appear to contain the three aforementioned component fluids within the hydrostratigraphic interval of relevance to active mining (Yeager et al. 2001, Siegel et al. 1990 and Noll 1989 for the Appalachian Basin; Knauf and Kumar 1983, Kumar 1983 and Knauth et al. 1980 for the Gulf Coast data). The three components plot well apart on a stable isotope plot. A global meteoric water line (GMWL) is added for reference.

Mixing models in Figure 1 assume sampling and analysis of a single control...
point related to an unabated mine leak. These simple models also assume a normal superposition of water types with ancient brine on the bottom, Pleistocene recharge in the middle and Modern water at the top. Each model starts at inflow inception with a water signature reflective of the deep ancient fluids found closest to the deep mine. Over time, the drawdown cone from the mine leak pulls in an increasing percentage of Pleistocene water up to 50% (arbitrary) resulting in a shift of the isotopic signature toward the lighter Pleistocene component. In as much as mining involves evaporites in both of these basins, the introduction of undersaturated Pleistocene fluids results in halite dissolution, thereby causing a substantial increase in Cl/Br ratio.

At the point in time of a 50:50 ancient brine and Pleistocene mixture, the base of the Modern water horizon is reached by the cone of depression, and the isotopic signatures change projection from the mid-point between the ancient and Pleistocene components towards the position along the GMWL for the local modern waters. Assuming a modern atmospheric 3H concentration of 10 tritium units (TU), detectable concentrations of 3H (approximately 1 TU) appear when the percentage of modern meteoric water in the mixture rises to 10%.

![Appalachian Basin (New York) Diagram](image1)

![U.S. Gulf Coast Diagram](image2)

*Figure 1* Mixing Models for the New York State Portion of the Appalachian Basin and U.S. Gulf Coast.
Conclusions and Recommendations

Routine sampling and analysis of mine shaft fluids and any waters discharging from roof and rib strata are recommended over the operational life of the mine, because doing so offers the potential to detect changes in fluid migration that could portend broadened hydrogeologic connections and greater risk of more substantial water ingress. Stable isotopes of oxygen and hydrogen, in combination with tritium and major ion chemistry, are helpful geochemical tools for monitoring such effects.

In some cases, the detected connection of mine leaks to shallow groundwater can be linked to a man-made conduit. Improperly abandoned boreholes, mining carried out too close to an overlying aquifer, or inadequate ground support of workings in the mine design are examples of potential man-made causes of hydrogeologic communication between mines and aquifers.

Conversely, some transmissive features connected to mine leaks are naturally-occurring. These include faults, fractures, dissolution features and formations with relict primary porosity. Many natural features can be detected during the characterization phase of mine development and during drilling of pilot hole testing for shafts. Geophysical surveys can be used to identify larger features that can be targeted for drilling.

We offer the following recommendations on how to respond to findings from routine sampling and analysis of mine water that suggest a growing connection of a mine or shaft leak to a major aquifer/source of fresh water. A technical plan for characterization and mitigation of a mine leak is optimized when several different types of data can be integrated into a comprehensive source water investigation. In addition to the isotopic and major ion analyses described in this paper, review of microseismic data would assist in determining where anomalies suggestive of rock damage are originating. Of course, availability of microseismic data necessitates that a monitoring network is installed and operating prior to a substantial leak breakout.

Evaluation of ground subsidence and mine closure data could reveal if there is a locus of unusual behavior. If there are specific suspicious areas identified, a drilling plan can be developed to target those areas. Drilled holes can be used as pressure-relief wells to take water off of the mine roof (if closure data are suggesting build-up of fluid pressure and seismic data are suggesting hydraulic fracturing) and/or for grout injection into damage zones to seal water.

Proactive grouting programs are recommended for all mines in sedimentary basins, but particularly for evaporite mines, to minimize potential for sudden increases in water inflow. A variety of grouts are useful for leak mitigation (Goodman et al. 2018). Rapid initial response and periodic maintenance grouting to manage inflows at low rates into evaporite mines are required to avoid mine-threatening ground damage. As an interim measure, some evaporite mines inject brine to minimize the amount of salt dissolution taking place while grouting programs are developed and implemented.

In non-evaporite mines, sufficient time will likely exist to carry out testing and grouting. However in evaporite mines, that luxury is not usually available as events can escalate out of control very rapidly. Some extenuating circumstances might include the possibility that the ability of the aquifer to produce water is limited and/or the overlying aquifer is sufficiently unconsolidated that sediment flows into and plugs the solution cavity. This process often creates sink holes.

Critical to the success of a leak mitigation grouting program is achieving a connection between the injection well and the mine leak. The connection can be demonstrated by correlating pressure/flow testing data with mine inflow data or directly by using dye or other tracers.

Mapping of a cone of depression around a mine leak is often a recommended endeavor. It should be appreciated, however, that during an emergency response, initially there will be too few wells to fully map the drawdown cone. Action plans must, therefore, be based on the multiple, independent lines of evidence that individually may be incomplete, but when integrated offer the best chance for a successful water mitigation program.
References


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The isotopic composition of hydrothermal waters and carbonate deposits in the adits of the Baksan Neutrino Observatory

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Abstract
The adit of the Baksan Neutrino Observatory explores the situation in the Baksan Gorge of the Kabardino-Balkarian Republic (Russia). There were opened several exits of thermal water in a fractured vein at the a distance of 3,700, 4,000 and 4,200 meters from the entrance. Various mineralization has formed from these thermal springs for more than 30 years. A qualitative set of minerals, isotopy of C and O carbonates, hydrotherms allow to suggest that carbon dioxide in the mine space has a deep nature, and salt composition of solutions was formed from the buried evaporite complexes.

Keywords: isotopic composition, hydrothermal waters, Caucasus

Introduction
The adit of the Baksan Neutrino Observatory (fig.1) explores the situation in the Baksan Gorge (Central Caucasus) of the Kabardino-Balkarian Republic (Russia). The tunnel of this adit has been drilling since the beginning of the 1970s in the muscovite-chlorite-quartz shales of Kurmotau mount. There were opened several exits of thermal water in a fractured vein at the a distance of 3,700, 4,000 and 4,200 meters from the entrance.

Various mineralization has formed from these thermal springs for more than 30 years. That is similar in morphology to the cave formations (fig. 2), which were formed from hot solutions (20-50 °C) and are mainly composed of calcite, as well as the constructed corallites of chlorine-sodium amphibole, magnesite, dolomite, magnesia calcite, tenardite, vanthgophyte, collectionjite, halite and sylvan. The authors selected water and rock material for research in June 2018.

Methods
The chemical composition of water. The water for analysis was taken in the adit from the unloading zone confined to cracks from 3 to 6 m long at a distance of 3800 m from the entrance. 2 hours after water sampling an abundant white crystalline carbonate precipitate fell from it. Chemical analysis of water was made at the State University of the Ural Branch of the Russian Academy of Sciences (analyst N.V. Bykova). The

Figure 1 Location of the Baksan Neutrino Observatory (Google Earth)

Figure 2 General view of sinter formations in the Neutrino
composition and morphology of the precipitated particles and other mineral formations were determined on a VEGA 3 LMH scanning electron microscope with an Oxford Instruments INCA Energy 250 / X-max 20 X-ray energy-dispersive microanalysis system for microanalysis (analysts E.P Chirkova, O.V Korotchenkova).

Analyses showed (Table 1) that the water discharged in the Neutrino gallery is characterized by a hydrocarbonate-sodium chloride (chloride-soda) composition with a salinity of 8.2 g/L.

Mineral sediment that fell within two hours from the sampled water was represented by two generations of calcite (fig. 3). The early ones form rhombohedral crystals with a smooth-faceted and splintery surface, the later ones form a sheen-like crystals and spherulites. They differ in chemical composition too. The early ones are characterized by the admixture of magnesium (0.02-0.11 formula units), iron (0-0.02), Sr (0-0.01), and the latter - magnesium (0-0.01 feed units), iron (0-0.01) and strontium (0.01-0.02) Ba (0-0.01).

The isotopic composition (δ¹⁸O, δ²Н) of thermal waters was δ¹⁸O -8.66 ‰, δD -86.12, which is close to the isotopic composition of the brines of the Alberta oil basin in North America. Analyzes of the isotopic composition of water was made at the University of Innsbruck (Austria) using laser absorption IR spectrometry on Picarro’s L-2130-i laser equipment, equipped with a WS-CRDS (Wavelength-Scanned Cavity Ring Down Spectroscopy) system, and carbonates on a mass spectrometer Delta PLUS XL (Fisher Scientific).

It is generally accepted that the mineral waters of the Greater Caucasus are formed mainly due to the infiltration of precipitation in the Glavny and Vredovoy Ridge. The enrichment of groundwater with carbon dioxide flowing through the faults from the basement during degassing of the mantle, thermometamorphism and magmatism. It is confirmed by the young age of the volcanic structure of Elbrus and the near-surface (5.8 km) position of the magma chamber (Bogatikov et al., 2002) which provoked the formation of numerous outcrops of sub-thermal carbonated mineral waters in the river valleys. A number of other reasons for determining the chemical specificity of the mineral waters of the Caucasus are indicated by Abayhanov (2010). On the one hand, it is an active carbon dioxide leaching, which leads to hydrolytic decomposition of feldspar and the formation of soluble carbonate salts (Na and Ca) and silica, and on the other, the involvement of normal and elevated salinity in the circulation of buried thalassogenic chloride waters of the Mesozoic sediments.

The isotopic composition of carbonates. Isotopic analyzes of carbon and oxygen was made at the Innsbruck Quaternary Group at the University of Innsbruck (headed by Academician of the Austrian Academy of Sciences, Professor C. Spötl ) on a Delta V mass spectrometer (Thermo Fisher Scientific) equipped with an automatic line for analyzing carbonates based on the GASBENCH interface as described in Spötl & Vennemann (2003). For a detailed study of the isotopic composition of stalagmite, the material for analysis was selected every 3 mm from every layer. We made 20 analyzes of stalagmite and 1 analysis of corallite stalactite. This samples are presented in fig. 4

In Fig. 5 you can see comparison of the isotopic composition of C and O of stalagmites and corallite stalactites from the Neutrino tunnel with the isotopic composition of marine limestones, seamy formations from the caves of the Urals and Alps, as well as

| Table 1 The chemical composition of fissure-vein waters in the Neutrino gallery |
|-----------------|------|------|------|------|------|------|------|------|------|
| Mineralization, mg / dm³ | pH   | dry residue, mg / dm³ | HCO³⁻ | Cl⁻ | SO₄²⁻ | Ca²⁺ | Mg²⁺ | K⁺ + Na⁺ |
| 7878          | 7,75 | 7595 | 2892,7 | 2287,1 | 142,4 | 138,8 | 2499,4 |
| 8213*         | 7,75 | 7930 | 3034,4 | 2287,1 | 142,4 | 138,8 | 2499,4 |

* - taking into account precipitation
travertines formed from the hot springs of Pamukkale (Turkey) and travertines from cold carbonic waters of the Tokhan-Upper source (Elbrus).

The relatively close isotope compositions of oxygen and carbon have carbonate sediments of the Tokhan-Upper (Elbrus) source, which are formed from cold (7–9°C) carbon dioxide water (Bychkov et al., 2007). However, it was noted that in the process of heating water to atmospheric temperature (18 °C), the deposited carbonates are enriched with a heavy isotope of carbon. Also, the travertines from the world famous source Pamukkale (Turkey) have similar values of the isotopic composition.

The isotopic composition of C and O stalagmites and corallite stalactites which formed by thermal water in the Neutrino tunnel differs from the usual sinter formations from the caves of the Urals and the Alps.

**Conclusions**

A qualitative set of minerals, isotopy of C and O carbonates, as well as mineralization (8.2 g/L) and hydrocarbonate-sodium-chloride composition, hydrotherms allow to suggest that carbon dioxide in the mine space has a deep (magmatic, metamorphic) nature, and salt composition of solutions was formed from the buried evaporite complexes.

**References**


Table 2 The isotopic composition of the newly formed carbonates from the Neutrino gallery

<table>
<thead>
<tr>
<th>№</th>
<th>Sample description</th>
<th>Isotopic composition, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\delta^{13}$С vs PDB</td>
</tr>
<tr>
<td>1</td>
<td>Stalagmite selected at 4000 m from the entrance.</td>
<td>6,16</td>
</tr>
<tr>
<td>2</td>
<td>Water temperature is 30 °C.</td>
<td>3,93</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1,82</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>1,54</td>
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<td>7</td>
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<td>2,32</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>1,70</td>
</tr>
<tr>
<td>9</td>
<td>Stalagmite selected at 4000 m from the entrance.</td>
<td>1,22</td>
</tr>
<tr>
<td>10</td>
<td>Water temperature is 30 °C.</td>
<td>3,69</td>
</tr>
<tr>
<td>11</td>
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<td>2,32</td>
</tr>
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<td>12</td>
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<tr>
<td>20</td>
<td></td>
<td>3,15</td>
</tr>
<tr>
<td>21</td>
<td>Stalactite selected at 3700 m from the entrance.</td>
<td>3,8</td>
</tr>
<tr>
<td></td>
<td>Water temperature is 20-25 °C.</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. Variations of $\delta^{13}$С and $\delta^{18}$O of carbonates from the Neutrino gallery (1 - stalagmite; 2 - corallite stalactite) and their comparison with the genetic associations according to Railsback, 2010 (with addition from authors): 1 - stalagmite; 2 - corallite stalactite
Shift of mine water inflow from fissured coal layer aquifer to thick overlying aquifers: a western Jurassic coal mine, China

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Abstract
The mining hydrogeological conditions of the Ordos coalfields disclosed by the active coal mines are actually various and more complicated. The Xiaojihan coal mine is located in the east of the Ordos and is turning into a more complicated hydrogeological status. The article presents evidences to prove the changes and explores the reasons for this phenomena. Increased inflow rates, dropped aquifer water levels, decreased mine water TDS, etc. indicated that the sources of mine inflow have really been shifting from the fissured coal-layer aquifer to the overburden J2a-J2z sandstone aquifers. The total mine water inflow still insistently goes up. This posed more serious challenges to mining safety. We should timely take measures to prevent it evolving into another mine water hazard.

Keywords: mine water inflow, Jurassic coal fields, shift, western China

Introduction
The Ordos Jurassic coalfields basin in the western arid China now is becoming the key base of China coal industry (National Development and Reform commission 2016). However, the more serious challenge are that the mining hydrogeological conditions disclosed by the active coal mines are actually various and more complicated.

The Xialjiao coal mine is located in the east of the Ordos basin. It is a fully mechanical modern coal mine, has the production capacity of 10 million tonnes and commenced coal mining in 2014. The main minerable coal beds of the coal mine lie in the upper part of the middle Jurassic Yan'an Formations (J2y), which are overlain by the middle Jurassic Zhiluo Formations (J2z) and An' ding Formations (J2a), the lower Cretaceous Luohe Formations (K1l) and the Quaternary sand deposits. As reported by the detailed coal exploration: (1) all the middle Jurassic and the Lower Cretaceous were half-consolidated; (2) while mining, the water interconnected zone would at most reach the J2z sanstone aquifers, which would resultantly be the water source aquifer and might drain a limited quantity of mine water owing to its weak water abundance; (3) the J2a and K1l aquifers are higher above the water connected zone; and (4) the type of mining hydrogeologic coditions at the Xiaojihan cola mine was calsified as simple.

However, as the earlier mine construction engineerings, including ventilation shaft, main roadways and first trial longwall face etc., were drawing near or passing through the J2y cola layer, there unexpectedly happened a seires of serious waterburst with high water pressure and big inrush rate. It was verified afterwards that the minerable coal beds were actually hard, fissured and fully water carring, i.e. rare fissured-coal-layer aquifers. It was observed that the rare fissured-coal-layer aquifers were being strongly dewatered and its water pressure were apparently lowering. The maximum total inflow at that time was up to 800 m3/h. The Xiaojihan coal mine was then re-classified as hydrogeologically medium complexity with a potential risk of rare fissured-coal-layer aquifer water inrush.

But 2-3 years later, more long wall faces were excavated and the mining continuously went western and deeper. Though the inflow...
from the coal-layer aquifer shrinked further, the total mine inflow at the Xijihan coal mine went up from about 700 m$^3$/h in 2013-2015 to 1200 m$^3$/h in 2018. Certainly there were inflow water sources other than the fissured coal-layer aquifer. The overlying roof aquifers of Zhiluo ($J_2z$) and An ding ($J_1a$) of the Middel Jurassic, which had previously explored to be bearing less ground water, began to contribute the most of total mine water inflow. We were forced to re-consider the mining hydrogeologic features of Xiaojihan coal mine.

**Methods**

Mainly from the perspective of a hydrogeologic practitioner and on the data basis of regular in situ observation, water level monitoring, mine water inflow measurement and water quality analysis, use the hydrogelologic methods to assess the situation happened at Xiaojihan coal mine.

**Analysis**

The evidence to prove the water sources of inflow shifting includes: (1) The total mine inflow at the Xijihan coal mine has gone up from about 700 m$^3$/h in 2013-2015 to 1200 m$^3$/h in 2018; There are certain inflow water sources other than the fissured coal-layer aquifer; (2) Driving the coal gateways of a langwall face had dewatered the coal-layer aquifer to almost depletion, then roof dripping water in the goaf side predominated current inflow drainage; The roof dripping water from the $J_2a$-$J_2z$ sandstone took account 77% of the total mine inflow; (3) the groundwater level of the $J_2a$ sandstone aquifer and the $J_2z$ sandstone aquifer has decreased up to 20m-40m since 2014; and (4) The TDS of mine water showed an obvious downwards trend. On this basis, we assessed that the hydrogeology condition at the Xiaojuhan coal mine got shifted and more complicated.

The Reasons for the changes of ming hydrogeological conditions at Xiaojuhan coal mine: (1) As the initial mining activities dewatering the fissured $J_2y$ coal-layer aquifer, the active underground mining areas were beginning to evolve into a groundwater “sink”; The “sink” was getting larger and larger with the subsequent mining engineering; (2) There were no ideally expansive and uniform aquifuge formaitions between the $J_2a$-$J_2z$ sandstone aquifers, which occurred lense-like in the Jurassic intraplate lake sedimentary basin; and (3) Though the $J_2a$-$J_2z$ sandstone aquifers were more than 120m above the $J_2y$ coal bed, coal excavation have actually caused much higher water interconnected zone than we had expected; The water interconnected zone had gone further upwards to the $J_2a$-$J_2z$ aquifers; Semi-consolidated feature of the Jurassic should account for the higher water interconnected zone (figure 1).

Features of current mining inflow at Xiaojuhan coal mine: (1) The inflow rate was still accumulatively increasing with the further expansion of mining area; and (2) It is diffilcut to find a geologic channel or target area to block the water recharge or to prevent the increase trend of mine water inflow.

![Figure 1 schematic map of hydrogeologic condition shifting at the Xiaojuhan coal mine](image)

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inflow. For the coal mines in this region, it is an unprecedented challenge.

**Conclusions**

Under certain condition, the mining hydrogeologic status of a coal mine might also be changeable. On the evidence of increased inflow rates, dropped aquifer water levels, already tiny decreased mine water TDS, etc., the sources of inflow at the Xiaojihan coal mine have really been shifting from the fissured coal-layer aquifer to the overburden J_2a-J_2z sandstone aquifers. It was the activities of initial mining and dewatering that gradually made the mining area a strong "sink", strengthened the originally weak hydrologic relationship between the J_2a-J_2z aquifers, and eventually induced the upper aquifers to discharge into the working face. It could be predicted that the water inflow would still be increasing. The situation was going worse. Could we timely prevent it evolving into a new kind of mine water accident? It is urgent.

**Acknowledgements**

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**References**

Isotopic Composition of Underground and Surface Waters at the Uzbekistan Tyubegatan Potassium Salts Deposit

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Abstract
To prevent water inflows in the mine workings, it is important to estimate the genesis of groundwater and its interaction with surface waters and groundwater of other horizons. At the Tubegatan potassium salts deposit (Uzbekistan), these tasks were solved by monitoring the isotopic composition of groundwater and surface water.

In samples of surface groundwater in the deposit area, the content of deuterium and oxygen-18 was studied. Water samples taken in the mines of the deposit have an isotopic composition typical to surface sources.

It been concluded that the identified brine appearance had a direct hydrodynamic connection with the overlying over-salt aquifers through a system of tectonic disturbances. This fact indicates the danger to the functioning of the mine.

Keywords: potassium salt deposit, isotopic composition of waters, genesis.

Introduction
The construction and operation of tunnels, mines, quarries and other mine workings are often complicated by strong and sometimes catastrophic water inflows. The integrated use of traditional hydrogeological, hydrogeochemical, geophysical methods and isotopy of natural indicators allows one successfully solve the problems of safe operation of mining enterprises.

One of the most promising ways for the application of natural isotopes is evaluation of the genesis of groundwater, the conditions of their supply and interaction with surface waters, as well as the interaction of groundwater from various horizons. The solution of these problems is of great practical importance, in particular, in mine hydrogeology in the study of the supply of groundwater involved in mine and quarry water inflows.

The main purpose of monitoring the isotopic composition of groundwater and surface water at the Tubegatan potassium salt deposit in Uzbekistan was to establish a possible hydrodynamic connection of the brines from the brine occurrence in the exploration production of the Dekhkanabad potash plant (DPP) with surface water and determine their genesis.

Methods
To identify patterns of distribution of hydrogen and oxygen stable isotopes on the territory of the Tubegatan field, samples of surface water (6 samples) and mine water (58 samples) were taken.

The analysis of the isotopic composition of water samples was performed on laser analyzer Picarro L1102-i for hydrogen and oxygen content in water using the method of laser infrared spectroscopy. The allowable discrepancy between two parallel measurements for oxygen-18 was 0.1 ‰ and for deuterium - 0.5 ‰.

The isotopic composition of hydrogen and oxygen is expressed in relative values δ²H and δ¹⁸O:

$$\delta = [(Rpr/Rstand)-1] \times 1000\%,$$

were Rpr and Rstand – ratio of ²H/₁H or ¹⁸O/₁₆O in the measured probe and in the standard, which is taken as the average ocean water (SMOW) (Dubinchuk 1988).

The results of the isotopic composition of hydrogen and oxygen in waters were obtained directly as a “δ” value relative to the standard SMOW (Ferronsky 2009), expressed in mg/L.

The Tyubegatan deposit of potassium salts are confined to the deposits of the Upper Jurassic, which form the core of the anticlinal uplift.
The complexity of the geological structure of the area is due to numerous disjunctive disorders, as well as the presence in the section of powerful reservoirs (limestone, sandstone, fractured and cavernous gypsum anhydrides, etc.). These facts determined the water content of some rocks in the sediments of the Upper Jurassic and Lower Cretaceous.

Numerous aquifers do not have a hydraulic connection between them and are separated by layers of impermeable clays and argillites. This is evidenced by the natural outputs of groundwater at various hypsometric heights. When aquifers are immersed on the wings of the anticline to a considerable depth, groundwater becomes pressurized with difficult water exchange conditions.

The regime of groundwater confined to the aquiferous sediments of the Lower Cretaceous and the Kimeridi layer of the Upper Jurassic depends on the amount and time of atmospheric condensation. The groundwater regime in Callovian-Oxford limestone is not related to the climatic conditions in the area of the deposit and is distinguished by its constancy in time (Maltsev 1965).

At the beginning of 2012, during mountain drift at mine workings of the DPP mine, brine manifestation was disclosed with a flow rate of up to 52 l/s. Promptly carried out measures to suppress the brine manifestation led to the minimization of its flow rate, which in November-December 2012 was 0.2 - 0.3 l/s.

The source of the brine manifestation was revealed in the middle part of the right wall of the excavation and lithologically confined to the interlayer of gray sylvinitie occurring in the industrial stratum (Fig. 1).

One of the primary tasks in detecting water manifestation in a potash mine is to determine the genesis of brines. This is the main sign by which the degree of danger to the vital activity of the mine is assessed.

In mining, postsedimentation, condensation and backfilling brines can be developed, which differ in chemical composition and numerical characteristics of the values of ionic ratios of chemical elements.

The chemical composition of all three types of brines is substantially affected by the material composition of the rocks with which they are associated.

Also, the brines contained in the lower part of the section of the super-salt rock can penetrate into the underground mine workings. Mining brine shows that have a

![Figure 1 The brine in the operational development in the direction of the panel number 2.](image-url)
hydraulic connection with supersalt waters, for a certain period from the moment of the start of entering the mine workings will practically not differ from the post-sedimentary brines. The dynamics of changes in their chemical composition will depend on the dynamics of water inflows and the volume of accumulated brines.

The complex method for determining the genesis of miner brines, which includes standard chemical analysis and additional determination of the isotopic composition of hydrogen and oxygen of various types of waters of the studied territory, is effective. This leads to a reliable establishment of their relationship with brines.

To identify patterns of distribution of stable isotopes of hydrogen and oxygen on the territory of the Tubegatan field from May 2013 to June 2014, samples of surface water (6 samples) and mine water (58 samples) were taken.

The isotopic composition of hydrogen and oxygen in groundwater and surface waters has no substantial distinctions. Thus, it is not possible to establish isotope ratios for different aquifers. Fig. 2 shows the actual data for the investigated area.

According to the regime observations carried out by the geological service of the DPP, the chemical composition of brines is sodium chloride (unlike the chloride-magnesium composition of brines found in the overlying sediments of surface salt). Substantial changes in the salt composition during the observation period are not found. The contents of easily soluble salts of CaCl₂, MgCl₂ vary from 3 to 4 g/L (CaCl₂) and from 8 to 9 g/L (MgCl₂). Constancy of the ratios of (KCl) x 10⁴ and NaCl is also noted. In addition, there are minor fluctuations in the amount of salts in the range of 330-370 g/L. The presence of dissolved hydrogen sulfide in groundwater has not been established, the chemical composition is relatively stable and there are no substantial changes.

As a result of the fulfilled work, the intervals of distribution of the deuterium and oxygen-18 contents in natural waters on the territory of the Tyubegatan potassium salt deposit and the conditions for the formation of groundwater (Blinov 2015) were revealed.

Conclusions

Water samples taken from the brine occurrence in the mining site of the DPP, represent the brine formed as a result of the penetration of atmospheric precipitation through the thickness of salt rocks. This conclusion was made because the samples have an isotopic content characteristic to the surface sources.

The detected brine appearance has a direct hydrodynamic connection with the aquifers lying in the suprasalt interval of the section through the system of tectonic disturbances that cut through the strata of rocks overlying the studied industrial formation.

This fact testifies to the threat of safe operation of the mine. The method of comparing the isotopic composition of groundwater and surface water is effective.

Figure 2 The ratio of stable isotopes δ18O and δD in selected samples.
for predicting catastrophic water inflows in underground mine workings.

References
ENVIRONMENTAL MONITORING
Abstract
A features study of organic pollution from wastes, mine water, and mining effluents caused by extraction and processing of various types of minerals has been performed. The organic pollution characteristics of waste and effluents from the mining industry within the Kizel coal basin and the Verhnekamsky potassium salt deposit differed in applied technologies of ore processing and beneficiation are considered. It has been found that along with natural organic compounds specific for extracted mineral raw materials, technological reagents are a substantial source of organic pollution of wastes and effluents. Laboratory waste leaching test has shown that transformations of organic matter into water-soluble forms is accompanied by reactions of biochemical and physicochemical nature leading to generations of new compounds which are absent in the host minerals. The environmental significance of organic compounds entering the hydrosphere was assessed. Some of them have been revealed to be the persistent organic pollutants which cause substantial pollution of surface water and groundwater connected with waste storage facilities of mining industry.

Keywords: mining waste, organic pollutant, leaching, dissolved organic matter composition, geochemical markers.

Introduction
One of the features of mining technogenesis is a sharp increase in the number of substances in geochemical circulation, leading to toxic components entering the hydrosphere. The most powerful source of pollutant emissions is mining wastes characterized by the accumulation of a wide range of hazardous components. Among the least studied pollutants are organic compounds, in most cases not included in control scopes. Despite the fact that, in many cases, these compounds belong to the category of micro impurities in the extracted mineral raw materials (Greenwood et al. 2013), the technologies used for its beneficiation and processing quite often lead to substantial organic pollution of the generated waste (Bachurin 2005). It is facilitated by the use of a wide range of organic reagents (collectors, modifiers, frothers, etc.) in the beneficiation technological processes. Many of the used reagents has been established to be complex mixtures of compounds (polycyclic aromatics, hydrocarbons, phenols, amines, etc.) and serve as a source of hazardous compounds in wastes (Bachurin et al. 2013). The interaction of natural and technological compounds leads to the formation of multicomponent organo-mineral complexes in wastes which have no natural analogs and require the investigations of their hazards and behavioral features in the environment. One feature of organic pollutants should be noted – the ability of rapid geochemical transformation under the influence of exogenous factors resulting in new transformation products (TPs) including a substantial proportion of unregulated chemicals many of which can be equally or even more persistent and toxic than the original substances (Bachurin et al. 2013).

Methods
Studies (Bachurin et al. 2013, 2014) have shown that the real environmental assessment of organic pollution within the hydrosphere of mining areas is possible only when taking into account the particular characteristics of the waste composition and the nature of their transformation in the water environment. Practical implementation of given...
A methodological approach was performed on the basis of laboratory studies of “waste – water” systems and an informational database created on the results of hydrogeochemical investigations in mining regions. This made it possible to obtain basic analytical characteristics of pollutants (geochemical markers), reflecting both the particular nature of the extracted raw materials and the technology of its beneficiation which control pollutants accumulation in wastes (Bachurin et al. 2013). A laboratory waste leaching test was carried out in static conditions by successive three-step dissolution of solid mixtures in distilled water (the initial ratio of water to waste is 30 : 1). This simulation imitates the precipitation effect on waste-rock dumps stored on the surface. In the case of some organic reagents using in the technological process, the composition of their aqueous solutions and the nature of transformation after 1, 7 and 21 days were investigated.

The main studied objects in the tests and experiments were the most capable to migration components of organic matter – bitumens, which constitute the sum of organic compounds extracted from an analyte by chloroform ($B_C$) or hexane ($B_H$). The investigations of bitumens were carried out using analytical chemistry methods allowing to judge the structural-group and individual composition of organic compounds: thin-layer chromatography TLC, FT-IR spectroscopy, gas chromatography–mass spectrometry GC–MS (Agilent Technologies 6890N, MSD 5975B). As additional criterions reflecting the level of organic pollution of the studied objects, we used total petroleum hydrocarbons ($TPH$), phenols, benzo(a)pyrene, Corg. A brief description of the results obtained for the two Urals mining areas is provided below showing differing composition of natural organic compounds in extracted minerals and the technologies used for ore preparation and beneficiation.

**Kizel coal basin** has been the oldest coal-mining region of Russia. Cessation of mining did not solve the complex environmental problems that emerged during the long-term basin operation. This is caused by continued mine water outflow to the surface with total discharge volume ranging from 1,328 to 2,650 m³/h. Effluents from waste-rock dumps are other sources of pollution, the total discharge of which reaches 27.9–37.3 m³/h. Like it was during the operation of coal mines enterprises, mine waters and effluents have an acidic reaction ($pH = 2-3$), sulphate composition and high content of iron, aluminum, and a number of microcomponents (beryllium, manganese, cobalt, nickel, etc.).

Information about organic pollution level of coal mining waste in the Kizelovka basin is practically absent. There is however, the recorded presence of bituminous substances ($B_C$ 0.30–12.33 mg/dm³), $TPH$ (0.05–1.87 mg/dm³), and low molecular weight aromatic hydrocarbons (0.09–0.39 mg/dm³) in mine drainage (Bachurin 2018). The content of chloroform extracted bitumens ($B_C$) in the rocks of 8 surveyed uneven-aged dumps is relatively small – 0.5–6.0 g/kg, of which $TPH$ accounts for 0.04–2.39 g/kg (2–13% $B_C$). Analysis of the hexane fraction of bitumens (BH) of the rocks using the GC – MS method have shown that the share of hydrocarbon compounds is 48-62%, most of which are represented by aliphatic structures (Table 1). Aliphatic hydrocarbons are presented by a series of $C_{11}$–$C_{43}$ with a maximum content of short-chain homologues of $C_{13}$–$C_{18}$. Aromatic structures (64.8–159.0 mg/kg) are predominantly polycyclic and are presented by alkyl-substituted biphenyl, naphthalene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, 3,4-benzpyrene (13–104 mg/kg). The heterostructures of bitumens of the waste-rock dumps are represented by a wide group of oxygen-containing compounds (O–), dominated by carboxylic acids and their derivatives. In some samples, a high content of sulfur-containing compounds (S–) was recorded that is explained by the high sulfur content in coal. Nitrogen- and halogen-containing structures (N–, Hal–) are present in a subordinate amount.

According to laboratory tests data, water extracts from waste rocks of dumps are characterized by the following criteria: the content of bitumen BC ranges between 0.60–2.35 mg/dm³, $TPH$ between 0.05–0.80 mg/dm³, and 0.002–0.10 mg/dm³. According to GC – MS, bitumens of water extracts from dump...
Table 1 The composition of bitumens (%) in wastes and effluents of the Kizel coal basin.

<table>
<thead>
<tr>
<th></th>
<th>Alkanes</th>
<th>Naphthenes</th>
<th>Arenes</th>
<th>O-</th>
<th>N-</th>
<th>S-</th>
<th>Hal-</th>
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<td>Rock of dumps</td>
<td>42.8-52.7</td>
<td>1.2-1.7</td>
<td>4.6-7.3</td>
<td>15.4-49.2</td>
<td>0.8-1.9</td>
<td>0-0.1</td>
<td>1.4-3.1</td>
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<td>Water extract</td>
<td>54.6-62.5</td>
<td>1.7-1.8</td>
<td>none</td>
<td>33.2-34.4</td>
<td>0-0.2</td>
<td>none</td>
<td>1.4-6.6</td>
</tr>
<tr>
<td>Leachates of dumps</td>
<td>16.0-24.2</td>
<td>0-1.1</td>
<td>0-0.5</td>
<td>65.1-65.4</td>
<td>6.5-9.7</td>
<td>0-4.1</td>
<td>0.1-10.1</td>
</tr>
<tr>
<td>Mining water</td>
<td>6.4-19.5</td>
<td>0.6-3.2</td>
<td>0-1.1</td>
<td>70.0-84.6</td>
<td>0.4-3.0</td>
<td>0-1.5</td>
<td>0.2-2.8</td>
</tr>
</tbody>
</table>

The study of the dump leachates composition confirmed a high loading of organic compounds in them: the content of bitumens $B_t$ is 0.80-11.38 mg/dm$^3$, $TPH$ – 0.20-1.75 mg/dm$^3$, benzene – 0.36-0.39 mg/dm$^3$, toluene - 0.11-0.17 mg/dm$^3$, phenols – 0.03-0.06 mg/dm$^3$. The abundance of amines, pyridines, indoles, and quinolines (0.2 mg/dm$^3$) which have quite strict health standards calls attention. At the same time, the bitumens of the dump leachates, in contrast to the waste rocks water extracts, are more oxidized. According to GC – MS, non-hydrocarbon structures dominate in the bitumens composition with a subordinate content of hydrocarbons represented mainly by n-alkanes of the C$_{17}$-C$_{35}$ series. Phthalates, which account for 12.2-51.4% of bitumens, dominate in the group of heterocompounds as well as in water extracts from rocks. The high content of these compounds, which, apparently, are products of the transformation of the aromatic structures, is due to their stability under conditions of hypergenesis. In addition, the leachates of the dumps carry into the hydrosphere a wide variety of other aromatic ecotoxicannts – alkylated biphenyls and anthracenes, pyrene, fluoranthene, halogenated benzenes, benzmams and benzonitriles, piperidines, arylsulphonic acids, etc. Besides the esters, other acid derivatives being products of deeper transformations of carboxyl, aliphatic and aromatic structures are also environmentally hazardous. Of their variety, amines and nitriles of acids, halogenated, and sulphonated esters are emphasized. Apparently, this phenomenon is caused by multiple precipitations events that affect rock dumps leading to aqueous phase entry not only of easily soluble compounds, but also the structures strongly associated with the mineral matrix.

The results mentioned above show that the changes of coal-bearing rocks in dumps under hypergenesis conditions lead to a chemical transformation of natural organic compounds with the formation of a wide range of structures predominantly of the oxygen-containing type with high solubility and migration capacity in a water environment (Bachurin 2018).

**Verhneamksky potash salt deposit.** The approved technology of potash processing in Verhneamks deposit provides for mineral’s liberation (sylvinite, carnallite) using halurgic or flotation beneficiation methods. The beneficiation of potash produces wastes such as tailings stored in salt dumps, clay-salt sludges and brines merging into a sludge storage. The highest level of organic pollution is typical for the clay-salt sludges ($B_{cl}$ – 0.73-3.0 g/kg, $TPH$ – 0.34-1.96 g/kg) due to accumulation of both natural organic of halopelites and technological reagents, most of which are categorized as synthetic surfactants (Bachurin et al. 2015). According to the GC–MS dates, saturated aliphatic and halogenated hydrocarbons of series C$_4$-C$_{44}$ dominate the low content of naphthene and aromatic structures (Table 2).

Aliphatic hydrocarbons consist of normal and branched alkanes, alkenes, and isoprenoids. Series of normal alkanes (27.1-
34.9%) consists of homologues $C_{13}^{\text{---}}C_{34}^{\text{---}}$ with a maximum content of $C_{18}^{\text{---}}, C_{17}^{\text{---}}, C_{20}^{\text{---}}$. Due to the fact that the short-chain n-alkanes are few suggests that accumulation of these structures in sludges causes by the technogenic effect. Heterocompounds include predominantly O-containing structures, in which aliphatic and napthenic alcohols, aliphatic, napthenic, aromatic ketones and acid derivatives are identified. Among the last, acetates and phthalates are particularly noteworthy, which held 40-44% of all heterocompounds. Apparently, the formation of these structures is associated with the destruction of polyaromatic hydrocarbons and alcohols that make up the process reagents.

According to the GC-MS data, the reagents used in the desliming stage (carbamide-formaldehyde resin, polyacrylamide “Akkofloc A-110”, aliphatic amines “Ethomeen”, glycol ether) represent a complex multicomponent mixture, which, along with the declared reagents, contain a wide spectrum other compounds. Physico-chemical processes occurring in the “reagent - water” system lead to substantial changes in the chemical appearance of watersoluble organics. The main transformation products of the technological reagents examined are polyethoxylated compounds (polyglycols, polyoxyalkanols, and their ethers, dioxolanes, dioxanes and crown ethers), ammonium compounds and nitrogenous heterocycles, hydrocarbon structures, including polycyclic aromatics (Bachurin et al. 2015).

The results of laboratory testing of sludge leaching showed that despite the hydrophobicity of organo-mineral complexes formed in the waste, a certain part of organic compounds (from 5 to 33%) is water soluble. The quantity of $B_c$ in the sludge-water extract ranges between 0.55-3.43 mg/dm$^3$, amines < 0.78 mg/dm$^3$, benzo(a) pyrene - 1.2-25.4 ng/dm$^3$. According to the GC – MS data, both the initial structure of the sludge and the products of hydrolytic processes are identified in the leaching products. The last ones consist of hetero compounds, with a total content from 69.5 to 84.0% $B_c$. Phthalates are distinguished by the total content in water extracts reaching 89%. Considering the low content of these compounds in water extracts of halopelites (less than 14%), it can be assumed that their appearance is associated with the reagents transformation in the aquatic environment. The increased content of these compounds in the aquabitumens, including brine of sludge storages, is most likely due to their high solubility and stability in aqueous solutions (Bachurin et al. 2015). Additionally, a group of carbohydrate compounds (derivatives of furanose, pyranose, galactose) was identified in the organic content of leached sludge, which is associated with the using of carbamide-formaldehyde resin in the technological cycle, and acetoacetic acid esters due to the transformation of flotation agents.

Research of clay-salt sludge - water extract shows that sludge is a potential source of a wide range of organic structures representing a “cocktail” of natural and technological compounds, and their transformation products entering the hydrosphere. The predominance of carbocyclic and heterocyclic compounds in the aquatic environment has shown that the biogeochemical transformations of natural and man-made organic waste occur mainly because of cyclization and condensation of structures which control the extent of migration and accumulation of pollutants. Among the compounds passing into the water phase, nanoscale crown ethers, aza- crown ethers, annihilates and napthenic

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### Table 2 Bitumens composition (%) of ores and wastes in Verhnekamsky potash salt deposit

<table>
<thead>
<tr>
<th></th>
<th>Hydrocarbons</th>
<th>O-</th>
<th>Hal-</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potash ores</td>
<td>83.3</td>
<td>7.1</td>
<td>3.1</td>
<td>6.4</td>
</tr>
<tr>
<td>Halite wastes</td>
<td>56.2</td>
<td>39.4</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Clay-salt sludges</td>
<td>50.0</td>
<td>37.5</td>
<td>8.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Liquid phase of sludges</td>
<td>8.2</td>
<td>89.8</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Brines</td>
<td>15.8</td>
<td>79.7</td>
<td>2.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
macrocycles, the uniqueness of which is due to the ability to form stable lipophilic complexes with cations of various metals and microelements, are found. The main markers of water pollution are polyethoxy structures represented by linear polyglycols, their esters and polyoxyalkols, and cyclic dioxolans, dioxanes and crown ethers. Among the other water-soluble compounds in clay-salt sludges it is interesting to note aliphatic halogen-containing structures of the C9-C18 series marking the syngenetic organics of halopellites, aliphatic and naphthenic hydrocarbons, polycyclic aromatics, aliphatic amines, ammonium compounds, and nitrogenous heterocycles, which are products of the transformation of flotation agents. We should note that most of these compounds are toxic substances, and has established hygienic standards, which allows them to be monitored according to regulated measurement techniques.

Conclusions

The results of the geo-ecological survey of the mining areas of the Ural show that industrial wastes contain natural and technogenic organic compounds that are readily soluble in water.

This causes the possibility of organic pollution of the hydrosphere in areas adjacent to waste storage facilities. In some cases, the content of water-soluble organic compounds exceeds the sanitary and health standards adopted in Russia (table 3).

The range of organic pollutants is largely determined by the processes of transformation of natural and technogenic compounds in the water environment. This requires special laboratory testing aimed at clarifying the leaching nature of organic compounds from waste and the possible transformation products. The subsequent environmental monitoring should be focused on the control of only those chemical compounds that may be dangerous to humans and to the environment (Chibwe 2017).

References


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**Table 3** Water-soluble organic compounds of mining wastes of the Ural

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Quantity, mg/dm³</th>
<th>MAC, mg/dm³</th>
<th>Hazard category</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPH</td>
<td>0,05-4,15</td>
<td>27</td>
<td>4</td>
</tr>
<tr>
<td>Benzene and homologues</td>
<td>0,34-0,58</td>
<td>0,5</td>
<td>2</td>
</tr>
<tr>
<td>Phenols</td>
<td>0,03-0,10</td>
<td>0,1 (phenol)</td>
<td>2, 4</td>
</tr>
<tr>
<td>Aliphatic alcohols, oxo-compounds C₇-C₄₄</td>
<td>0,05-0,64</td>
<td>0,25 (propanol)</td>
<td>1, 4</td>
</tr>
<tr>
<td>Phthalic acid, phthalates</td>
<td>0,12-9,34</td>
<td>0,2 - 1,0</td>
<td>2</td>
</tr>
<tr>
<td>Nitrogen-containing C₇-C₁₈</td>
<td>0,35-0,96</td>
<td>0,05-0,1 (amines)</td>
<td>2, 4</td>
</tr>
<tr>
<td>Organic sulphur</td>
<td>0,02-6,38</td>
<td>0,2×10⁻³ (propentiol)</td>
<td>3</td>
</tr>
<tr>
<td>Halogenated hydrocarbons C₇-C₁₈</td>
<td>0,03-4,92</td>
<td>2,5×10⁻³ (tetrachlorhexane)</td>
<td>4</td>
</tr>
<tr>
<td>Aromatic N-, O-, S-containing</td>
<td>0,65-0,80</td>
<td>0,1 (naphthol)</td>
<td>2, 3</td>
</tr>
</tbody>
</table>

Abstract

Microbes are rarely part of river assessment and mine closure programs because their ecology is complex and methods are not standardised. The aims of this paper are to 1) develop standardised collection and analysis protocols for riverine microbes, 2) determine if microbial communities correlate to environmental condition in mine-affected rivers, and 3) apply the ‘system variability’ closure approach to microbes. In two Australian rivers, the user-friendly collection protocol was tested on benthic and pelagic assemblages and pebble biofilms. Benthic and pelagic microbial assemblages varied spatially and temporally which correlated with environmental variables. However, more research is needed before microbes are incorporated into monitoring and closure.

Keywords: freshwater microbe protocol, ecological indicator, system variability, mining rehabilitation, Hunter Valley

Introduction

There has yet to be a systematic effort to incorporate microbes into river assessment programs because their broad-scale spatial and temporal variability is not well-researched, and the identification technology and collection methodology is still not routine. Microbes represent the majority of Earth’s biodiversity, play key roles in aquatic biogeochemical processes, and are extremely sensitive to even small inputs of contaminants (Sims et al. 2013). Advances in the field of environmental genomics facilitated 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).

Aquatic macroinvertebrates (for example) are well-known ecological indicators for mine-affected rivers, but are not ideal, because identifying macroinvertebrates by their morphological characteristics is time-consuming. Although advances in DNA sequencing have shown great potential for identifying macroinvertebrates more rapidly (Carew et al. 2013), macroinvertebrates may not be ideal indicators. Unlike microbial processes, macroinvertebrates (and other multi-cellular taxa) may exhibit a substantial lag between exposure and effect detection due to lifecycles and/or sampling framework. More critically, macroinvertebrates cannot directly identify the effect – unlike the microbes (Druschel et al. 2004). For example, mining-related discharges have created new metal-rich niches that select for metal-tolerant and sulfate-reducing microbes and genes (Kang et al. 2013). Different successional stages of microbial communities may signal when a past effect occurred – knowledge of that would be useful when examining known affected sites. Essentially, we now have potential ecological indicators that can inform faster, cheaper, and more sensitive monitoring protocols but there are no standard methods.

Previously, we proposed a model (the ‘system variability’ approach) for setting rehabilitation goals and evaluating the condition of highly modified environments without reference sites and pre-impact data (Blanchette et al. 2016). This model used multivariate statistics to compare rehabilitated sites to overall local ecosystem variability, rather than reference site...
characteristics. We tested the model using biophysical data from river diversions in the Hunter Valley, New South Wales, Australia, and found that data from diverted and non-diverted sections of river were substantially different, potential management actions could be identified, and site trajectories were mapped – in some instances towards closure (Blanchette and Lund 2017). This model gave us a more holistic view of the ecology of the river system, and lends itself to studying microbial assemblages and biogeochemical processes.

Therefore, the aims of this research were to 1) develop standardised collection and analysis protocols for riverine microbes, 2) determine if microbial communities correlate to environmental condition in mine-affected rivers, and 3) apply the ‘system variability’ closure approach to microbes (Archaea and Bacteria) in two Australian rivers. A user-friendly standardised collection protocol (Aim 1) is important because it increases data reliability across space and time. Determining if microbial communities statistically correlate to environmental condition (Aim 2) is critical in assessing whether they can be reliable ecological indicators (sensu Kurtz et al. 2001)

**Methods**

**Overview** – Hydrology and catchment (Hunter Valley, NSW, Australia, Bowman’s Creek; BC, and the Goulburn River; GR) were as per Blanchette and Lund (2017). Briefly, these naturally intermittent rivers were diverted to facilitate coal mining. Complex hydrological conditions in both diversion and downstream sites resulted in treefalls and excessive growth of aquatic reeds, benthic siltation and further alteration of in-stream habitats (Blanchette and Lund 2017).

**System Variability approach to developing closure criteria** – APPENDIX I.

**Biophysical data** – River sites (Bowman’s Creek; 12 sites, Goulburn River; 20 sites) were sampled during an annual hydroperiod (2016-2017, GR; four times, BC; twice). GR had a trapezoidal channel, whereas the BC diversion had been constructed with more ‘natural’ attributes. Within each river, sites were clustered into a priori groups (‘zones’) based on gross biophysical similarity (see Blanchette and Lund (2017)). In situ water quality (turbidity, pH, conductivity, temperature, ORP) and soil measurements (pH, ORP), flow, water collected for metal and nutrient analysis, percent cover of in-stream habitat and riparian condition was collected as described in Blanchette and Lund (2017). Sediment size was determined according to a phi scale (McMullen et al. 2011).

For each site, benthic sediments (7 to -3 phi) were analysed for bioavailable metals and nutrients (Na, Mg, K, Fe, Al, S, Ca, P, Mn, Cr, Co, Ni, Cu, Zn, Cd, Pb) at the Edith Cowan University Analytical Chemical Laboratory and CSBP Perth. At ECU, sediments were dried (40°C), ground by hand in an agate mortar and pestle, passed through a 500 µm sieve and digested according to US EPA protocol 3050B for elemental analysis (Thermo Fisher Scientific iCAP QICPMS, 7600 ICPOES). Total N (Rayment and Lyons Method 7A5) and total organic C (acidification method 6B1) (Rayment and Lyons 2011) were analysed at CSBP Perth.

Microbe collection protocols – Benthic sediments (7 to -3 phi), pebbles (-5 phi) and water were collected from sites and times as above for DNA sequencing and OTU identification (Goulburn River; \( n_{\text{water}} = 77, n_{\text{sediment}} = 78, n_{\text{pebbles}} = 16 \), Bowman’s Creek \( n_{\text{water}} = 24, n_{\text{sediment}} = 21, n_{\text{pebbles}} = 18 \)).

Benthic sediments (for microbes and nutrient analyses) were collected at 25 equidistant points along the 50 m transect (site) using a modified sterile syringe to ensure only the top 1 cm was retained for analysis. In-stream differences (e.g., shading, hydrological habitats including dry sections, aquatic plants) were proportionally represented among the 25 samples, which were manually homogenised in a plastic bag such that each bag represented conditions at one site. Samples were placed on ice, then at -20°C for transportation and -80°C for storage.

Where benthic sediment surface area was dominated (or co-represented) by pebbles, 25 individual stones were collected roughly equidistantly along the 50 m transect. Pebbles from the same site were homogenised, transported and stored as per sediments.

When present, a water sample was collected from each site at approximately 5
cm beneath the surface with a sterile bottle without disturbing the benthos. Water was filtered on site (Durapore membrane filters, 0.22 µm, Merck Millipore) under gentle vacuum pressure until filter clogged. On site, the filter was transferred to a sterile petri dish, finely sliced using an autoclaved blade, and placed into a sterile Eppendorf tube for storage and transport as per sediments and pebbles.

**Laboratory processing and OTU identification** – DNA extraction, PCR, sequencing and OTU identification was performed by the Australian Genome Research Facility (AGRF). Unlike benthic and pelagic samples, biofilm on pebbles required liberation prior to DNA extraction. All pebbles were scrubbed with an autoclaved toothbrush, rinsed with autoclaved distilled water and elutriate filtered as per pelagic samples. It was impossible to treat samples from different habitats exactly the same prior to DNA extraction.

DNA extraction was performed by the AGRF using a DNeasy PowerLyzer PowerSoil Kit (Qiagen). Briefly, PCR amplicons were generated using specific primers (Target; 341F-806R, Forward(341F): CCTAYGGRBGCASCAG, Reverse(806R): GGACTACNNGGGTATCTAAT) and conditions (Target region; 16S: V3-V4, Cycle; 29, Initial; 95°C for 7 min., Dissociate; 94°C for 30 s, Anneal; 50°C for 60 s, Extension; 72°C for 60 s, Finish; 72°C for 7 min.), with AmpliTaq Gold 360 mastermix (Life Technologies, Australia) for the primary PCR. A secondary PCR to index the amplicons was performed with TaKaRa Taq DNA Polymerase (Clontech). The resulting amplicons were measured by fluorometry (Invitrogen Picogreen) and normalised. The eqimolar pool was then measured by qPCR (KAPA) followed by sequencing on the Illumina MiSeq (San Diego, CA, USA) with 2 x 300 base pairs paired-end chemistry.

Paired-ends reads were assembled by aligning the forward and reverse reads using PEAR (version 0.9.5) (Zhang et al. 2014). Primers were identified and trimmed. Trimmed sequences were processed using Quantitative Insights into Microbial Ecology (QIIME 1.8) (Caporaso et al. 2011) and UPARSE (Edgar 2013). Using USEARCH, sequences were quality-filtered, full-length duplicate sequences were removed and sorted by abundance. Singletons or unique reads in the data set were discarded. Sequences were clustered followed by chimera filtering using the “rdp_gold” database as the reference (Cole et al. 2014). To obtain the number of reads in each OTU, reads were mapped back to OTUs with a minimum identity of 97%. Using QIIME, taxonomy was assigned to OTUs using Greengenes database (version 13_8, Aug 2013) (DeSantis et al. 2006). Samples were rarefied at 17,000 reads for calculating dissimilarity between samples using weighed & unweighed Unifrac metrics.

Note that the benthic and pelagic samples were completed as part of one independent sequencing run, and the pebble biofilm as a second sequencing run. Therefore, in this paper, data were analysed separately. Future tests will re-run the similarity matrices of all three habitats simultaneously to ascertain significant differences (if any).

**Data analysis** – Non-metric multidimensional ordination (NMDS) in PRIMER visually displayed the microbial assemblage data (see Blanchette and Lund (2017) for biophysical data).

In this research, hypothesis tests on OTU weighted (abundance and presence/absence) Unifrac genetic distance data were conducted with a PERMANOVA (9999 permutations with a Euclidean distance; zone, time and habitat (pelagic, benthic, pebble) were fixed factors with site as a random factor nested in zone and time) in PRIMER (Anderson et al. 2008)). Where factorial interactions were significant (p < 0.05), results were interpreted with caution and within the context of subsequent pairwise analyses (see Anderson et al. 2008). Pseudo-F is reported hereafter as F.

Biophysical data was normalised and a resemblance matrix among zones created using Euclidean distance. Microbial assemblage data (relative abundance at the OTU level) similarity among zones was created using Bray-Curtis dissimilarity. Correlations between microbial assemblage data and biophysical parameters were analysed using RELATE (Spearman’s rank; rs, p < 0.05; 9999 permutations) and BEST (BVSTEP) with a
Results and Discussion

Pearson's correlation in PRIMER. Biophysical data was log-transformed and a Draftsman's plot allowed detection and subsequent removal of parameters for highly auto-correlated (> 0.95) variables. Characteristics of dominant microbes (relative abundance) were described at the Family level.

Samples from different riverine habitats (benthic, pelagic, pebble biofilm) were collected (Aim 1), genetic material was well-amplified, and OTUs were identified using established databases (Aim 1). Soil and pelagic assemblages were significantly correlated with environmental variables (Aim 2). Examples of how the system variability approach could be applied to the data were explored (Aim 3), which could inform future environmental monitoring and closure programs.

In both the Goulburn River (GR) and Bowman’s Creek (BC), there were significant effects of zone (GR; $F_{1, 7} = 7.10, p < 0.01$, BC; $F_{1, 3} = 2.69, p < 0.01$), time (GR; $F_{3, 9} = 9.78, p < 0.01$, BC; $F_{1, 3} = 4.62, p < 0.01$), and habitat (GR; $F_{1, 102.1} = 102.1, p < 0.01$, BC; $F_{1, 25.2} = 25.2, p < 0.01$) on microbial assemblages (weighted Unifrac distance OTU) at sites. NMDS showed a strong separation between pelagic and benthic OTUs in both rivers (Figures 1a and 1b). Essentially, microbial assemblages were different enough across space and time to be 'identified' with different zones over the hydroperiod.

A pairwise analysis for zone in the Goulburn River indicated that across all times, most comparisons of benthic microbial assemblages were significantly different ($p < 0.03$) with the exception of those found...
upstream and in the ‘rehab,’ and upstream and in the discharge sites. The relationship between Goulburn River sediment OTUs and sediment chemistry variables was significant ($r_i = 0.372, p < 0.01$), with separation along NMDS axis 1 correlated to *in situ* ORP ($r = 0.71$) and *in situ* pH ($r = 0.60$) to the discharge and downstream sites, and Pb, Cr, Al, Na, Fe, Mg, and Cu ($r \geq -0.5$) to the diversion sites. Across all sites and times, the taxon in Goulburn River sediment samples with the highest relative abundance at the Family level (total n Families was 827) were the Hyphomicrobiaceae (Alphaproteobacteria), of which many Genera are primarily involved in C and N cycling (Wang et al. 2016). Future work would explore the potential presence of indicator taxa in zones, and how they correlate with changing environmental conditions.

In Bowman’s Creek, pelagic microbe assemblage composition was different between times (May and December 2016; $F_i = 5.56, p < 0.01$) and across space (zone; $F_i = 2.21, p < 0.01$). Two diversions were sampled in Bowman’s Creek. Pelagic microbial assemblages in the North Diversion were significantly different to those upstream, whereas assemblages in the West Diversion were not significantly different to those upstream or downstream. Pelagic microbial assemblages were significantly correlated to water quality variables ($r_i = 0.435, p < 0.01$) (Figure 1d); higher concentrations of Ca were associated with May 2016 ($r = 0.69$) and higher total C ($r = 0.68$), Pb ($r = 0.67$) and DOC ($r = 0.64$) were associated with December 2016.

Across all sites and times, the OTUs in Bowman’s Creek pelagic samples with the highest relative abundance (n Families = 666) were the Synechococcalesaeae (Phylum Cyanobacteria), which can cause nuisance freshwater blooms with nutrient input and salinity variations (Muir and Perissinotto 2011). The domination of cyanobacteria and correlation of assemblages with Ca, carbon and other variables associated with evapoconcentration, decomposition and catchment run-off suggest that seasonality should play a key role in monitoring and closure planning.

In both the Goulburn River and Bowman’s Creek, there was no effect of zone (GR; $F_i = 0.25, p = 0.82$, BC; $F_i = 0.99, p = 0.41$) or time (GR; $F_i = 0.65, p = 0.65$, BC; $F_i = 0.91, p = 0.38$) on microbe assemblages from pebble biofilms. Biofilm assemblages were dominated by *Exiguobacterium* sp. (Order Bacillales) of which there are currently two distinct genetic groups: the psychrophiles, (from cold environments such as permafrost) and the thermophiles (from warm environments such as hot springs) (Vishnivetskaya et al. 2009). In contrast with benthic and pelagic OTUs, pebble biofilm assemblages were stable over space and time despite changing environmental variables. Therefore, biofilms may not be ideal ecological indicators in these systems.

Conclusions

Ecological indicators are only useful if there are clear and defensible links between the indicator and ecological function (Kurtz et al. 2001). Microbes are challenging to use as ecological indicators because (for example) they have complex lifecycles, ‘species’ is a challenging definition, modes of reproduction can be flexible, and community interactions are complex. Here we did not test for gene presence or expression and microbial ecological function could only be speculated. Future work could incorporate metabolomics and proteomics, which would involve laboratory cultures, potentially undercutting the ecological ‘gains’ made with the culture-free techniques of this study. Cell counts may negate the effects of within-sample relative abundances, although staining techniques (e.g.) can also introduce bias, especially when working with multiple unidentified taxa.

There are management concerns with freshwater benthic ecosystems in mined catchments (*sensu* Kurtz et al. 2001). We explored the use of microbes as ecological indicators, and how they may be used in river monitoring and assessment. We collected and identified OTUs from different habitats in dry and wet river beds (Aim 1); important for seasonal river systems which form a large proportion of global river networks (Datry et al. 2018) yet are often overlooked in monitoring programs (Steward et al. 2018). In the case of soil and pelagic microbes, assemblages correlated to environmental variables (Aim 2). We also provided examples
of how the system variability approach could be applied to the data (Aim 3). By virtue of their fast lifecycles, sensitivity to changing conditions, and ease of collection and identification, benthic and pelagic microbe assemblages hold promise as ecological indicators. However, more research is needed before microbes are incorporated into monitoring and closure programs.

**APPENDIX I – System variability approach to developing closure criteria.**

The system variability approach to developing closure criteria employs multivariate ordination - a data reduction and clustering technique traditionally used in ecology - as an applied management tool. A successfully rehabilitated site would lie within the river’s ‘normal’ variability, which is sustained and tracked over time (c.f., ‘reference sites’ in Blanchette et al. 2016). Determining if a rehabilitated site is within the variability of the system is a testable hypothesis; a null hypothesis of no significant difference between sites/assemblages is $p > 0.05$ using permutational MANOVA (Blanchette et al. 2016). Previously, we applied our model to biophysical data in the Hunter Valley rivers (Blanchette and Lund 2017).

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Aquifer Variation Characteristics of Coal Overlying Strata by Time-lapse Resistivity Monitoring

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Abstract
The coal mining areas of Western China are facing serious shortage of water resources and fragile ecological environment, high-intensity coal mining results in ground subsidence and overburden destruction, the structure of underground aquifer is destroyed and the groundwater level is lowered. The time-lapse electric prospecting method is applied to dynamically monitor the underground aquifers in different periods of modern coal mining. Time-lapse resistivity monitoring carries out multiple 2D electric prospecting for the same stratum at certain time intervals. Time-lapse resistivity monitoring involves many aspects such as data acquisition, processing, interpretation and inversion. The research district is located in Shendong mining district in Shaanxi Province. 4 times resistivity data acquisition is determined, the time node respectively is pre-mining, mining and post-mining as well as post-mining deposition stable period, the duration of this time-lapse data acquisition is 10 months. The research result shows that the aquifer variation of overlying strata have self-recovery capability with the development of modern coal mining process, the self-recovery capability gradually strengthens from coal seam roof upward to the near surface, the self-recovery capability of near-surface strata is relatively strong, while the roof of coal seam is most weak.

Keywords: aquifer, coal, overlying strata, time-lapse, resistivity, monitoring

Introduction
The coal mining areas of Western China are facing serious shortage of water resources and fragile ecological environment, high-intensity coal mining results in ground subsidence and overburden destruction, the structure of underground aquifer is destroyed and the groundwater level is lowered. It will not only cause the contradiction between the supply and demand of water, but also bring a certain effect to the ecological environment. The time-lapse electric prospecting method is applied to dynamically monitor the underground aquifers in different periods of modern coal mining, in order to research the influence of coal mining on overlying aquifer and groundwater.

Time-lapse resistivity monitoring carries out multiple 2D resistivity prospecting for the same stratum at certain time intervals, in order to study the temporal-spatial variations of aquifer characteristics of overlying strata. Time-lapse resistivity monitoring involves aspects such as data acquisition, processing and interpretation and inversion.

Research area overview
The research district is located in Shendong mining district in Western China’s Shaanxi Province. The strata of mining area from old to new have Yanchang Formation of Upper Triassic (T3y), Fuxian Formation of Lower Jurassic (J1f), Yan’an Formation of Lower-Middle Jurassic (J1-2y), Zhiluo Formation of Middle Jurassic (J2z) and Cenozoic sediments (Q).

The strata of mining area are generally monocline strata dipping into west with a dip angle of about 1-3°, where faults are rare and structure is simple. The thickness of bed rock is 180-200m and that of unconsolidated formation is 10-25m.

The mined coal seam of 12407 working face in mining area is Coal 1-2, of which the depth is 190-220m, the average thickness is 4.81m and the dip angle is 1-3°, and the coal seam is stable as well as the structure is simple.
12407 working face stope uses approach of full-seam mining, longwall mining and caving type roof control, in which the mining height is 4.5m, working face length is 300m, the footage is 3600m, the average daily mining footage is 12-13m and the monthly total footage is 390m-400m.

Aquifers monitoring principle
The resistivity of the underground stratum is not only related to the physical characteristics and water content of the stratum, but also closely related to the structural state and deformation and destruction of the stratum. The resistivity of the rock layer increases with the increase of the degree of rock failure in the case of the rock layer is not hydrated. The resistivity of the rock layer varies with its water content, the higher the water content of the same rock layer is, the lower the resistivity, the apparent resistivity of the overlying strata changes before and after the coal seam mining, and the electric property is different with the change of coal seam and strata caused by mining failure and different water content. Therefore, resistivity parameters are used to identify water abundance and its variation under different mining conditions of overlying strata.

Time-lapse resistivity data acquisition method
Time-lapse resistivity monitoring studies aquifer variation of overlying strata in coal mining through repeated resistivity prospecting at different time periods. Data acquisition is chosen to be carried out in different phases of coal mining, i.e. performed before mining, during mining and in deposition stable period after mining respectively. The duration of this time-lapse data acquisition is 10 months, the working footage positions corresponding to data acquisition time are shown in Figure 1.

The first acquisition started when Coal 1-2 of 12407 working face hadn’t been mined and the coal seam was in original state, and the acquisition was background survey for strata. The second acquisition was carried out 4 months later, when nearly half of Coal 1-2 of 12407 working face had been mined, and half area of the working face was goaf and the other maintained unmined. Strata of goaf was in mining state and coal seams adjacent to the mining area would be influenced by mining while coal seams that were far away from the mining area maintained unmined. The third acquisition was conducted 2 months later, when Coal 1-2 of 12407 working face had been totally mined up, and the working face became a goaf completely and the strata were in mining state. The fourth acquisition was then implemented 4 months later, when strata of 12407 working face was totally in post-mining deposition stable period.

Resistivity discrepancy analysis during coal mining
The resistivity profile is obtained through the inversion of the apparent resistivity of the collected data, and the 3D data cube is formed by using the visualization image of multiple line data. The resistivity distribution of the aquifers is obtained by the target layer subdivision of the 3D data cube, and the water bearing capacity of the overburden aquifer and the water bearing change law of the coal seam under the influence of the mining are analyzed.

Figure 2 shows geoelectrical profiles derived from processing those 4 acquired resistivity data.

According to the geoelectrical profile of first acquisition, 3-4 resistivity strata are distributed in the underlying strata of surface; the surface has one relatively high-resistivity thin bed and 20-30m underneath, there is one inhomogeneous low-resistivity stratum; generally, the bed rock section has the resistivity distribution of coal measure strata and the roof bears water in some local areas.

On the profile of second acquisition, 4-5 resistivity strata are distributed in the underlying strata of surface, the resistivity of surface sand zone fluctuates locally, the zone 20-30m below surface generally shows a resistivity distribution of low-resistivity stratum; Influenced by working face mining, the resistivity of coal roof fluctuates locally and the local resistivity of areas near mining working face increases.
On the geoelectrical profile of third acquisition, 4-5 resistivity strata are distributed in the underlying strata of surface, the resistivity of surface strata increase relatively, the zone 20-30m below surface generally shows a resistivity distribution of low-resistivity stratum; the resistivity of coal roof influenced by working face mining fluctuates locally.

On the geoelectrical profile of fourth acquisition, 4-5 resistivity strata are distributed in the underlying strata of surface, the resistivity of strata located in the middle of survey lines is relatively higher and the sand and soil are relatively dry. The zone 20-30m below surface generally shows a resistivity distribution of low-resistivity stratum with inhomogeneous thickness; The resistivity of coal roof fluctuates, which indicates the water content of water-bearing sandstone strata of roof decreases, which may be resulted from water charging of goaf.

**Shallow aquifer variations during coal mining process**

Within the research area, those surface water-bearing formations with a depth of 15-50m are called shallow aquifer. It can be found through comparing resistivity slices (Figure 3) of shallow aquifer during coal mining that before mining, due to a small brook exists in the middle of shallow aquifer (Fig.3(a)), its underlying strata are water saturated and water bearing of other zones is poor; during mining (Fig.3(b) and Fig.3(c)), mining activities lead to electric property changes of subsurface aquifers, the resistivity increases a little bit and water bearing deteriorates in general; during post-mining deposition stable period (Fig.3(d)), resistivity of subsurface aquifer decreases and its water-bearing distribution basically recovers to the pre-mining state.

**Aquifer variations of coal roof during coal mining process**

Figure 4 shows the resistivity slices of roof aquifer during coal mining. It can be found...
through comparison that before mining, the roof has multiple inhomogeneous aquifers (Fig.4(a)), of which the local water bearing is good; when influenced by mining (Fig.4(b) and Fig.4(c)), roof water infiltrates downward and roof resistivity increases, the water bearing of roof aquifer deteriorates, after post-mining deposition stable period, water bearing of roof doesn’t recover (Fig.4(d)) and generally is poor.

Conclusions
Influenced by coal mining, resistivity of shallow aquifer increases in the mining process, in post-mining deposition stable period, local ground water of the aquifer infiltrates, resistivity decreases, and its water bearing basically recovers to the pre-mining state. Water bearing of coal roof become worse during mining. This indicates that water bearing self-healing capability of shallow strata is higher, while that of roof strata adjacent to the coal seam mined is lower.

Acknowledgements
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References
Abstract
This paper presents results of a biota study carried out in the brine discharge area of Ludmilinskaya brine well (Solikamsk). Eight taxa of pennate diatoms and two species of invertebrates were identified during the study. Most of the identified taxa belong to cosmopolitan benthic zones with varying degrees of halobility.

Keywords: brackish water, diatoms, invertebrates

Introduction
Recently, studies of the biota of water bodies with increased salinity in areas of industrial pollution with potassium production waste have been conducted in Perm Krai (Martynenko, 2017; Martynenko et al., 2017; Khayrulina et al., 2017; Khayrulina, Baklanov, 2018). Brackish inland water bodies usually have unstable salinization conditions and vary in ecological features with a certain species composition (Hartog, 1967). In such water bodies with extreme habitats, specific biocenoses develop which may greatly differ in species composition in different areas (depending on the distance from sources of water-soluble salts in the form of salt springs and discharges of old brine wells). Human effect is usually seen as a factor contributing to biodiversity reduction although there are examples evidencing the opposite trend (Barinova et al., 2000). This paper shows the results of a preliminary study of the biotic component directly in the area of saline solution discharge.

Methods
The material for this paper was several benthic samples taken in March-April 2019 from several parts of the stream flowing from Ludmilinskaya brine well (5-10 meters far from the wooden casing pipe). Ludmilinskaya brine well (59°39′28.5″N 56°46′58.6″E) was drilled in 1906 within the Troitsky (Solikamsky) salt-making plant to determine the formation depth of rock salt and was equipped in 1910. The well was operated until 1923 when the enterprise was closed. It was not restored after the Russian civil war. Since the liquidation of the enterprise, brines from the well have moved with gravity, with their flow rate depending on the season. In 2011, the borehole environment was refurbished and the wellbore was sealed with gravel mixture for safety purposes. According to the references (Kurnakov et al., 1917), the salinity of the water pouring out of the well was 260 g/L in 1917. Water mineralization in 2017 amounted to 12 g/L (Khayrulina et al., 2017). According to our data, the mineralization of the well water has decreased to 8 g/L by mid-March 2019. The reasons for the decrease in the source mineralization remain unknown yet.

Diatoms were identified according to Zabelina et al. (1951). Environmental and geographical characteristics of algae are provided by the paper according to Barinova et al. (2000). Species of invertebrates were determined using appropriate field guides (Chekanovskaya, 1962; Key to freshwater..., 1995). The materials were examined using optical (binocular microscope MBC-10, stereomicroscope Leica MZ16) and electron probe (scanning electron microscope VEGA 3 LMH with a system of X-ray energy dispersive microanalysis Oxford Instruments INCA Energy 250/X-max 20) methods at the laboratory of the local geology of natural resources of the Mining Institute, Ural branch of the Russian Academy of Sciences.

Results
The recorded water salinity in the area of well discharge is close to the limits of salinity
of 5–7 g/L, at which the minimum species diversity is observed (Remane, 1971). Only eight diatom taxa were found in the samples, including some species from different halobility categories (Tabl.).

Raphless diatoms *Synedra pulchella* and *S. tabulata* dominate among the identified algae (Fig. 1, a–e). These two types were not listed among algae found in the rivers of Perm Krai (Martynenko, 2017; Belyaeva, 2013; Belyaeva, Pozdeev, 2005), but are part of some algal floras of water bodies in the Asian part of Russia. *Fragilaria pinnata* (Fig. 1, f, g) was numerous in our samples; this species predominates in the alluvial ripal zone epilithon of the Chusovaya River and samples of the upper area of the Kama Reservoir (Belyaeva, 2013; Belyaeva, Pozdeev, 2005). As the species of a single raphless alga could not be identified, we preliminarily classified it as a teratological form of one of the species of *Tetracyclus* (given the fact that most species of this genus can exist in an acidic environment) (Fig. 1, h).

Among raphid diatoms, findings of numerous *Navicula cryptocephala* and *N. protracta* (Fig. 2, c–h) and a single finding of another species of this genus *N. peregrina* were recorded (Fig. 2, b). The latter was identified to be a variation of kevingensis, which is characterized by closer striae (7–8 in 10 µm). All these species were found in saltwater bodies of Perm Krai (Zabelina et al., 1951; Martynenko, 2017), *N. cryptocephala* and *N. peregrina* were found in samples from the central stretch of the Kama Reservoir (Belyaeva, 2013).

*Surirella striatula* (Fig. 2, a) is a species of diatoms new to the algal flora of Perm Krai. According to the environmental classification of the diatoms, this species is a halophile (Barinova et al., 2000), while it is a euryhaline organism according to others (Yatsenko-Stepanova et al., 2014). In Russia, *S. striatula* was discovered at least in three modern algal floras of the Black Sea (Balycheva et al., 2017), the Tuzlukkol River (Orenburg Oblast) (Yatsenko-Stepanova et al., 2014), and the Bolshaya Smorogda River (Volgograd region) (Burkova, 2016). This species, as well as *Synedra pulchella* and *S. tabulata*, were most likely brought to the area of the northeastern part of Perm Krai by migrating waterfowl.

*Eucyclops macruroides* Lilljeborg, 1901 (Fig. 3, a–c), which belongs to freshwater species (Key to freshwater…, 1995), was found in the samples. However, there is evidence of this species being found in the mesohaline waters of the Danube (Zorina-Sakharova et al., 2014). Our findings also confirm that the species can live in brackish waters. Beside the copepods, oligochaete *Lumbricillus lineatus* Müller, 1771 was found in the samples (Fig. 3, d–h). This species is euryhaline, meaning it can live both in fresh waters and in extreme conditions of oceanic salinity (Chekanovskaya, 1962).

**Conclusion**

It is the first time that biota at the place of saline solution discharge of Ludmilinskaya well was studied, low species diversity was found in both flora and fauna. Among

<table>
<thead>
<tr>
<th>Taxon/ Environmental and geographical characteristics</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fragilaria pinnata</strong> Ehr.</td>
<td>P-B</td>
<td>10-35</td>
<td>ind</td>
<td>hl</td>
<td>alf</td>
<td>b</td>
</tr>
<tr>
<td><em>Navicula cryptocephala</em> Kütz.</td>
<td>B</td>
<td>-</td>
<td>-</td>
<td>i</td>
<td>alb</td>
<td>k</td>
</tr>
<tr>
<td><em>Navicula peregrina</em> (Ehr.) Kütz.</td>
<td>B</td>
<td>-</td>
<td>-</td>
<td>mh</td>
<td>alf</td>
<td>k</td>
</tr>
<tr>
<td><em>Navicula protracta</em> Grün.</td>
<td>B</td>
<td>-</td>
<td>-</td>
<td>mh</td>
<td>ind</td>
<td>k</td>
</tr>
<tr>
<td><em>Surirella striatula</em> Turp.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>hl</td>
<td>-</td>
<td>-</td>
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<tr>
<td><em>Synedra pulchella</em> (Ralfs) Kütz.</td>
<td>Ep</td>
<td>-</td>
<td>-</td>
<td>i</td>
<td>-</td>
<td>k</td>
</tr>
<tr>
<td><em>Synedra tabulata</em> (Ag.) Kütz.</td>
<td>B</td>
<td>-</td>
<td>-</td>
<td>mh</td>
<td>ind</td>
<td>k</td>
</tr>
<tr>
<td><em>Tetracyclus</em> sp. *</td>
<td>B</td>
<td>-</td>
<td>-</td>
<td>i</td>
<td>acf</td>
<td>a-a</td>
</tr>
</tbody>
</table>

*Christian Wolkersdorfer, Elena Khayrulina, Svetlana Polyakova, Anna Bogush*
Figure 1 The diatoms (Araphinales). Ludmiliskaya well, Solikamsk, Russia (03.-04. 2019). a, b – Synedra pulchella; c, d, e – Synedra tabulata; f, g – Fragilaria pinnata; h – Tetracyclus sp.

Figure 2 The diatoms (Raphinales). Ludmiliskaya well, Solikamsk, Russia (03.-04. 2019). a – Surirella striatula; b – Navicula peregrina; c, d, e – Navicula cryptocephala; f, g, h – Navicula protracta

the discovered diatoms, halophilic species (Surirella striatula), mesohalobe species (Synedra tabulata) and species indifferent to salinity (S. pulchella) were found that had not been previously recorded in the water bodies of Perm Krai. The finding of Eucyclops macruroides confirms the limits of the species tolerance with respect to salinity to be broad.

Acknowledgements
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References
Figure 3. Invertebrates. Ludmiliskaya well, Solikamsk, Russia (03.-04. 2019). a, b, c - Eucyclops macruroides; d, e, f, g, h - Lumbricillus lineatus s.l.


From remediation supervision to long-term surveillance – Ground and surface water monitoring at a former uranium processing site

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Abstract
Starting in 1990, the clean-up of the former Crossen uranium mill near Zwickau in Germany has been a focal point in the Wismut remediation program which is dedicated to the legacy of large scale uranium mining and milling in East Germany.

The discharge of treated water, but also the still remaining release of contaminated seepage into aquifers and surface streams require the monitoring of the water-borne environmental impact. Key contaminants include uranium, arsenic and radium, accompanied by molybdenum, sulphate, chloride, hydrogen carbonate and sodium.

The current remediation monitoring is based on radiation protection licences and permits issued under water law. With the transition towards post-remedial and long-term activities after 2020 the monitoring requirements will substantially change regarding key function and scope. The presented paper describes the existing water monitoring system and key findings of the previous monitoring period. Finally, site conditions, constraints and remaining uncertainties for post-remedial monitoring will be discussed.

Keywords: ore processing, tailings pond, uranium, arsenic, radium, monitoring, groundwater, surface water

Introduction
The second largest tailings management facility (TMF) of the former East German uranium mining industry (former SDAG Wismut) is situated at Crossen and Helmsdorf near the city Zwickau, Saxony. Ore processing and the deposition of residues occurred on both sides of the river Zwickauer Mulde. First, three smaller tailings ponds (TP) were piled up from 1950 to 1958: Crossen (0.3 million tons), Dänkritz I (6.6 million tons) and Dänkritz II (1.2 million tons). After the depletion of storage capacity TMF Helmsdorf (49 million tons) was started in 1958 and worked until 1989.

Site remediation included
- the decommissioning of the processing plant including area clean-up (finished in 2001), other facilities on the left side of the Mulde were already dismantled before 2001;
- the relocation of the huge Crossen waste pile (3.3 million cubic meters) including the underlying older tailings from the floodplains of the Zwickauer Mulde river to the Helmsdorf TMF (terminated in 2018) and the rehabilitation of the footprint and reuse as a renaturalized floodplain;
- and the dry stabilization of the TMF itself on 200 hectares (to be finished in 2021).

The technology of in situ decommissioning includes the expelling of pond water, interim covering of the tailings surface, dewatering of the fine tailings, re-contouring of dams/ponds and final covering including re-vegetation (Neudert & Barnekow 2006). The water management strategy involves the treatment of contaminated pond, ground- and seepage water (Laubrich et al. 2018).

The discharge of treated water, but also the still remaining release of contaminated seepage into aquifers and surface waters require the monitoring of the water-borne environmental impact.

With the transition towards the implementation of long-term tasks, the requirements regarding function and scope of the environmental monitoring will change.
Geological-hydrogeological site characterization

The Crossen-Helmsdorf site is located in the western part of a permian molasse basin between the Erzgebirge in the south and the Granulitgebirge in the north, which is based on old Paleozoic and Precambrian basement. The discontinuously outcropping sediments of the Upper Lower Carboniferous up to the Oberrotliegend II are continental sediment deposits of the eroded Variscan orogen.

The underground of the Helmsdorf TMF is determined by rocks of the Mülsen formation of the Oberrotliegend, which is intensively tectonically stressed in the vicinity of Helmsdorf TMF. The characteristic tectonic structural pattern combines structures which strike in ENE-WSW, NW-SE, N-S as well as NNW-SSE direction (fig 1).

Based on intensive drilling work from 1998 to 2003 and the gradual commissioning of groundwater monitoring wells during the rehabilitation period, it was recognized that all ENE-WSW striking fault zones on the eastern flank of the Helmsdorf TMF are involved in groundwater runoff affected by the tailings facility. Morphologically, these structures are visible through valley cuts, such as the Oberrothenbacher, Wüster-Grund, Niederhohndorfer, Zwischengrund and Trischgrund valleys. These structures extend into the area of the Zwickauer Mulde floodplain and pave the way for contaminated groundwater (Möckel & Neudert 2004).

The completely remediated Dänkritz I TP is located in an area of tertiary loose sediment deposits, having been subject to intensive sand and gravel extraction in earlier times. Tailings were deposited inside an exploited gravel pit. The clastic materials represent a pore aquifer of good water permeability along a SW-NE directed palaeo-channel. The relief of the underlying Rotliegend surface determines the groundwater flow direction within the Tertiary sediments towards the Zinnborn/ Zinnbach creek. Due to a high uranium contamination of groundwater downstream of the Dänkritz I TP, two extraction wells went into operation in 2002/2003, whose water is treated together with seepage water of the TMF Helmsdorf in the water treatment plant (WTP) Helmsdorf.
The Dänkritz II TP, also situated inside of an exploited gravel pit, is not subject to the obligation of Wismut GmbH. The remediation will start in the near future.

The other objects (Crossen waste dump, processing plant and further industrial area) are located in the floodplain of the Zwickauer Mulde. It is characterized by quaternary loose sediments in the subsurface, which are extensively covered by alluvial loam.

**Basics of monitoring networks development**

Starting in 1990, first measuring networks of each compartment (water, air, soil) were installed in order to identify pollution sources and to describe their environmental impacts. After the deduction of remediation needs a selection of substantial (key) measuring points for the water path are defined as basic monitoring network which is legally based on the specifications of the REI Bergbau (1997). These points concisely characterize the site and serve for long-term observation. By setting limit values, water and radiation protection approvals determine the requirements for self-control with regard to parameters and sampling frequency.

Aspects of monitoring tasks are summarized in table 1.

The remediation procedure requires the observation of each individual object, the compliance with limits and a flexible adaptation of monitoring elements to the clean-up progress. In expectation of the end of the physical remediation work the complex monitoring network will be reviewed and adapted to the needs of the post-remedial or long-term phase. In conjunction with resulting (long) time series the long-term monitoring network should reflect the success of remediation activities (Kreyßig et al. 2008).

**Configuration and modification of key monitoring network**

A key measuring network is composed of measuring points, which are needed for a sufficient characterization of the hydraulic and hydrochemical system behaviour in time during aftercare (Sporbert et al. 2006).

Decisive for the selection of key measuring points is the comprehensive knowledge of the geology and hydrogeology of the respective remediation object and the pathes of influence. All relevant aquifers or water-bearing units influenced by these objects be considered. Based on the groundwater flow regime, groundwater inflows and outflows are assigned to the object. The monitoring of the pollutant source (e.g. tailings pond) must be included in case of in-situ-remediation (Möckel 2006).

With the help of key monitoring networks, the fundamental, spatially substantial influences of groundwater by objects of Wismut GmbH are to be tracked in the long term and to be judged in terms of their dispersion dynamics as well as their trend behavior.

In the course of the transition from remediation to long-term monitoring, the water monitoring serves for:

- Evidence of hydraulic and geochemical stability after completion of remediation,
- Exclusion of a trend reversal of already decreasing or stable concentration values in groundwater,
- Prevention of health problems for the population from contaminants spreaded through the groundwater path, which could possibly lead to restrictions on its use for human consumption.

During the initial phase of the rehabilitation project until 2003, the groundwater surveillance network at the Crossen/Helmsdorf site embraced more than

<table>
<thead>
<tr>
<th>Table 1 Aspects of monitoring tasks</th>
<th>Classification of monitoring activities</th>
</tr>
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<tbody>
<tr>
<td>Monitoring tasks:</td>
<td>screening, remediation, long-term</td>
</tr>
<tr>
<td>Temporal tasks:</td>
<td>before, during, past remediation</td>
</tr>
<tr>
<td>Object tasks:</td>
<td>background, source, path, effect</td>
</tr>
<tr>
<td>Permit tasks:</td>
<td>basis, remediation, after care</td>
</tr>
<tr>
<td>With respect to extent:</td>
<td>person-related, source-related</td>
</tr>
<tr>
<td>With respect to time:</td>
<td>limit-related, trend-related</td>
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</table>

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
600 groundwater monitoring wells. The remediation progress with the gradual completion of individual objects led to the initial establishment of a key monitoring network at site Crossen/Helmsdorf in 2006 with 129 groundwater and 10 surface water measurement points (Möckel 2006) (tab. 2).

With a view to the termination of the physical work (predicted for 2021), an optimized monitoring network has been established in 2018 which is dedicated to reflect the effect of the individual objects on the aquatic environment. The network can be understood as an optimized monitoring system for the immediate post-remedial and the long-term surveillance periods. It takes into account the hydrogeological site conditions, regulatory requirements, and cost aspects. Most recently, the Crossen key monitoring network involves 74 groundwater wells and 8 surface/seepage water monitoring stations (Möckel & Greif 2018). Table 2 shows the development of the number of measurement points in the individual objects.

The decline of 2018 compared to 2006 is particularly evident at the measuring points in the dams. This is related to the reduction of geotechnical investigations after complete removal of the freewater. Figure 2 shows stable or slightly decreasing uranium concentrations along the groundwater discharge channels allowing a gradual reduction of measuring points.

On the industrial area (temporary ore storage facility and assoziated technical structures) located at the left side of the Zwickauer Mulde remediation was completed in 2001. The uranium concentrations in groundwater are stable at a low level. Here, the measuring points of the key measuring network could be decommissioned. On the other hand, contamination in the groundwater can still be detected along the processing site (radiometric, chemical processing) on the right side of the Zwickauer Mulde, as residual materials had remained in the underground. The groundwater monitoring should be continued here with less measuring points. The waste dump Crossen is in the final stage of remediation, hence the temporal evolution must be further observed with the existing sampling sites.

**Table 2** Number of measuring points of the key monitoring network in 2006 and 2018.

<table>
<thead>
<tr>
<th>Object</th>
<th>Structure and path</th>
<th>2006</th>
<th>2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>dam body (polluted source)</td>
<td>23</td>
<td>12</td>
</tr>
<tr>
<td>Tailings pond Helmsdorf</td>
<td>tailings underground (geogenic background)</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Helmsdorf fault zone (upstream)</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Steinigtgrund fault zone (upstream)</td>
<td>2</td>
<td>1</td>
</tr>
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<td>Engelsgrund fault zone (upstream)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Oberhohndorf fault zone (upstream)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Nord - Süd – jointed zones (up-/downstream)</td>
<td>5</td>
<td>1 / 6</td>
</tr>
<tr>
<td></td>
<td>Oberrothenbach fault zone (up-/downstream)</td>
<td>3</td>
<td>1 / 6</td>
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<td>Zwischengrund fault zone (downstream)</td>
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<td>tailings body/dam (polluted source)</td>
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Stratigraphy: \( ^{p} \) permian (Rotliegendes), \( ^{q} \) quaternary, \( ^{t} \) tertiary, \( ^{a} \) anthropogenic
According to the 2018 key monitoring plan, quarterly measurements of groundwater level and annual groundwater sampling are required. In the case of surface water measuring points, the sampling frequencies range from monthly to quarterly. The parameter spectrum includes in-situ parameters, macro constituents, trace elements and radionuclides.

**Use of key monitoring network and systematic long-term studies**

Due to the long-term character of the monitoring programs, the concentration data series obtained reflects the spatial and temporal remediation status of the individual objects. In combination with the discharges, an accounting and thus an assessment of the relevance of individual emissions to the environment becomes possible. For the Crossen-Helmsdorf site, the following tasks can be derived from the current data:

- Examination of the groundwater quality for inflow, development within the pollution source and along outflow channels (e.g. fig. 2),
- Examination of surface water quality, including compliance with environmental quality standards in water and suspended matter in the surface water body according to the EU Water Framework Directive (currently no standard for uranium),
- Determination of water quality and amount of seepage and groundwater sub-streams to be treated as a precondition for effective water treatment,
- Balancing of the partial flows and determination of loads from point sources in relation to the increase in load in the receiving waters (Zwickauer Mulde), indirect estimation of loads from diffuse sources,
- Designation of the performance of the water treatment via the pollutant retention from the water system (also with regard to supraregional effects, in this case for river Elbe).

Analysis of long-term data series provide a powerful tool for the evaluation of the remediation success. Figure 3 shows, that the commissioning of the WTP Crossen (1995) in the middle course and the WTP Schlema-Alberoda (1998) in the upper course of Zwickauer Mulde led to the reduction of uranium emissions and consequently the improvement of water quality in the Zwickauer Mulde as shown at site Crossen-Helmsdorf.

![Figure 2](image)

**Figure 2** Uranium concentrations in groundwater along Wüster Grund disturbance (permian) in dependence of distance to TMF Helmsdorf
Outlook
Depending on the future development, the network will be subject to regular revisions, with the goal of further optimization. Key monitoring networks should be reviewed at least every 10 years. Within one of the next adjustments at site of Crossen-Helmsdorf the consolidation of all remaining requirements should be checked.

References
Abstract
The Earth's surface collapses are a serious hazard on salt mine areas. Electromagnetic methods are characterized by a number of substantial informative capabilities within salt deposits. Electromagnetic monitoring technology has been developed on the base of electrical and electromagnetic sounding. Analysis of the experimental monitoring surveys results allowed to determine a number of predictive criteria and indications of the salt karst processes in electromagnetic fields, including the expressed dynamics of water mineralization change, gas-dynamic and subsurface subsidence-collapse cyclicities. The obtained information has been used as a basis for a dynamic geoelectrical model of collapse formation.

Keywords: monitoring, salt mines, prediction, electromagnetic sounding, electrical methods, dynamic geoelectrical model

Introduction
Development of monitoring technologies to determine and predict possible negative processes is an important problem these days. One of such negative processes is the formation of collapses and subsidence of the Earth's surface as a result of intensive karst processes caused by natural and anthropogenic reasons. The salt karst process is extremely intensive. The examples of this are the collapses and subsidence occurred during potash deposits mining in Canada, USA, Russia, Germany and other countries. Geological, geophysical, hydrogeological, geodetic and other methods are applied to provide the safety of salt deposits exploration (Contrucci et al. 2011; Land and Veni 2012; Pain et al. 2012; Siemon et al. 2012). The difficulty of their implementation is connected with the necessity to analyse many factors including physical-geological conditions of the investigated territory and various phenomena associated with the karst processes as well as with peculiarities and contrast of their manifestation in physical fields.

This paper deals with the results of a research aimed at developing an electromagnetic monitoring system adapted to the Upper Kama salt deposit conditions (Russia, Perm region). The acute need for these investigations was connected with the flooding of one of the mines accompanied by a series of subsequent collapses (fig. 1). The geological section of the investigated depth interval includes the potash salt strata, rock salt beds, clay-marl complex, limestone-sandstone complex, and quaternary sediments (Andreichuk et al. 2000). There are up to four aquifers within the oversalt strata with quite high water content. The lower part of the clay-marl complex and the evaporate strata, isolating the aquifers from the mines, are referred to as a waterproof complex (Andreichuk et al. 2000). The top of the evaporate beds within the investigated territory can be found at a depth of 140-180 m, however, the potash salt layers and mine system are located at a depth of approximately 200-230 m. An important peculiarity of the investigated area is the position of a large part of mines within the city. Their location increases both hazardous level of possible negative phenomena and relative difficulty of the implementation of geophysical monitoring methods.

Methods
Electromagnetic methods have unique informative capabilities within salt deposits. Electrical resistivity depends on such physical properties as porosity and water
content of rocks, it is sensitive to changes of water mineralization and gas content, which are associated with the salt karst process development.

Under the conditions of the Upper Kama salt deposit the water mineralization changes from 0.5-1 g/L (oversalt aquifers of the limestone-sandstone strata) to 400-450 g/L (saturated brines in the salt rocks dissolution zone) (Andreichuk et al. 2000). So electrical resistivity of water can decrease by a factor of hundreds (to 300-400) as a result of the mineralization rising in the salt dissolution zone.

The same contrast of electrical resistivity change is connected with the gas content of rocks. Due to the dielectric properties of gas the increase of the gas content of rocks upon filling the voids can lead to the electrical resistivity rise of hundreds of per cent. Salt rocks contain (in adsorbed, molecularly connected, nonassociated condition) a substantial volume of gas of different types (hydrogen sulfide, carbon dioxide, methane, and others). The distortion of salt crystal structure generally occurring as a result of its dissolution leads to gas accumulation and gas dynamic processes.

To monitor the physical condition of rocks in the depth interval from the Earth’s surface to the productive part of the salt strata a complex of complementary methods has been developed. It contains: 1) electromagnetic sounding based on the use of controlled source (CSEM) and industrial electromagnetic fields (industrial magnetic field method, IMF) (Kolesnikov and Laskina 2015) which provide an opportunity to investigate the salt rocks layers; 2) direct current method (DC) which allows to control the oversalt part of geological section; 3) stationary electrical monitoring system, aimed at the predictive assessment of the negative processes development stage in anomalous areas determined by the complex of the EM and DC methods. The stationary monitoring systems are based on the DC method with the use of multielectrode array, commutator and specific software (Kolesnikov et al. 2017). It provides an opportunity for real time spatial-temporal control of the physical condition of oversalt geological section with the required measurement period, safety of work and data transmission via the Internet.

For the analysis of the survey results in addition to electrical resistivity the following dynamic interpretation parameters are used: a) relative difference $\Delta_{i,1}$ between obtained values $\rho_i(r)$ for i-th and initial $\rho_0(r)$ stages of survey; b) velocity of the electrical resistivity change $v_i$ for the time period $\Delta t_{i,i+1}$ between i-th and (i+1)th surveys; c) dynamic activity which is the sum of amplitudes of variations $\delta_{i}(r,t)$ exceeding the noise level ($\delta_0$) determined in the process of test measurements.

**Experimental surveys**

Developed monitoring complex was applied to investigate several areas (approximately 2 km$^2$ each) within the flooded mine territory. The surveys were conducted on 1080 investigation points annually. A complex analysis of the results obtained for all investigated areas allowed us to form a general scheme of the salt karst processes.

![Figure 1 The first collapse (a) and example of the following collapses (after 4 years) (b).](image-url)
Figure 2 shows the results of the monitoring of the salt strata with the help of the IMF method. It demonstrates the typical formation of the decreased resistivity anomaly with an extension of the zone and increase in its intensity. One of the most likely reasons of the formation of this zone is the increased intensity of salt rocks dissolution in this depth interval, causing the extension of the cavity and the rise in mineralization of water, filling the mines. It is typical for the initial stage of possible collapse formation.

The following dynamic of resistivity variations can be accompanied by a number of other processes. We suppose that the most substantial of them are the so-called cyclic processes, which are evident in a periodic dramatic resistivity increase in a certain part of the geological section followed by a decrease in the anomalous effect as well as by some specific phenomena in the overlying sediments. Such processes were observed as a result of regional DC and EM surveys and stationary monitoring systems application.

Regional surveys were conducted once a year on the most of the investigated territory. It allows to recorde only general behaviour of the dynamic process accompanied by a set of indications in salt and oversalt parts of the section and determine probable nature of the most intensive spatio-temporal changes in the electrical resistivity of the medium (with the intensity to 300-900 %). At the same time, stationary monitoring systems implemented at anomalous sites (identified by the results of regional monitoring surveys) detected the repetition of these processes with a relatively reduced intensity (on average 15-20%, in some cases up to 100-150 %) with an interval from 15-20 days to 1.5-2 years showing the periodical changes in electrical properties. The cyclicity is explained by the increased sensitivity of electrical resistivity to changes in water mineralization, density and gas content of rocks within the zones of increased rocks fracturing. Each process has its own peculiarities in the electromagnetic field. Analysis of the anomalous effect and the dynamics of the electrical properties variation, observed within the determined subvertical fractured zones, showed that there exist two types of cyclicity: 1) gas-dynamic; and 2) subsurface subsidence-collapse.

The most probable reason of the first type of cyclicity is the substantial increase of the gas content of rocks in the oversalt strata, caused by the the distortion of the gas-shield
properties of the covering salt rocks and the subsequent outburst of gas accumulations, formed as a result of the salt rocks dissolution. This process leads to a substantial increase in the electrical resistivity of the near salt strata. The existence of the subvertical fractured zones in the overlying sediments contributes to gas migration, in a number of cases up to the Earth’s surface, causing the gradual decrease in the anomalous effect with time as a result of the gas emission from substrata.

Some examples of the gas-dynamic cyclicity are shown in Figure 3. It reflects the observed dramatic resistivity increase (to 300-400 %) in 2013-2014 in the near salt strata with the traceability of the anomalous zone in the overlying sediments and the following relative decrease of resistivity in 2014-2015.

The second type of cyclicity is connected with the processes of subsurface collapse. It manifests itself as a formation of a dramatic resistivity increase zone within the salt karst area without well-defined anomalous features in the overlying sediments in the initial time period. This process is the evidence of the possible rocks density rise and is typical for the subsurface rocks collapse in the interval of the karst cavity.

Verification example of this is the precollapse process, detected by a stationary monitoring system in a potentially dangerous area, considered in the results of the analysis of the gas-dynamic cyclicity, which appeared two years before a small collapse (fig. 3). In contrast to the gas-dynamic cyclicity the stationary monitoring system indicated a dramatic resistivity increase in the near salt strata (to 800 %) without the well-defined anomalous effect in the overlying sediments (fig. 4). This manifestation, which is typical for the subsurface subsidence-collapse cyclicity, was observed 14 days before a small collapse in this place. The reason for it is the distortion

Figure 3 Sections of the apparent resistivity (a, b, c) and velocity of the resistivity change (d, e) 2012-2014 on the territory of the collapse occurrence (area 2).
of the physical-mechanical properties and a breakdown of the overlying rocks in the karst cavity under the influence of gravity.

Analysed examples show that the defined types of cyclicity, detected within the subvertical zones of the fractured rocks, are important diagnostic features for the predictive estimation of the position and time of possible collapse formation. The time interval between the beginning of the subsurface subsidence-collapse phenomena and the Earth's surface collapse occurrence depends on the depth of cavity formation and physical condition of the overlying sediments. Geodetic survey has been applied as one of the methods for the verification of the karst development zones, determined by the electromagnetic methods. Comparative analysis of the defined electrical diagnostic features of karst processes has shown the further spatial correlation with the zones of the intensive subsidence of the Earth’s surface.

As a result of the analysis of experimental monitoring investigations conducted in 2012-2016 a predictive dynamic geoelectrical model of the development of the collapse formation process under the conditions of the flooded mine territory has been created. The model shows four basic stages.

1. The first (initial) stage corresponds to the beginning of the formation of an intensive salt rocks dissolution zone in the productive interval. It is reflected by a decreased resistivity area with a tendency towards a rise in the anomalous effect.

2. The second (progressive) stage is characterized by the increased intensity of the distortion of the covering salt rocks and overlying strata. It is indicated in the resistivity survey results as: a) increased dynamics of the waterproof strata resistivity change; b) decrease in relative electrical resistivity in the waterproof strata with the cyclical processes of resistivity variations in the oversalt sediments, caused by the likely disturbance of the gas-shield properties of salt rocks and gas migration; c) traceability of the previously determined zones of decreased resistivity in the productive interval, indicating the absence of substantial rock collapse in this depth interval.

3. The third (precollapse) stage corresponds to the beginning of the subsurface subsidence-collapse processes. The typical features of this stage: a) decrease in the anomalous effect in the salt strata,

![Figure 4](image-url)
associated with a density properties increase as a result of the likely filling of the brine-filled cavity by the breakdown material; b) cyclicity of resistivity variations, which is typical for the subsurface subsidence-collapse processes; c) subvertical zones of decreased resistivity in the overlying sediments, showing intensive fracturing of rocks; d) tendency to the resistivity decrease in the waterproof strata and overlying rocks, connected with a possible increase in the water content of these rocks.

4. The forth (collapse) stage is characterized by intensive dynamics of the subsurface subsidence-collapse cyclicity in the oversalt strata with the tendency towards the approach to the Earth's surface.

Conclusions

Developed electromagnetic monitoring technology allowed us to determine important criteria to predict salt karst processes including two types of cyclic resistivity variations: gas-dynamic and subsurface subsidence-collapse. Formed dynamic geoelectrical model of these processes can substantially increase the accuracy of salt karst prediction.

Acknowledgements

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Stakeholder Participation in Sulphate Monitoring in Lake Nuasjärvi, Finland

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Abstract
Stakeholder participation in environmental monitoring may enhance the data collection process. The paper presents a pilot study of a stakeholder participation in water quality monitoring and explores reliability and validity factors of measurement results. In a pilot project at the Lake Nuasjärvi the community members used a mobile phone data management platform application to report commercial quality colorimetric reagent strips readings on site. The objective of the pilot was to assess preliminary monitoring solutions performance in field settings and to gather stakeholder experience in order to identify needs for further studies and to understand different stakeholder profiles and their needs.

During the pilot, a pilot group of five users observed selected monitoring points at lake Nuasjärvi. The results were collected from the measurement devise to an information management platform. To minimize data unreliability, the calibrated primary data was run through a set of comparable datasets to identify and eliminate deviations.

Keywords: citizen observations, stakeholder participation, environmental assessment

Introduction
In 2012 a local mining operations at Talvivaara in Sotkamo municipality, Finland, nickel and sulfate leaked into a nearby water bodies. Due to damaged dam structures a water discharge exceeded the permitted quantities both in water volumes and in the allowed contaminant loads. In aftermath of the incident, the responsible corporation initiated a new discharge pipeline plan leading to a bigger water body, the lake Nuasjärvi, to prevent future environmental violation.

The pilot project intended to increase the amount and the availability of water quality data and to support stakeholder communications prior to the pipeline construction. (Accident incident reporting center, Onnettomuustutkintakeskus 2014) The field piloting for citizen observation in sulfate monitoring was carried out during during eight weeks in summer 2016. The pilot campaign was designed by Measurepolis Development (part of KAMK University of Applied Sciences since 7/2016), PHD Nordic Oy and SYKE.

One of the objective of the pilot was to build social capital in water quality measurement procedures among the community residing in the lake area, hereafter referred to as 'affected population'. Five households in the affected area were selected to participate in the pilot. Three were house owners and two were summertime residents. The screening questions included asking about previous participation and willingness to participate in a field experiment.

The selected participants had no prior professional training in water quality monitoring. They participated in a practical training session regarding the use and the readings of reagent strips, how to use the smartphone application to transfer the data, the monitoring sequence and the data management model. They also visited the monitoring sites and were informed of possible factors influencing accurate data...
readings. After the initial training, the selected household carried out the data readings and transfer independently.

The stakeholder participation pilot took place prior to the installation of a water discharge pipeline. Presumably attitudes of the affected population could have been influenced by the widespread media attention to the previous environmental accidents. All participants reported having followed up media discussion regarding the previous environmental accidents.

Data gathering and the analysis process

In the pilot project affected community members used a mobile phone data management platform (PHDSight) application to report commercial quality colorimetric reagent strips results on site. The PHDSight is developed by PHDNordic (SME) and Finnish Environmental Institute (SYKE). The strips used in piloting were commercially available sulphate monitoring strips with sensitivity level of 220 pm, which was adequate to detect the possible exceeding of the permit limit control for total sulfate, but not the normal variation inside the environmental permit limit. Pilot users took two weekly readings for eight weeks.

In addition to building building social capital in water quality monitoring among the affected population, in general, the objective was also to gather field experience of monitoring devices, the strips, and to assess their usability and technical field performance. (PHD2018)

The selected monitoring method, whereas the basic principle is presented in Picture 1, consists of commercial colorimetric reagent strips. Smart phone camera is used to capture the readings with a calibrated color panel stabilizing the possible background lightning variations. The readings include location and time in order to show the results for a specific timely periods on a map. The colourmetric readings are transformed into numeric values and then transmitted using smartphones into information management solution PHDSight and the Finnish Environmental Institute’s database. Picture 2 shows the selected monitoring spots on the map and Picture 3 shows an example of a single measurement result. To avoid data gathering reliability

![How it works](https://example.com/how-it-works.png)

*Picture 1 Monitoring concept setup (courtesy PHDNordic).*
issues, the colorimetric readings are calibrated and the measurement readings, i.e. the primary data, is run through a comparable data set to identify and eliminate deviations.

The local information interface transfers the colorimetric information in the numerical values. In the pilot the numerical values were not shown locally before computing them. This was to prevent misleading conclusions in case of unaccurate or faulty measurement results.

In addition to industrial discharge, other factors, such as the seasonal rainfalls or swamp drainings, might influence the pH and sulphate levels in water bodies. Other uncertainty factors related to the selected method include reagent materials, incorrect measurement procedures, external circumstances (e.g. temperature or pH) or even misinformation provided in purpose.

No incidents which could have compromised field readings took place during the pilot. All participants were able to carry out the readings, to transfer the reading results and to receive the measurement reports in timely manner. All captured values
were in the range of environmental permit values, meaning no early warning indications occurred. Thus, no early warnings were initiated. A reading value out of the range of acceptable sulphate levels would have prompted an early warning protocol including a repeated measurement.

Individual measurement readings were not shared with the affected population participating in the field measurement readings. Instead, we shared the summary data and a report with the stakeholders, who had participated in the field data gathering.

In addition to the five affected households, we conducted unstructured experts interviews prior to, during, and post the field pilot. The interviewees included two industry (mining) representatives, the environmental permit authority representative, a local municipality administrator representative.

The mining industry representatives were responsible for environmental sustainability. It was agreed to keep the stakeholder participation field experiment separated from the mining corporation’s activities. Nevertheless, industry representatives expressed their concern of ‘sabotage’ of monitoring by stakeholders participating in the field readings or by outsiders. However, they also expressed interest to incorporate stakeholder participation in their own practices as a way to strengthen the collaboration with community and as a way to build social capital and trust. The piloted measurement device and measuring protocol could be used in the internal corporate water quality monitoring. Colourmetric reagents for monitoring of various contaminants are widely available and the data processing could be tailored to the industrial needs. To sum up, the industry representatives found both, the actual measurement process and the stakeholder participation, something they were willing to explore further in the future.

The public sector representative expressed concern of the possibly distorted information. In the interview the public sector representative expressed views that the pilot might lead to an opinionated general discussion among the public and in the media. “No matter what you measure, the discussion could twist the results and conclude that toxicity is present because there is a need to measure it. Moreover, the measurements cannot be trusted because they are conducted by the affected community members. As a rule, environmental monitoring should be left with the public sector authorities, and that reporting of the results requires the authority asserted by the public sector.” Please note that this views are expressed by an individual public sector official and do not reflect the general official public sector statement.

The Centre for Economic Development, Transport and the Environment has the oversight function of the environmental permit. The representative stated that accuracy and validity needed to be explicitly outlined in the field data collection. Nevertheless, similarity to the industry’s willingness to experiment with the new monitoring concept, the public sector expressed interest in utilizing stakeholder participation, and view it as an opportunity to provide background information for the environmental permit control procedures.

Results – Pilot case experiences on usability and field performance of sulphate monitoring as stakeholder participation

Technical field performance of the selected monitoring setup was adequate and no incidents which could have compromised field readings took place during the pilot. All participants were able to carry out the readings, to transfer the reading results and to receive the measurement reports in timely manner. All readings were recorded in the database.

All captured values were below the detection limit, meaning no early warning indications occurred. Thus, no early warnings were initiated. A reading value out of the range of acceptable sulphate levels would have prompted an early warning protocol including a repeated measurement and further involvement of accredited measurement protocol. The sensitivity of the available reagent strips follows the environmental permit value limit for exhaust water and some exceedings have been reported during the 2012 incident.
Pilot user interviews showed positive experiences on the usability; none of the pilot users found difficulties in the use of the selected monitoring solution. The pilot users found the participation as an interesting and motivating act, and volunteered to participate also in future if similar activities take place.

Other stakeholder interviews raised up underlying questions related to possible wider adaption of the method; industrial representatives saw the method as a possible additional part in their internal operations and community trust building rather than as a part of environmental permit control. Authority representative saw the method as a supportive part for their background operations, when the possible uncertainties related to a single measurement are not in a critical part. All the other interviewed stakeholders, others than the pilot users, stressed the need for careful information management protocol in order to mitigate the risk for distribution of intentionally distorted information.

**Conclusions - Stakeholder Participation in Monitoring as a Component of a Wider CSR and Sustainability Protocols**

Affected community members described the participation in environmental field monitoring as a positive experience. Similar positive experiences in ICT assisted citizen observations have been reported in previous studies. (Gharesifard & Wehn 2014) Affected community members reported that the active participation strengthened their sense of being active members in their community. They commented the polarized and opinioned media coverage and reflected it on their experience carrying out environmental field monitoring. Participants suggested that stakeholder participation in carrying out environmental monitoring could enhance the information available to general public.

In conclusion, while recognizing possible validity and reliability issues we postulate that stakeholder participation in environmental monitoring may provide valuable additional data to enhance the more traditional monitoring conducted by environmental authorities and industry representatives. Involving affected communities in field data readings allows more comprehensive data gathering and monitoring of larger and also environmentally sensitive areas. Stakeholder participation offers a relative cost-effective method of field data gathering compared to the monitoring conducted by expert firms. While monitoring by contracted experts is usually conducted on one-off basis, affected communities and other stakeholder could conduct monitoring in regular basis. A comprehensive data analysis aids to eliminate data deviations and improves the reliability of the field data.

In this field study we piloted stakeholder participation in the environmental monitoring by engaging community members to conduct water quality readings. The concept has wider potential and more studies are warranted to explore new ways, how affected population could actively participate in sustainability monitoring instead of just serving as a passive audience receiving information from environmental agencies, industry representatives, local authorities and media. The stakeholder participation in monitoring activities not only has the potential to provide more frequent and more nuanced primary data, but also to cover wider areas than typically are covered by monitoring protocols. Furthermore, stakeholder participation could be included as a standard component of a wider CSR approach, and even as an activity of community engagement in SLO and FPIC processes.

In conclusion, active participation in the monitoring processes creates trust in the monitoring process. Stakeholder participation in environmental monitoring processes builds social capital and could be incorporate in the industry CSR practices. In fact, stakeholder participation involves affected population in obtaining the very social licence to operate.

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The Internet of Things and Issues for Mine Water Management

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Abstract
The Internet of Things and the Smart City offer an unprecedented distribution of sensors for the collection of data, including data on water quality. We qualitatively examine this application for mine water monitoring and remediation.

We examine current discussion and deployment to anticipate application of new data technologies relating to water and mining activity.

Keywords: Internet of Things, IoT, Sensors, Water Quality, Wireless

Introduction
Present mine water monitoring systems
According to (Drobniewski and Witthaus 2017), mine water monitoring consists in part of monitoring water level and composition to avoid adverse effects on natural and public life. Understanding the composition and level is done through manual tests with water level probes and samples that are gathered and returned to the surface for analysis. This presents the unique opportunity for integrating real-time sensing in the form of Internet of Things (IoT) devices, capable of providing contemporaneous and repeated measurements, along with networking technologies that can provide infrastructure, fault tolerance, and a communications backbone to surface systems and management.

Overview of IoT trends
Devices that fall into the IoT category include traditional “smart home” devices, such as light switches, locks, cameras, and security devices. However, many additional device classes can be counted, as more control and measurement devices are being found on traditional and industrial network systems, such as SCADA networks (Chikuni and Dondo 2007). As such, many of these interconnected devices are equipped with their own network address, and managed or monitored by a centralized controller which is capable of capturing and processing the data from the networked nodes. This indicates that industrial-application devices can also be considered IoT devices, as distributed sensing and control makes its way into application spaces that were not considered viable just a few years ago.

Capabilities and benefits
IoT devices come equipped with four main functions that distinguish them from ordinary sensors, controllers, or actuators. The first is the presence of a dedicated network interface, using a variety of technologies, such as 802.11 (WiFi), 802.15.4 (Zigbee), or a variety of other infrastructure or mesh network radios (Alliance 2007, Jo Woon, Ho Young et al. 2007). The second element is an external controller that is able to use the network infrastructure to communicate with the IoT device. This can be a combination of dedicated hardware or servers, a dedicated server in conjunction with a mobile device, a dedicated controller with multiple access nodes, or other combinations of systems and interfaces. The third element is an actuation and/or sensing system, which either interrupts electrical circuits, performs measurements via sensors, or has physical outputs that are capable of modifying its environment. Lastly, the fourth component is an integrated microprocessor and software combination capable of intelligently monitoring its state of operation, communicating with the controller, and performing the requested modifications of its physical state so as to serve as a functional device.
Networking
With all four elements present and functional, we must briefly understand how networking fits in to the picture. Most modern wireless networking operates within a reasonable line-of-sight (LOS) set of constraints. Though WiFi and cell networks can easily traverse some structural walls in buildings, sufficient density of building materials or distance from a transceiver will render wireless signals unusable to a connected device due to path loss fading and shadowing. Because of this, there is a substantial caveat for using IoT devices in a strongly-constrained environment, such as a mine, for sensing.

A way to ameliorate path loss and shadowing is through the use of intermediary nodes that act as signal repeaters, effectively bridging the network around obstacles. An entire category of IoT networking technologies permits this to occur, using peer-to-peer, dynamic mesh networking. Several such protocols exist, including 802.15.4, the ZigBee protocol (Akkaya and Younis 2005). Clear advantages exist in the sense that these devices provide infrastructure via their ad-hoc network meshes, as well as fault tolerance by routing requests through as many networks as possible. Thanks to these advancements, along with the careful positioning of repeater infrastructures, we believe that IoT-like devices will easily serve as a new class of monitoring device for mine water management.

Legal Aspects
A regime of safety with the Internet of Things is part and parcel of administrative regulation for ensuring public safety. Governance of cyber-physical systems is squarely within the notion of the information polity, the laws and regulations and practices and procedures that order life in society. The challenge is mapping these within any particular domain from the features and aspects generally of the technology and the regulatory regime (Losavio et al. 2017, Losavio et al. 2018, Losavio et al. 2018). This holds for issues of mine safety and mine water management.

As with information security in particular, public safety begins generally by identifying the elements to be secured; with information systems, and particularly to computers, networks and the Internet we look at characteristics to be secured, such as authenticity, integrity, access control, confidentiality, and privacy. Device safety and reliability is of primary importance generally within the Internet of Things, and critical to systems for mine safety and monitoring. But how that device is used by a person can compromise the devices safety to others. Accountability for misuse may be very important.

(Charou et al. 2010) found from three test sites that the ability to remotely sense and report data can allow for the monitoring and identification of sources of pollution and the areas affected, including changes in land use and water bodies. High-resolution satellite remote sensing data and GIS integrated with geospatial databases were sufficient to provide this for long-term environmental management and monitoring for mining area reclamation.

(Li and Liu 2009) described the effectiveness of wireless sensor networks in underground coal mine monitoring via a mesh sense or deployment. There Structure-Aware Self-Adaptive wireless sensor network (SASA) could detect structure variations caused by underground collapses.

Commentators have begun to realize extraordinary benefits that may be presented by the Internet of Things. (Pickup 2017) noted:

The Internet of Things, especially through wearable technology, will produce extraordinary improvements in productivity and safety. Notable is the SmartCap sensors in a ballcap that can monitor worker fatigue levels via a cellular network, anticipating future technologies for worker health and safety. Another area of development is the integration of location and environmental monitors for ventilation and devices for equipment maintenance.

Mielli (2013) opined that the Internet of Things within the mining space might be seen as an extension of industrial control systems integrated into a broader area of operations for the mine (if not all). These would include the miners themselves, their equipment and censorious for activities within the mine.
These would enhance mine safety, including via environmental response monitoring and enhance efficiency by the optimization of activities. And as with the Smart City integration, this would provide for “Smari Asset Management” to monitor and optimize the use of capital-intensive systems within the mine.

Most optimistic are the comments of Alexandre Cervinka, founder and CEO of Newtrax, that the future of mining was here with the Internet of Things (Newtrax 2018). He found that the most important aspect of IOT implementation was the real-time monitoring of activities, including ecological and environmental issues of mine ground, air and water. IOT will also offer better systems management of machines and safety for personnel via the expanded deployment integration of sensors and the analytics to best utilize that data to identify efficiencies, risks and benefits.

IoT Devices and Sensing
As mentioned in the Introduction, wireless sensor network devices that fit into the IoT realm must feature four components that indicate their adherence to the IoT space. According to (Drobniewski and Witthaus 2017), modern sensing systems for mine water quality monitoring can be in the form of installed probes, based on modified deep-sea observation devices. As they are large devices, these systems are excellent candidates to be retrofitted with mesh networking technologies that would permit distributed monitoring of a number of mine water sites of interest. When properly equipped with repeater technologies, these probes would be capable of producing self-sufficient networks that can route data reliably from probe to destination controller, as well as route back the necessary control and monitoring commands that are needed to keep the probe operational. As such, these probes can be modified to meet all four conditions of IoT device characteristics, provided server architecture is provided.

Wireless Sensor Networks and Power Infrastructure
To expand on the coverage concerns related to path loss and shadowing, underground mines present a unique connectivity challenge, as rock and soil is not typically an easy barrier for wireless networks, particularly if the content of these obstacles is ferrous. We propose that each mine is a unique case, and that there exists no “one-size-fits-all” networking technology that is applicable to each case. For instance, in surface-based mines, where the water quality is easily observable above-ground, traditional infrastructure-based networks may be sufficient. However, in underground environments, both monitoring nodes and network repeaters must be presented in such a way that data is reliably sent and received. This carries further complications that power supply may not be readily available, both to the measuring instruments (which are IoT devices), and/or to the repeater nodes.

A variety of networking technologies exist to solve these problems. For instance, the ZigBee protocol is both a long-distance and a low-power network architecture, which needs only minimal power to operate (Alliance 2007). ZigBee can operate in both infrastructure and mesh networking modes, which means that the low power consumption makes it ideal for battery-powered devices. Furthermore, network routing protocols, such as the Ad-hoc On-demand Distance Vector routing protocol (Perkins and Royer 1999), means that nodes are able to “find” each other every time a datagram must be sent from node to controller or vice versa. These “on-demand” methods are well-suited to systems that have infrequent traffic, such as mine water monitoring systems, and can thus serve as applicable candidates to modernize data acquisition and control in otherwise difficult operational environments.

Network Security
Of course, each networked node serves as a potential access point for unauthorized access. Mine water monitoring, because it can be relatively infrequent compared to traditional computer and mobile networks, can be protected via a number of systems. The first of these is an anomaly-based intrusion detection system. Work by (Lauf, Peters et al. 2010) has demonstrated that anomaly detection is effective in determining when intrusions have taken place in systems exhibiting periodic
behaviors. Furthermore, with the advent of formal verification methods, as shown in [Sabraoui], the network nodes themselves can classify and understand verified and validated data and commands which can only be transmitted by valid software and network combinations. Security aspects exist anywhere that a wired or wireless system is present. However, we also believe that proper protocol and security service integration can provide sufficient protection for these application-specific network technologies, provided that the protocols and software are regularly maintained and updated when vulnerabilities are discovered.

**Legal Concerns**

A regime of safety with the Internet of Things is part and parcel of administrative regulations for ensuring public safety, of which the regulation of the extremely dangerous internal environments of mining and the external damages collateral to mine operations are vital. Governance of cyber-physical systems is squarely within the notion of the information polity, the laws and regulations and practices and procedures that order life in society. The challenge is mapping these within any particular domain from the features and aspects generally of the technology and the regulatory regime. Public begins generally by identifying the elements to be secured; with information systems, and particularly to computers, networks and the Internet we look at characteristics to be secured, such as authenticity, integrity, access control, confidentiality, and privacy. Device safety and reliability is of primary importance generally within the Internet of Things, and critical to systems for mine safety and monitoring. But how that device is used by a person can compromise the devices safety to others. Accountability for misuse may be very important.

And these map between elements of a program for information security and the security components of criminal and civil justice. Prevention is promoted by the criminal justice goals of deterrence, rehabilitation and incapacitation of the human offender; similarly, money damages within the civil justice system encourage accountability. Rehabilitation in particular may support detection and recovery as the skills of the rehabilitated offender are used in monitoring and analysis of the effect of attacks.

Yet the public and private information spheres itself continues to grow and grow, creating new risks and opportunities. This can be seen in the various both internal and external deployments of sensors relating to mine activity and potential wealth of actionable data from the Internet of things deployed within and without mining environments.

Table 1, below, notes the various sensors and data from mine systems that may integrate with the Internet of Things.

If we consider the relative data spaces between that which is “private” and that which is “public,” eg., the data which is extant, aggregated and subject to analysis, we have an evolving situation of danger relative to these data spaces.

This identifies both the richness and benefits of the IOT deployment within mines and mining environments as well as regulatory issues that must be faced. Within either the civil or criminal justice system, it is essential that system testing assure reliability. Failure of these critical systems as to internal mine safety and external mine water environmental damage will, at the least, expose the mining enterprise and makers of the IOT mine systems to civil liability (monetary damages). Given the exceptionally dangerous environments, inside and out of the mine, failure of these systems that leads to death or serious physical injury can lead to criminal liability for those same parties as well as anyone using the systems who either intentionally or through gross negligence fails to use them to ensure minor and environmental safety.

It is important to consider the privacy implications of the deployment of these systems. While deployment within a mining environment may generally avoid privacy concerns, use of the data generated may raise questions of liability. But as the systems may also be deployed externally in relation to environmental monitoring, that data may begin to intrude into private spheres of the community for which there is no clear demarcation of both proper conduct and potential legal liability.
Lastly, it is vitally important to consider the liability for the failure to implement these systems. As the power and utility of IOT for mines increases while the cost to decrease, from the cost of sensors and networks to the cost of the analytics, mining operators will have difficulty justifying a failure to use them. Where these technologies could’ve avoided death, serious physical injury and environmental devastation, a callous failure to deploy them only held against the mine operator and be indicative of their liability for injuries to others. The 2019 Vale Brazil mine dam failure demonstrates the huge human and environmental cost in system failures that could have been avoided.

**Conclusions**

The sensor networks contained within the Smart City paradigm may be used to address water management and monitoring issues. The deployment of IOT in mining is only now beginning, with primary focus on operational safety and improved efficiency as part of the Industrial Internet of Things. Mine water issues are not yet primary concerns for the use of this technology.

Given the utility of the Internet of Things and the benefits for water management seen in the Smart City paradigm, the industrial Internet of Things as deployed for mine water management they offer substantial advantages in time, cost and efficiency. The deployment of inexpensive sensors, independent or part of wider sensor arrays, can provide real-time monitoring of conditions, including at upstream points we are rapid remediation may be possible. The lessons from general IOT deployment in mining are equally applicable for mine water management can inform system design.

Properly integrated, the Internet of things will allow great advances in the management of wine water and environmental issues as well as the improvement of minor safety and mine efficiency.

**Acknowledgements**

The authors thank Perm State National Research University for hosting this conference and giving us the opportunity to develop these ideas. The authors, in particular, we thank Prof. Svetlana Polyakova for her work in administering this conference and advising us regarding it.

**References**


**Table 1 - Data Life in the Mine and Mine Environs**

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Data</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-person miner IOT devices</td>
<td>data alert, environment monitoring, service, navigation, tracking.</td>
<td>Direct-Location, mine environmental conditions, miner health</td>
</tr>
<tr>
<td>Capital equipment IOT devices</td>
<td>speed, acceleration, braking, safety device usage, vehicle status, operational status</td>
<td>Direct-Location, use activity, potential criticalities</td>
</tr>
<tr>
<td>Telephony/ messaging</td>
<td>Telephony activity</td>
<td>Direct-associations, content, activity</td>
</tr>
<tr>
<td>Internal Security Cameras</td>
<td>Identification, time, location, mine activity</td>
<td>Direct-Location, identification, actions, associations</td>
</tr>
<tr>
<td>Public Security Cameras</td>
<td>Identification, time, location data, external products</td>
<td>Direct-Location, identification, actions, associations</td>
</tr>
<tr>
<td>Internal Sensor Network</td>
<td>Mine environmental activities, personnel and equipment action</td>
<td>Direct-external environmental status, identification, location</td>
</tr>
<tr>
<td>External Sensor Network</td>
<td>Environmental activities and downstream effect</td>
<td>Direct-external environmental impact</td>
</tr>
</tbody>
</table>
Mielli, F. (2013). “The Internet of Things (IoT) and… Mining operations?”.
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The models for the description of highly mineralized brines behavior in surface water bodies

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Abstract
One of the most widely used approaches to the disposal of wastewater, including mine water, is to remove them to surface water bodies in order to reduce pollutant concentration due to dilution process. Most of the dilution methods are based on evaluation of mixing processes with neutral buoyancy while the behavior of heavy highly mineralized brines is fundamentally different. For this reason, most of traditional methods for calculating the dilution which regulate the procedure for the discharge of wastewater to surface water bodies are incorrect. This paper discusses new approach based on hydrodynamic models in 3D formulation in non-hydrostatic approximation.

Introduction
Today one of the world’s largest Verkhnekamsk potash and magnesium ore deposits is being actively developed. The main production facilities for the development of this field are located within the Solikamsk-Berezniki industrial hub. Until recently, only PJSC Uralkali was engaged in the development of the field, but at present other large companies are actively involved. As a result, the total production volume can reach more than 20 million tons per year. With the current enrichment system adopted at the considered potash enterprises, the specific volume of excess brines is about 1 m\textsuperscript{3} per ton of final products (Lepikhin 2012). Such high production volumes, with the current technologies, will inevitably have a substantial environmental impact, its individual components. Surface water bodies are subject to the greatest load, which is related to the specifics of the adopted technological process of both ore mining and extraction of useful components from it. The task of minimizing the effect of such a large amount of polluted wastewater forms one of the main environmental problems of the Perm region.

This task is strongly complicated by the fact that the behavior of discharged highly mineralized brines differs qualitatively from that of the sewage with neutral buoyancy. Because of that, traditional methods for calculating the dilution processes presented in regulatory documents governing the procedure for the discharge of wastewater to the surface water bodies are incorrect. Our investigations have shown that the discharge of excess brines without their effective initial dilution, due to their high density, results in a significant inhomogeneity of the pollutant depth-distribution in the Kama reservoir. In some areas of the Kama reservoir, the concentration of pollutants in the bottom area is more than an order of magnitude higher than that in the surface horizons. This creates a real danger not only for habitat of benthic hydrobionts, but also for water supply systems. Since the end caps of water intakes, due to the need to ensure their work during the deep winter low water period, are located, as a rule, at a considerable depth, a danger to their stable work is created.

The hydrological regime of the Kamsky reservoir changes very substantially during the year, particularly, the flow rate defining the intensity of hydrodynamical processes in reservoir could vary in more than 20 times. In these conditions, numerical simulation on modern supercomputers becomes the main tool for solving the considered problem.
the present paper we discuss the validity and efficiency of different models and methods for the description of highly mineralized brines behavior in surface water bodies using the example of the Kamsky reservoir. New, very efficient computational technology, combining the calculations in 1D, 2D and 3D formulations, is suggested. The models are verified using the comparison of calculated mineralization fields with the results of field measurements of distribution of specific electric conductivity of water.

**Dilution models**

In order for dilution models to be sufficiently effective, they must account for the characteristic features not only of water bodies, but also of the effluent itself. Taking into account that the Kama river (Kama reservoir) in the area of the Solikamsk-Berezniki industrial hub has a very complex hydrological regime, being a zone of variable backwater from the Kama hydroelectric station, and the withdrawal brines are characterized by high density, substantially higher than the density of fresh water, a three-level modeling scheme of the processes under consideration was adopted. This three-level scheme has been successfully applied to solve a wide range of water quality formation problems in reservoirs, taking into account density stratification effects (Lyubimova 2010, Lyubimova 2014, Lyubimova 2016, Lyubimova 2018).

The first level is a hydrodynamic model, built on the basis of the Saint-Venant system of equations in one-dimensional formulation for the site covering the entire Kama reservoir from Tulkino to Kama HES with a length of 350 km. For its numerical solution, the software product HES-RAS v.4 was used. As the boundary conditions for this model we used the flow rate in the input section of the Kama river (at Tyulkino settlement), flow rates of the major tributaries: Yaiva, Kosva, Inva, Obva, Chusovaya, Sylva rivers, and water level (and/or flow rate) in the Kama HES upstream. As a result of the calculations, the distribution of the hydraulic characteristics of the flow for the entire computational domain is obtained. On its basis, the boundary conditions for the second level model are estimated.

The model of the second level is based on a well-studied system of shallow water equations, including the system of the momentum equations of shallow water momentum and the continuity equation in a two-dimensional formulation. For the numerical solution of this system of equations, the licensed software product SMS v.10 (SMS Tutorial 2006) was used. As the boundary conditions for this model, the flow rate at the upper gauge and the water level at the lower gauge are specified. The morphometry of the computational domain was determined on the basis of our detailed bathymetric investigations. This model was developed for the upper part of the Kama reservoir and includes all the main sources of pollutants from the water users of the Solikamsk-Berezniki industrial hub. A characteristic feature of the studied water body is its complex morphometry. For its adequate setting, the computational grid included more than 40 000 elements. In modeling pollutant transport processes, the flow rate of the discharged brines and the content of pollutants in them were used as input data. At the same time, the calculated parameters themselves, primarily the characteristics of the velocity field, obtained on the basis of this second level model, determine the boundary conditions for the third level model.

In the general case, the use of transport models in the two-dimensional approximation is sufficiently correct, if the discharged wastewater does not form substantial areas with substantial density stratification in water bodies. Otherwise, it is necessary to use transport models in the three-dimensional approximation. These models, because of their much greater complexity, are less frequently used in solving problems of the assessment of anthropogenic impacts on water bodies.

**Modeling of the transport of highly mineralized brines in the three-dimensional approach**

A characteristic feature of discharged excess brines is their substantial mineralization (about 300 kg/m$^3$) and, accordingly, high density (about 1200 kg/m$^3$). Due to the suppression of vertical turbulent pulsations,
heavy brines can propagate to considerable distances without decreasing markedly concentrations. To study the effect of density stratification on the processes of dilution and transport of highly mineralized brines, modeling was carried out within the framework of the three-dimensional approach. The discharge of excess brines from a slit-like discharge outlet near the surface oriented across the river bed was considered.

The calculations were performed using the commercial package ANSYS Fluent, which implements the finite volume method. A k-ε turbulence model was used. The equations for turbulent kinetic energy and dissipation rate took into account the contribution of density stratification effects. A detailed description of the calculation algorithm can be found in (Lyubimova 2010, Lyubimova 2014, Lyubimova 2016, Lyubimova 2018).

The computational domain was a rectangular parallelepiped containing one source in the form of a rectangular water outlet with the height equal to 1 m and width equal to 1 m located at the surface of the water body in the center of the computational domain relative to the side walls. The height of the computational domain was 10 m, width 40 m, length 300 m.

At the lower boundary of the computational domain corresponding to the bottom, the no-slip conditions and the absence of impurity flux were set. The upper boundary of the region corresponding to the free surface of the fluid was considered undeformable; the conditions for the absence of a normal component of velocity and tangential stresses, as well as the condition for the absence of an impurity flux were set on it.

At the input of the computational domain, a uniform over cross-section velocity of the main stream, having one non-zero component, and a constant concentration equal to the background concentration of the impurity in the river were set. At the exit, the boundary conditions of the vanishing of the derivatives with respect to all variables were set. At the outlet a constant brine flow rate and impurity concentration were set. On the lateral boundaries of the computational domain, the conditions for the equality of the zero derivative of the velocity along the normal and the absence of impurity flux were set.

We considered the quadratic density dependence on concentration, constructed for the brines of potash enterprises (Vostretsov 2008): $\rho(c) = 999.993 + 0.6678 c - 0.00001229 c^2$ ($c$ is the brine concentration, g/l), while the density changes in depth reached 10%. As the initial state, the background concentration and velocity of the main flow were uniformly distributed over the flow cross section.

The calculations were carried out in the framework of the unsteady approach.

The grid was built using the Gambit 2.4.16 program, while the computational domain was divided into cells with the decrease of grid cell size near the outlet. The main calculations were carried out using a grid consisting of approximately $4 \times 10^5$ elements.

When carrying out model calculations, the discharge velocity was taken to be $U = 1$ m/s, the main flow velocity was $V = 0.1$ m/s, the salinity of the withdrawn brines varied from 1 to 300 g/L, the background salt concentration in the receiving reservoir water was taken 0.2 g/L.

Calculations showed that brine dilution processes differ substantially from hydrodynamically passive impurities dilution. As can be seen from Fig. 1, there is a substantial non-uniformity of the distribution of the impurity in depth: a heavy impurity accumulates at the bottom and, due to the occurrence of a “blocking” layer, is carried by the flow, almost without decreasing concentration, for very large distances.

For comparison, we present in Fig. 2 the results of calculations for the case of neutral buoyancy, when the density of the discharged brines coincides with the density of water in the river.

When organizing the release of wastewater in the warm period, when the water area of the Kama river is not covered with ice, the location of the outlet near the surface is of considerable interest when it is much easier to organize the initial dilution. The performed model calculations for this scheme of organization of the outlet are presented in Fig. 3.

As follows from the presented results, at high concentrations of discharged brines
without special measures in the bottom areas, stable zones of unacceptably high pollution will be formed, propagating to long distances.

**Conclusions**

As a working tool for evaluating the efficiency of various brine removal schemes, a complex hydrodynamic model of the Kama river (Kama reservoir) has been developed on the basis of a combination of one-, two- and three-dimensional formulations. Near brine releases, the calculations are carried out within the framework of a three-dimensional model, taking into account the substantial
inhomogeneity of the calculated parameters over the depth. At larger distances, when the concentration of contaminating ingredients is more homogeneous in depth, it is most efficient to use models in a two-dimensional approximation. At the same time, the results of simulation in two-dimensional approximation determine the boundary conditions for the model in three-dimensional approximation. In turn, the boundary conditions for the model in two-dimensional approximation are determined on the basis of model calculations in the framework of one-dimensional approximation.

Figure 3 Behavior of highly mineralized brines in the reservoir-receiver at different concentrations of the discharged brines \((c=100, 50, 5, 1 \text{ g/L})\). Velocity of flow in water body is \(V=0.2 \text{ m/s}\).
of the chemical composition of water. At the same time, traditional systems for organizing scattering water outlets require substantial adjustments.

It is important to work out the configuration of the scattering water outlets most effective for specific structural conditions on the basis of three-dimensional hydrodynamic modeling.

References


Abstract
There are a vast number of abandoned old flooded mines in Europe, with inadequate information of their current status. Exploring and surveying such mines is both unfeasible and hazardous for human divers. UX-1 is an autonomous robotic platform for survey and exploration of such mines. In this work, we present the design, implementation and testing of the guidance and navigation system of UX-1. The system has been tested using a software-in-the-loop and hardware-in-the-loop techniques, and in a real mine environment.

Keywords: underwater robots, flooded mines, mine exploration

Introduction
The total number of flooded mines in Europe is unknown. The estimations range from 5000 up to 30000. Many of such mines may still have considerable amounts of raw materials and minerals that were disregarded during the operational lifetime of the mines due to low commercial value that made their further exploitation economically unfeasible. An example of these materials is fluorite, which until recently was considered a waste mineral in many lead-zinc mines but now is on the EU list of critical raw materials (European Commission, 2017). The dependency on the import of the raw materials, geological uncertainty, growing costs of exploration, technological and economic feasibility of mine development are problems for which the EU is actively trying to find a solution.

After the discontinuance of mining activities, the maintenance systems stopped, the dewatering pumps were turned off and if there was no drainage system present, the closed mines tended to get flooded. The database developed by European Federation of Geologists (EFG) counts 8174 flooded metallic mines deeper than 50 meters, distributed in 24 different European countries. The last available information regarding the status and layout of many of those mines dates from decades (and in some cases from even more than one century) ago, resulting in a rather incomplete and imprecise data.

Additionally, the depth of those mines poses severe limitations on the possibilities of their exploration, since human cave diving can be dangerous or even lethal in harsh deep mine conditions.

For the above mentioned reasons, robotics imposes itself as a good solution for a non-invasive flooded mine exploration. By using an autonomous robotic system for gathering valuable geoscientific and spatial data, the strategic decisions on re-opening abandoned mines can be supported by real data which cannot be gathered in any other way.

The serious development of autonomous underwater vehicles (AUVs) began in the 1970s. They have shown a big potential for a variety of tasks, including oceanographic surveys, sea floor mapping (Iscar et al. 2018) and air crash investigations, such as the use of AUV ABYSS and Bluefin-21 AUV in search of missing airplanes Air France Flight 447 and Malaysia Airlines Flight 370 (Geomar 2009; LeHardy 2014). Most of the mentioned applications relate to open water environment, which imposes almost no restrictions on the size and shape of the robot.

One of the first autonomous system to explore and map a subterranean cavern was DEPTHX robot. During its deployment in 2007 the vehicle explored four cenotes in Sistema Zacatón in Tamaulipas, Mexico (Gary et al. 2008). The operating environment allowed the limitation-free design with no
The project UNEXMIN investigates the utilization of the capabilities of a fully autonomous underwater vehicle for exploration and 3D mapping of flooded mines. Considering that the dimensions of the tunnels can be as narrow as 1.5m, the robot must be small and have high maneuverability to be able to navigate through them. The developed UX-1 is a robot specifically tailored for abandoned mine exploration, designed taking into account the aforementioned space limitations (Figure 1). The robot needs to be able to fit into small mine openings, to resist high pressure when operating at a certain depth and to avoid getting entangled with obstacles such as ropes or cables encountered during the operation. The main characteristics of the UX-1 robot are briefly outlined in Table 1.

Autonomous mapping of underwater mines is a relatively new and challenging task. The main problem is the localization and navigation due to the attenuation of Global Positioning System (GPS) and radio-frequency signals. These limitations coupled with the harsh and unstructured nature of the underwater environment are the cause of the limited number of real working robots for the case of mine exploration.

This paper describes the navigation and guidance software architecture embedded in the UX-1. This system has been tested in a controlled environment using a software-in-the-loop (SIL) and hardware-in-the-loop (HIL) techniques, and in the real mine.

**Robot hardware architecture**

The mechanical design of UX-1 is chosen to meet certain requirements, to wit: high maneuverability, minimum drag, reduced size, and long autonomous missions (Zavari et al. 2016). Its spherical shape of 60 cm in diameter is chosen in order to satisfy the two first requirements. Furthermore, the spherical design allows translation symmetry in all directions without changing the heading of the UV. The hull is a machined aluminum pressure hull designed to endure water pressure up to 50 bar. The robot is equipped with a ballast system for driving through long vertical shafts up to 500 m. Moreover, the robot has a pendulum system which uses substantial restrictions on the size of the robot.

![The UX-1 robot.](image)

**Table 1 Characteristics of the UX-1 robot.**

<table>
<thead>
<tr>
<th>Features</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hull dimension</td>
<td>Sphere 0.6 m diameter</td>
</tr>
<tr>
<td>Weight</td>
<td>≤ 106 kg</td>
</tr>
<tr>
<td>Maximum speed</td>
<td>0.5 m/s</td>
</tr>
<tr>
<td>Maximum operating depth</td>
<td>500 m</td>
</tr>
<tr>
<td>Maximum pressure</td>
<td>50 bar</td>
</tr>
<tr>
<td>Autonomy</td>
<td>≤ 5 hours</td>
</tr>
</tbody>
</table>

*Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)* 691
batteries as weight to produce the pitching movement which is otherwise not possible with the current thruster configuration.

The instrumentation that the robot carries can be roughly divided into two categories: navigation equipment necessary for basic robotic functions and scientific instrumentation for collecting geological data. The first group includes thrusters, an inertial measurement unit (IMU), a Doppler Velocity Log (DVL), a structured light system (SLS), a multibeam profiler sonar (Kongsberg M3), pendulum and ballast systems, batteries and a computer. The second group contains a water sampler, conductivity and pH measuring units, a sub-bottom profiler, a magnetic field measuring unit, UV fluorescence imaging and multispectral imaging units. As it can be noted, only indirect geological data collection methods are included, due to the special environmental characteristics that make it impossible the direct contact with the surrounding of the probe. The detailed configuration of the sensor instrumentation is out of the scope of this paper.

Robot software architecture

The software is organized modularly into four modules: Sensor Fusion (SF), Simultaneous Localization and Mapping (SLAM), Low-Level Control (LLC), and Guidance, Navigation and Control (GNC), whose interactions are depicted in Fig. 2a. Each module is developed by a different team of developers, so special attention has been devoted to the interface between them to ensure a smooth integration. We refer the reader to the Deliverable 3.1 of the project for further details.

The Robot Operating System is chosen as a middleware (an abstraction layer between the hardware and the software) due to its modularity, good hardware support (drivers) and its messaging system which simplifies the communication between different modules of the software.

The SF module is responsible for providing pose and perception, while using the components of SLAM module. Internally, this module is composed by three submodules: Pose Estimation, Sensor Perception and Data Acquisition and Registration (acquiring the data from all the sensors).

The SLAM module receives Pose and Perception information (provided by the SF module) and provides corrected map data and global localization of a robot.

The LLC module is a simple module consisting of two monolithic programs running the two microcontrollers which, according to the low-level commands received, directly control the actuators.

The GNC module will be explained in the next section and the rest of the paper will be focused on this module, in particular, the robot autonomous guidance and navigation system.

Guidance and Navigation Software Architecture

In order for a robot to accomplish a task, it needs to “understand” the environment, i.e. what it looks like and where the robot is therein. A map is a representation of the environment and it should contain enough information for a robot to accomplish the tasks of interest.

The GNC module has four main submodules: Mission Planner, Guidance, Navigation, and Control. These submodules depend on the Sensor Fusion and the SLAM from which the GNC module obtains the map, robot pose, and robot global
localization. In Fig. 2b a simplified diagram of the GNC module architecture is depicted. The rest of the paper focuses on the first three submodules; the Control module is out of the scope of this paper.

The Mission Planner is the highest level submodule in charge of configuring the overall strategy. This module takes as an input a set of planned actions, which depend on whether the mine has already been explored and mapped. In the case of an unknown map, the action is explore, and if the map is known and available, the action is go to point. The go to point action is comprised of a goal location and possibly a science goal, such as water sampling or gamma-ray measuring. The actions are fed sequentially into the guidance submodule.

Guidance submodule has different behaviors depending on the action. In the case of the go to point, this submodule extracts the goal location from the action. If the action is explore, the goal location is computed taken into account constraints such as the duration of the mission and/or spatial coverage. Once the goal location is known, the submodule plans the trajectory to move the robot from the current to the goal location taking into account the kinematic restrictions of the robot and the positional requirements of the scientific data collection action. An example of a scientific data collection action imposing a specific positional requirement is multispectral image capture, which requires maintaining a certain distance to the mine wall during the operation.

The calculated trajectory in a form of waypoints is further sent to the Navigation submodule. This submodule generates velocity profiles, i.e. a waypoint and the information on how to traverse it with respect to time, which are finally transformed into low-level control commands by the Control submodule.

In Figure 3, a high level description of algorithmic steps performed by the Mission Planner, Guidance and Navigation submodules is depicted.

Results

Testing the described software architecture is challenging because of its complexity and various groups being involved in its development making the robot not always available for each group. Furthermore, real experiments can be expensive, time-consuming, dangerous, or even impossible to test under all conditions. Therefore, in order to evaluate our GNC module we have performed a series of tests gradually increasing the complexity of them. Firstly, using a Software-in-the-loop (SIL) technique, then Hardware-in-the-loop (HIL) and finally in a real mine. In Fig. 4, a visual description of the SIL and HIL is depicted.

For the SIL tests, the simulated modules are SLAM, SF, and LLC. Gazebo simulator\(^3\) is used for modeling the dynamics of the robot and the sensor data. All the inputs to the GNC modules are simulated and its output, LL commands, is sent to the Gazebo which controls the simulated robot. The advantage of the SIL is possibility to test GNC module with various mine structures without having the real robot in our hands.

For the HIL tests, the actual robot is used and the experiments were performed in the pool with the dimensions 10×6×5 m. The simulated module is SLAM and partially SF, while the LLC is real. The real inputs to the GNC module are LL feedback and robot position. The sensors related to the map building are simulated and its readings are inputted from Gazebo. The advantage of this tests is using the real robot in the controlled environment with low risks of damaging the equipment while bypassing the readings of some sensors for map building in order to simulate different mine structures.

In Fig. 5, two examples of different mine structures are shown. The structure on Fig. 5a has been used for the HIL tests and is designed as a scaled prototype of the uranium mine Urgeirica in Portugal with the dimensions fitting the available pool for testings. The structure on the Fig. 5b has been used in the SIL tests which poses no limitations on the size of the mine structures. It represents a real sized mine Kaatiala in Finland where the first field trials took part.

In Fig. 6 an example of the trajectory planning is depicted. In Fig. 6a, a current

\(^3\) GAZEBO http://gazebosim.org/
Conclusions and Future Work
This paper introduces the autonomous robotic platform UX-1 developed in the European project UNEXMIN for underwater exploration of flooded abandoned mines. Special emphasis is placed in the link between the stringent operational conditions that such a hostile environment represents and the decisions, regarding both the physical characteristics of the robot and its software architecture, made during its design phase.

The details provided in this paper focus on the submodules responsible for robot guidance and navigation, and on the different incremental frameworks deployed to test them. In such incremental test frameworks different parts of the architecture of the complete robotic platform are substituted for simulations, allowing therefore to test all the

Figure 3 High level description of the Mission Planner, Guidance and Navigation submodules.

Figure 4 SIL and HIL.

Figure 5 Mine structures used in (a) Hardware-in-the-loop and (b) Software-in-the-loop testings.
interactions and communications between the guidance and navigation submodules and the rest of modules of the system in different development stages of the complete platform. In this way, testing at three different levels of completeness is designed and run, wherein testing the complete software and hardware platform in a real mine represents the last and final operational level in the development of UX–1. Results of partially simulated architectures and preliminary results corresponding to the complete platform level are presented in this paper. Future campaigns in several abandoned flooded mines are planned (Urgeirica uranium mine in Portugal and Ecton copper mine in UK), which will soon lead to an extensive evaluation of the complete platform in different mines with different peculiarities and specific details.

Acknowledgements

The UNEXMIN project has received funding from the European Union’s Horizon 2020 research and innovation programme under Grant Agreement No. 690008. The authors thank M. Pici for the help with the review of the paper.

References


Figure 6 Example of trajectory planning (a) Current position of the robot (b) Built map and the planned trajectory (c) View without the visualization of the map.
Abstract

This study was carried out on the territory of Verkhnekamskoe potash deposit in the Lyonva Valley. The Verkhnekamskoe potash mining led to accumulation of large quantities of mining wastes negatively affecting the environment. These wastes are mainly presented by the slurry storage facilities, salt tailing piles and brines. Water-soluble minerals were easily weathered and formed drainage water of the Na–Cl composition that polluted groundwater. As a result of ground water salinization, a substantial transformation of soils was observed around potash mining area and in the river valleys. Two types of the transformed soils were defined in that area: 1) saline alluvial gleyed humus chloride-sodium-magnesium-calcium soil; 2) secondary saline alluvial clay-loam sulfate-chloride-sodium-calcium soil.

Keywords: salinization, soil, groundwater and surface water, environmental monitoring

Introduction

Mining activity is associated with the storage of huge volumes of waste that have a negative effect on the environment. At most potash mines, up to 70% of mined rock is stored on the surface as a wastes (Environmental Aspects of Phosphate and Potash Mining 2001).

The solid halite wastes are deposited as tailings piles, that consist of >95% of NaCl. The fines such as clays and the insoluble fraction in the form of clay-salt slurry and excess brines are pumped to slurry storage facilities. The clay-salt slurry is composed of 35-40% of water-soluble salts and 60-65% insoluble clay material. The high total dissolved solid (TDS) concentration of water streams is due to the high content of soluble salts in the salt tailing piles. Brines infiltrate through the slurry dumps and salt tailings piles into groundwater. Salinization of surface water and groundwater in potash mining regions has been studied by a large number of researchers (Arle and Wagner 2013; Baure et al. 2005; Bel’tyukov 1996; Liu and Lekhov 2013; Lucas et al. 2010).

Other substantial issue is soil salinisation due to rising water tables. Salt accumulation in soil layers occurs when the water tables are shallow (particularly <4 m from the surface) and the groundwater salinity becomes progressively higher due to evapotranspiration. Usually this situation occurs in valley floors of the landscapes in arid ecosystems (Rengasamy 2006; Greene et al. 2016; Fitzpatrick, 2008; Salama et al., 1999).

For the healthy ecosystem functioning, the soil must fully fulfill its ecological functions. Technogenic effect such as salinization causes some changes of the physicochemical properties of soil, that leads to transformation of soil, plant and fauna. The main goal of this paper is to investigate the soil salinization induced by the Verkhnekamskoe potash mining.

Study area

Our studies were carried out on the territory of the Verkhnekamskoe potash deposit in the Lyonva Valley (fig. 1).

The study area is situated on the left bank of the Lyonva River in the vicinity of slurry storage. The slurry storage site came into production in the mid-1970s. A clay-based seal was used to protect groundwater aquifers from contamination. The large amount of precipitation, rugged topography, and cold climatic conditions promote active migration of water-soluble salts into the groundwater.

Effluents seeping through the bed of the slurry storage site were discharged directly into the underlying Quaternary (Q) and Sheshminsky (P1ss) and led to groundwater
salinization (Na–Cl type, mineralization of 5.9–29 g/L) (Khayrulina and Maksimovich, 2018). When saline groundwater met confining beds, it seeped to the surface in the river valleys and polluted surface water and soils.

**Methods**

In seepage areas in the Lyonva River valley, soil samples were taken in soil profile cuts in 2017 year. The morphological and physicochemical methods were used to assess the ecological state of the soil.

Morphological analysis was carried out according to classification and diagnosis of soils of Russia (2004). Physico-chemical analysis of soils included:

- Soil pH was analysed by pH-meter. Soil organic matter was determined by wet-combustion Tyurin method (Theory and practice 2006).
- Soil acidity was determined by the Kap-pen method, based on treating of soil sample with sodium acetate in concentration 1 mol/dm³ and then titration of soil extract with alkali solution.
- Exchangeable cations was determined by the Kappen-Gilkowitz method, which is processing of soil samples with a certain amount of 0.1 N HCl and then titration of soil extract with 0.1 N NaOH (Theory and practice 2006).

- Cation exchange capacity (CEC) in carbonate samples were determined by the barium chloride method (Theory and practice 2006).
- Mobile phosphates and potassium were determined by Kirsanov method (Theory and practice 2006), based on the extraction of mobile phosphates and potassium from the soil with a solution of 0.2 M HCl. Then mobile phosphates were determined as a blue phosphorus-molybdenum complex on a photoelectrocolorimeter and potassium – on flame photometer (Mineev, 2001).

The quantity and quality of soluble salts were determined in water extractions of soil samples, followed by determination of anions and cations. Carbonates were determined by back-titration with sulfuric acid; the Na⁺ concentrations in water extraction were determined by flame photometer; and concentrations of Ca²⁺, Mg²⁺ were determined by titration method with Trilon B (disodium dihydrogen ethylenediaminetetraacetate); sulphate ions calculated as a difference between the amounts of cations and anions (Mineev, 2001).

**Result and Discussion**

In the floor of the Lyonva River Valley we two transformed soils were observed instead of zonal alluvial humic gley soils. The first type
of soils was a saline alluvial gleyed humus chloride-sodium-magnesium-calcium soil consists of three horizonts and covered by vegetation, dominated by the graminaceous and umbrella species. A top 20 cm was a gray-humus horizon AYrs (colour is gray-brown). It was densely intertwined with roots at the depth of 10 cm, and the roots were rare below 10 cm. The soil colour became darker at the depth of 14 cm and soilstructure was cloddy. A pale gray color and rust-stains were observed from the depth of 18 cm. Gleyed soil Cg was formed in the depth of 20–70 cm. This horizon had a brown colour, rust-stains and iron-manganese nodules. An alluvial gleyed horizon CG with bluу-grey colour and rust-stains was identified from the depth of 70 cm. Then the colour became blue-grey without rust-stain below 100 cm.

Soil chemistry revealed the salt load linked to a high mineralized ground water. The highest ion concentrations (instead of HCO₃⁻) were detected in low horizon at the depth of 70–80 cm (tab. 1). The soil water extract had much higher levels of Cl⁻ and Na⁺.

A second type of transformed soil was secondary saline alluvial clay-loam sulfate-chloride-sodium-calcium soil were formed in the seepage areas in the floor of the Lyonva River Valley. The top layer (=3 cm) was an iron-bearing crust without any vegetation. A gray-humus horizon AYs (3-15 cm) consisted of black gel-like phasis with a high content of plant residues. A gley loamy horizon G (15-70 cm) had a gray colour with rust-stains

The content of water-soluble ions in the second type of soil substantially exceeded their amount in the first soil. In a layer of 0–3 cm, The maximum content of water-soluble ions was observed (tab. 2) in the top layer of the second type of soil, that decreased slightly with depth. These extremely high ion concentrations are associated with salt waterlogging.

The soils were characterized by a high CEC. Its variability depends on the difference in the amount of organic carbon and in the particle size distribution (tab. 3). There was a substantial variation in the content of nutrients, for example, a very high content of potassium and phosphates were detected on the top layer of the second type of soil.

### Table 1
Ion composition of the water extract from the alluvial humus gleyate chloride sodium-magnesium-calcium saline soil.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Depth</th>
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<tbody>
<tr>
<td></td>
<td>5-15 cm</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>76.0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>20.4</td>
</tr>
<tr>
<td>Na⁺</td>
<td>39.1</td>
</tr>
<tr>
<td>K⁺</td>
<td>7.8</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>11.6</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>330.1</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 2
Ion composition of water extract from the saline secondary sulfate-chloride sodium-calcium

<table>
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<th>Ion</th>
<th>Depth</th>
</tr>
</thead>
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<td></td>
<td>0–3 cm</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>3260</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>720</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2500</td>
</tr>
<tr>
<td>K⁺</td>
<td>9500</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>11</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>14420</td>
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<tr>
<td>SO₄²⁻</td>
<td>8107</td>
</tr>
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</table>
### Table 3 Physico-chemical properties of researched soils.

<table>
<thead>
<tr>
<th>Soil name</th>
<th>№</th>
<th>Layer, cm</th>
<th>С₀rg, %</th>
<th>pH_{H₂O}</th>
<th>pH_{KCl}</th>
<th>CEC</th>
<th>Soil acidity</th>
<th>P₀₂</th>
<th>K₀₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saline secondary¹</td>
<td>1</td>
<td>0-3</td>
<td>5.9</td>
<td>5.91</td>
<td>5.84</td>
<td>71.0</td>
<td>2.5</td>
<td>15.7</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-15</td>
<td>5.8</td>
<td>6.75</td>
<td>6.70</td>
<td>37.3</td>
<td>1.1</td>
<td>0.8</td>
<td>150</td>
</tr>
<tr>
<td>Alluvial soil²</td>
<td>2</td>
<td>0-15</td>
<td>5.4</td>
<td>5.85</td>
<td>5.42</td>
<td>82.7</td>
<td>13.3</td>
<td>3.5</td>
<td>27</td>
</tr>
<tr>
<td>Alluvial soil³</td>
<td>3</td>
<td>0-15</td>
<td>9.8</td>
<td>5.59</td>
<td>5.19</td>
<td>36.2</td>
<td>7.7</td>
<td>3.8</td>
<td>55</td>
</tr>
<tr>
<td>Alluvial soil⁴</td>
<td>4</td>
<td>0-15</td>
<td>1.7</td>
<td>4.31</td>
<td>3.38</td>
<td>64.0</td>
<td>9.4</td>
<td>2.5</td>
<td>15</td>
</tr>
</tbody>
</table>

1 - secondary saline alluvial clay-loam sulfate-chloride-sodium-calcium soil;  
2,3 - saline alluvial gleyed humus chloride-sodium-magnesium-calcium soil;  
4 – alluvial humus gleyate chloride sodium saline soil.

### Conclusions

For the study of the environmental effect of potash mining, the assessment of soil properties is an effective indicator of ecological and geochemical changes in the studied landscapes. The main transformational factor for the soils studied in the river valleys of the Verkhnekanekskoye salt deposit is salinization, which was identified throughout the soil profile. As a result of polluted ground water distribution the zonal alluvial humic gley soils were transformed to saline alluvial gleyed humus chloride-sodium-magnesium-calcium soil and secondary saline alluvial clay-loam sulfate-chloride-sodium-calcium soil. The main causes of soil salinization are a mining subsidence and a rising water table.

### Acknowledgements

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Tyurin IN (1931) Novel transformation of the volumetric method to determine humus using chromic acid. Pochvovedenie. No.5-6, p. 36-47.
Natural Environmental Pollutants in the Black Shale Zones

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Abstract

The main natural sources of water contamination in the areas of black shale rocks in the western slope of the Urals are considered. They are characterized by the presence of various toxic elements due to sorption activity by carbonaceous matter. A substantial increase in their concentrations with the transition to readily soluble forms occurs in the weathered rocks and karst cavities. The latter are eroded by streams, and solutions or suspensions with a high content of toxic elements are transported over long distances. Their most substantial concentrations are found in the clayey weathered rocks (especially for Zn, Hg, Pb, Ni, As, Cu, V). In many parts of the world the territory of black shale rocks are areas of intensive mining activity, the ecological condition of which requires constant monitoring.

Keywords: black shale formation, weathered rocks, toxic and radioactive metals

Introduction

The industrial and mining enterprises are usually considered as the main sources of contamination of natural waters. The latter are widely represented in such mining regions as the Urals and cause the intensive pollution of the environment. For example, substantial masses of toxic elements enter the natural waters and atmosphere in the Urals when developing copper and gold deposits. Difficult environmental conditions are sometimes created due to the air migration of fine asbestos. A high chromium content is observed in the waters of the areas where chrome ores are mined, etc.

Many deposits of diamonds, noble metals, copper, coal and other minerals have already been exploited, but substantial areas remain occupied by mining dumps. Suffice it to note the large areas of waste heaps left after the cessation of the development of a coal deposit in the Kizelovsky basin. There is a diverse complex of toxic elements in the natural waters of these areas.

There are high concentrations of toxic elements in certain areas of the Urals the sources of which are natural objects in addition to the technogenic contamination of natural waters. These include, first of all, specific rocks and mineral occurrences of minerals. O. Gryaznov (2014) shows typical associations of toxic and other small elements in the Urals rocks. In particular, a very wide range of toxic elements (Ta, Nb, Be, Mo, Pb, Zn, Co, Ni, Cr) is associated with alkaline feldspar metasomatites, which are widespread in the Urals.

Many toxic elements are concentrated in sulfides. They are not resistant to chemical weathering agents and are easily destroyed by oxidation, and toxic elements are converted into colloidal or true solutions. Being unstable to chemical weathering agents sulfides dissolve easily, and toxic elements become the components of colloidal or true solutions. Then they are deposited on certain geochemical barriers in the process of migration, where they may be concentrated.

The complexes of black shale formations, widely represented in the Urals, have long attracted attention as a promising source of useful minerals. Black shale rocks contain carbonaceous matter, which is a natural sorbent of potentially toxic metals, including toxic and radioactive ones. The weathered rocks are formed in the process of destruction of black shale rocks, in which the toxic components are accumulated. The weathered rocks are easily eroded by rivers and interseasonal water flows.
A concrete example is the area of the black shale rocks of the Fedotovskaya suite (Upper Riphean) on the western slope of the Middle Urals. This territory is a part of the Gornozavodsky district of the Perm Region with intensively developed mining activities of different profiles, saturated with numerous mining and production wastes. Earlier, gold and diamond deposits were developed on the territory, as a result of which a huge amount of dumps had been accumulated.

Methods
In the process of studying the material composition of the black shale rocks of the Fedotovskaya suite and the weathered rocks overlying them on the western slope of the Middle Urals, the content of toxic metals and radioactive elements was determined using electron probe spectroscopy methods. The JSM 6390LV scanning electron microscope (Jeol) with INCA 350 x-act energy dispersive device (Oxford Instruments) and the X-ray fluorescence spectrometer S8 TIGER (Bruker) are used. The main mineral forms of occurrence for toxic elements and their transformations into secondary products in the processes of chemical weathering have been investigated. In total, about 100 microprobe and over 1800 X-ray fluorescence analyses were performed.

Results
The minerals that carry most of the toxic metals in black shale rocks are sulfides. The mineral with many toxic elements (Ni, Co, As, Sb, Bi, Se) is pyrite. The total content of toxic impurity elements in pyrite is usually 0.3-0.5%, sometimes up to 2-3%. In addition to pyrite, many other sulfides containing toxic elements are presented in black shale rocks (galena, sphalerite, arsenopyrite, cinnabar, cobaltite, etc.) (tab. 1).

The form of occurrence for uranium in the black shale rocks of the Fedotovskaya suite is mainly uraninite, confined directly to inclusions of carbonaceous matter (fig. 1). The presence of uranium and thorium in organometallic compounds is assumed. Mercury is found in the form of droplets of native mercury, amalgams, and as part of aggregates with the participation of gold and silver micro- and nanoparticles. The mercury concentrator is probably carbonaceous as an active metal sorbent. It is also possible for it to enter the deep faults from the mantle during periods of tectono-magmatic activation of the territory (for example, in the Early Mesozoic).

The study of the distribution of toxic elements in the section of black shale rocks allows us to draw the following conclusions. Their concentrations within the black shale strata vary in wide limits, depending on

Table 1 The average content of toxic elements in the sulfides of the black shale strata of the Fedotovskaya suite and detrital weathered rocks, %.

<table>
<thead>
<tr>
<th>Elements</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>18.11</td>
<td>20.36</td>
<td>19.67</td>
<td>15.87</td>
<td>15.19</td>
<td>44.56</td>
<td>53.45</td>
<td>53.41</td>
<td>39.64</td>
<td>34.51</td>
<td>19.66</td>
</tr>
<tr>
<td>Fe</td>
<td>9.29</td>
<td>6.13</td>
<td>4.33</td>
<td>0.60</td>
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<td>36.17</td>
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<td>33.76</td>
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<td>0.48</td>
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<td>0.82</td>
<td>0.84</td>
<td>0.18</td>
<td>0</td>
<td>0</td>
<td>25.59</td>
<td>0.28</td>
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<tr>
<td>Zn</td>
<td>-</td>
<td>-</td>
<td>0.51</td>
<td>0.82</td>
<td>0.17</td>
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<td>-</td>
<td>-</td>
<td>61.27</td>
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<td>As</td>
<td>32.18</td>
<td>42.46</td>
<td>42.26</td>
<td>4.11</td>
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<td>Ni</td>
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<td>0.73</td>
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<td>0.14</td>
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<td>Co</td>
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<td>Bi</td>
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</table>

Amount: 87.42 99.18 98.94 100.01 99.39 96.52 99.67 99.87 98.99 99.69 99.44

Note: 1-3 - cobaltin, 4-5 - galena, 6 - galena in pyrite, 7-8 -pyrite, 9 - chalcopyrite in pyrite, 10-11 - sphalerite.
Analyst B.M. Osovetsky.
the content of carbonaceous matter, the degree of metasomatic changes in the rock, hydrothermal and effusive activities. Metal concentrations decrease sharply in the calcite interlayers. For example, for zinc they are reduced to 16 ppm, instead of the usual concentration, ranging from 66 to 194 ppm (tab. 2).

The processes of substantial redistribution of toxic elements have been occurring in the weathered rocks. At the same time, they are usually insignificant in the detrital weathered rocks of aleurite composition and only for some elements marked changes are noted. Thus, the concentrations of V, Cr, and Co in the detrital weathered rocks are sharply reduced compared with those in the black shale rocks (see tab. 2).

The carbonaceous matter and sulfides are easily decomposed in the weathered rocks of the clay composition, and their components often become an integral part of colloidal solutions. Almost all toxic elements are found here. Galena in the weathered rocks decomposes to form easily soluble corkite \( \text{PbFe}_{3}\left[\text{SO}_4\right]\left[\text{PO}_4\right](\text{OH})_6 \). The secondary pyrite of a colloform structure is also formed in the weathered rocks, in which high concentrations of some toxic metals are observed. Extremely high concentrations of zinc, nickel, vanadium, and lead have been found in individual layers of the weathered rocks (tab. 3).

The active migrant in the clay weathered rocks is mercury. The mineral forms of Hg occurrence are very diverse, including Hg,Sn, Hg,Pb, HgAu and other amalgams. The gold-mercury aggregates with globular structure, which are formed as a result of gradual merging of mercury droplets and

<table>
<thead>
<tr>
<th>Interval, m</th>
<th>V</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Sn</th>
<th>Sb</th>
<th>Pb</th>
<th>Th</th>
<th>U</th>
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<td>2.5-5.0</td>
<td>9</td>
<td>2</td>
<td>0</td>
<td>27</td>
<td>45</td>
<td>74</td>
<td>25</td>
<td>8</td>
<td>6</td>
<td>7</td>
<td>15</td>
<td>3</td>
<td>1</td>
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<tr>
<td>5.0-8.0</td>
<td>8</td>
<td>0</td>
<td>2</td>
<td>20</td>
<td>20</td>
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<td>17</td>
<td>8</td>
<td>6</td>
<td>6</td>
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<tr>
<td>8.0-20.5</td>
<td>49</td>
<td>13</td>
<td>7</td>
<td>32</td>
<td>45</td>
<td>160</td>
<td>15</td>
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<td>11</td>
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<td>61</td>
<td>10</td>
<td>44</td>
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<td>18</td>
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<td>15</td>
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<td>4</td>
</tr>
<tr>
<td>30.5-44.0</td>
<td>58</td>
<td>59</td>
<td>8</td>
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</tr>
<tr>
<td>44.0-46.0</td>
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<td>58</td>
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<td>3</td>
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<tr>
<td>55.4-107.0</td>
<td>87</td>
<td>44</td>
<td>12</td>
<td>49</td>
<td>28</td>
<td>194</td>
<td>19</td>
<td>3</td>
<td>1</td>
<td>36</td>
<td>6</td>
<td>3</td>
<td>17</td>
</tr>
</tbody>
</table>

Note: N is the number of analyses (hereinafter). Analyst K.P. Kazymov.
capturing of micro- and nanoparticles of gold, are characteristic new formations in the clay weathered rocks. On the way to such aggregates, clay, iron, silica, and other substances are also often captured. The fact of the formation of such aggregates is an evidence of the active migration of mercury. The gold-mercury phases gradually decompose with the release of mercury in the native state and in the gas phase, as evidenced by the numerous pores on the surface of the aggregates (Fig. 2).

An important role as an accumulator of toxic elements is played by karst cavities filled with the weathered rock products. They are found in large quantities in carbonate rocks in contact with black shale. There are very few toxic elements directly in carbonate rocks. But in the products of the weathered rocks displaced into karst cavities their concentrations sharply increase (for example, zinc percentage reaches 330 mg/L) (tab. 4).

According to the data of the Gornozavodsky municipal district in the spatial planning scheme for 2008, the Upper Riphean-Vendian aquifer complex is represented by hydrocarbonate and sulphate-hydrocarbonate sodium, calcium and magnesium waters with mineralization of 0.06-0.07 g/L, the upper Riphean-Vendian terrigenous aquiferous complex hydrocarbonate and sulphate-hydrocarbonate magnesium-calcium waters with mineralization of 0.02-0.05 g/L, rarely up to 0.2 g/L, the Klyktan terrigenous-carbonate aquifer complex presents detecting bicarbonate-calcium-magnesium water with a salinity of 0.1-0.3 g/L, complex uneven aquifer intrusive rocks represented hydrocarbonate (sodium, magnesium, calcium) to water with a mineralization 0.1 g/L. The trace element composition of surface waters in the study area is given in table 5.

Conclusions
The zone of black shale rocks on the western slope of the Middle Urals is characterized by elevated concentrations of toxic elements in the weathered rocks eroded by water courses. These natural sources of environmental contamination by the nature of their effect on ecosystems are almost as important as man-made sources.

Table 3 The average content of pollutant elements in the Early Mesozoic clay weathered rocks, ppm.

<table>
<thead>
<tr>
<th>Interval, m</th>
<th>V</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Sn</th>
<th>Sb</th>
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<th>U</th>
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<td>6.0-14.0</td>
<td>75</td>
<td>16</td>
<td>27</td>
<td>111</td>
<td>61</td>
<td>695</td>
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<td>21</td>
<td>15</td>
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<td>4</td>
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<td>6</td>
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<td>4</td>
</tr>
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<td>41.5-42.0</td>
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<td>0</td>
<td>14</td>
<td>23</td>
<td>14</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>17</td>
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<td>1</td>
</tr>
<tr>
<td>44.3-49.3</td>
<td>34</td>
<td>11</td>
<td>0</td>
<td>12</td>
<td>36</td>
<td>21</td>
<td>5</td>
<td>4</td>
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<td>35</td>
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<td>19</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>75</td>
<td>1</td>
<td>3</td>
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<tr>
<td>54.6-59.0</td>
<td>73</td>
<td>10</td>
<td>0</td>
<td>16</td>
<td>18</td>
<td>13</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>22</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

Analyst K.P. Kazymov

Figure 2 Gold-mercury aggregate: A - general view, B - porous surface
Black shale strata are widespread in the world. They are either already areas of active mining or are in the process of economic development. As to the western slope of the Urals, natural sources of environmental contamination can have a substantial effect on the ecological condition of the territory.

An important task is to develop a comprehensive environmental monitoring program in the areas of black shale rocks with an assessment of the contamination level of natural waters and bottom sediments with radioactive and toxic components.

**Acknowledgements**

The authors are grateful to S. Suslov, an employee of Geokarta-Perm JSC, for providing stone material and M. Volkova, K.P. Kazimov, staff of the Perm University Nanomeralogy Sector, for participating in sample preparation operations and performing analytical studies.

**References**


Phylogenetic diversity of microbiota of sediments, water and coastal surface technogenic formations of soda sludge storage (Berezniki, Perm region, Russia) ©

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²Perm State National Research University, Bukireva, 15, 614990, Perm, Russia

Abstract
The phylogenetic diversity of the microbial community was evaluated using metagenomic sequencing. The objects of the study were water, sediments and coastal surface technogenic formations of the soda sludge storage facility of the soda plant “Soda”, Berezniki (Perm region, Russia). The bacterial communities of the all samples were dominated by representatives of two classes: Bacilli and Gammaproteobacteria. At the same time, differences in the species diversity of microbiocenoses were noted. The water samples with a pH of 12.6 were characterized of lowest biodiversity, where the basis of the microbial community was only 3 classes: Bacilli (57.51%), Gammaproteobacteria (29.79%) and Clostridia (4.55%). The most diverse microbial community (8 classes) was noted in the soda sediments; the pH of these samples was 11.

Keywords: alkalophiles, sludge storage, microbiocenosis, metagenomic analysis

Introduction
Soda Lakes as extreme habitats are the object of study for a long time, and interest in their research does not decrease. Such sources are unique aquatic ecosystems characterized by high salt concentrations and pH values (Kompantsseva et al. 2007). Despite these dual extreme conditions, most lakes are highly productive ecosystems with a fully functional microbial community (Sorokin et al. 2011). Considerable interest for understanding the functioning of soda lakes as a separate type of ecosystem is the study of microbiocenosis (Grant 2006).

Microbiological studies that were carried out in soda-salt lakes showed that they have an active alkaliphilic microbial community, which is not found in other ecosystems (Shargaeva et al. 2014; Egorova et al. 2011). Unlike natural alkaline lakes, formed from tens of thousands of millions of years ago, sludge storages with an extremely alkaline and saline environment have existed only decades. The microbiocenosis of alkaline biotopes of anthropogenic origin is interesting in plan of studying the mechanisms of secondary adaptation to alkalization and high salt concentration.

The purpose of this study is to learn the phylogenetic diversity of the sludge storage facility of the Berezniki soda plant (Perm region).

Objects and methods
Samples for physical, chemical and microbiological studies were taken from the territory of the existing sludge storage “Soda” plant in the Berezniki city (Perm region, Russia). The sludge storage is located on the northwestern outskirts of Berezniki city on the left bank of the Kama river. The area of the current map is about 155 hectares. According to rough estimates, the volume of sludge in the storage currently exceeds 10 million m³ (Blinov et al. 2003). Sampling of water, sediment and coastal surface formations was carried out in September 2017. Samples before DNA extraction were transported and stored for a short time at 4°C. Preparations of the chromosomal DNA of bacteria were obtained by the phenol method modified for the isolation of DNA from actinomycetes (Hunter 1985). For screening bacterial microbiota, a metagenomic analysis of the samples was carried out on the 16S rRNA
genes on the MiSeq (Illumina) platform. Sequencing of the V3-V4 region of the 16S rRNA gene was performed following 16S Metagenomic Sequencing Library Preparation protocols. (https://support.illumina.com/content/dam/illumina-support/documents/documentation/chemistry_documentation/16s/16s-metagenomic-library-prep-guide-15044223-b.pdf).

Sequencing was performed at the the Illumina MiSeq Systems (Illumina, USA) according to the manufacturer’s instruction with 2x250 bp paired-end runs. We used software trimming v0.3 for read trimming and FastQC v.0.10.128 for quality control. Raw sequence data were processed and analyzed using QIIME (Quantitative Insights Into Microbial Ecology, Version 1.9.1) software (Caporaso et al. 2010) and Ribosomal Database Project (RDP) http://rdp.cme.msu.edu/. To obtain the necessary PCR fragments, 2 rounds of PCR were used. The nucleotide sequences of the main primers for the 16S rRNA region V3/V4 were used: Forward Primer = TCGTCGGCAGCGTCAGATGTGTATAAGAGACAG and Reverse Primer = 5’ GTCTCGTGGGCTCGAGATGTGTATAAGAGACAGTACHVGGGTATCTAATCC. Primers were synthesized in Evrogen LLC (Russia). PCR was performed with the Tersus PCR kit (Evrogen, Russia). The first round of PCR was performed in 25 μl of the reaction mixture containing 10 μl of 10x buffer; 2,5 μl dNTP; 1 unit of Tersus polymerase activity; 1 μl of chromosomal DNA, 20 pmol of primers, and H2O up to 25 μl. The reaction was carried out in the amplifier “T-100”, the company “Bio-Rad”. Amplification mode: 95°C - 2’([95°C - 30”; 57°C - 30”; 72°C - 30"] 10 cycles) 72°C - 5’; 10°C. The approximate length of the PCR product (after annealing the adapter and the terminated MID) was 530 bp. After the second round of amplification, the presence of PCR products was also checked in a 1,5% agarose gel. After imaging the fragments, each amplicon was double-cleaned with AMPure XP particles. Then, the concentration of each amplicon was evaluated using the Quant-it Picogreen dsDNA Assay Kit, and the amplicons were mixed in an equimolar amount to a final concentration of each amplicon in the pool of 5 ng.

The ionic composition of the medium was investigated using the Kappel-105 capillary electrophoresis system, and the elemental composition was studied using a Shimadzu AA-6300 atomic absorption spectrometer, in accordance with the manufacturer’s instructions.

**Results**

Metagenomic analysis of samples taken from the territory of the sludge storage (water, coastal surface technogenic formations and sediment) was carried out. Representatives of 8 classes were identified in the studied samples, among which 2 classes of Bacilli (up to 57,51%) and Gammaproteobacteria (up to 31,51%) occupied a dominant position.

In the soda sediment, at pH 11, the most diverse microbial community was noted, the basis of which consist representatives of 8 classes: Gammaproteobacteria (20.34% of the total), Bacilli (18,71%), Alphaproteobacteria (16,39%), Clostridia (7,49%), Betaproteobacteria (6,23%), Actinobacteria (4,75%), Deltaproteobacteria (3,73%), Sphingobacteria (3,53%) (fig.1). The dominant cation was a calcium cation, the dominant anions were carbonates, bicarbonates and chlorides, which was caused by the production process of soda obtaining.

In samples of coastal surface formations, the microbial community turned out to be less diverse. Representatives of 4 classes were found here: Bacilli (45,60%), Gammaproteobacteria (31,51%), Betaproteobacteria (6,89%), Clostridia (5,29%), despite on the fact that the conditions were less extreme (pH 8) (fig.2). These formations, obviously, arise when soda
is washed on natural soils. The content of calcium cation in these samples is reduced by 4 times, carbonates are not detected, and the content of hydrocarbonates is comparable to that in the sediment. The concentration of chloride ions is reduced by 7.5 times.

In water samples, the basis of the microbial community was only 3 classes: 
**Bacilli** (57.51%), **Gammaproteobacteria** (29.79%) and **Clostridia** (4.55%) (fig.3). The decrease in biodiversity can be due both to an extreme increase in pH (up to 12.6) and to the fact that in the adhered state on the sediment particles, microorganisms are more resistant to adverse factors.

It is established that the dominant species are **Staphylococcus sciuri** and **Acinetobacter baumannii**, the DNA of which in different samples ranges from 14.38 to 47.21% and from 7.91 to 24.60% of the secreted metagenome, respectively. It should be noted that the number of representatives of **Staphylococcus** in all samples was higher than **Acinetobacter**.

Representatives of the genus **Staphylococcus** are gram-positive facultative anaerobes, chemo-organotrophs with an oxidative and enzymatic type of metabolism. **Staphylococcus sciuri** is able to ferment sugar to cellobiose, which is a distinctive feature of this species. It also possesses pronounced saccharolytic, caseolytic and gelatinase activities. These properties and the absence of a pathogenicity factor characterize them as the most ancient, capable of existing in an abiotic environment (Deryabin 2000).

The genus **Acinetobacter** includes strictly aerobic non-fermenting catalase-positive oxidase-negative gram-negative immobile prototrophic bacteria with G + C content in DNA from 39 to 47% (Wang et al. 2014). Acinetobacteria are characterized by a universal metabolic activity, which ensures their ecological plasticity. Substances used as source of nutrition of acinetobacteria are very diverse: simple carbohydrates, oil, human tissues (Bergogne-Berezin et al. 2008).

Also in the literature note the high lipolytic activity of acinetobacteria. They have a set of lipases, at which the optimum action of most lipases lay in an alkaline environment. High activity and a wide range of substrates for acinetobacterial lipases justified their use as industrial detergents (Aehle 2007).

**Clostridia** are very important organisms for modern biotechnology. Extracellular enzymes produced by these bacteria are able

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**Figure 1** Diversity of microbial community in the soda sediment.
Figure 2: Diversity of microbial community in samples of coastal surface formations of soda sludge storage.
to degrade or hydrolyze biopolymers such as starch or cellulose (Schwarz et al. 2004).

Representatives of the genus *Sphingomonas*, chemotrophic, strictly aerobic alphaproteobacteria, known for their ability to decompose hydrophobic polycyclic aromatic hydrocarbons and express hydrolytic enzymes (Zhou et al. 2016), also constitute a substantial proportion (3.77%) of soda sediment among the dominant microorganisms.

Thus, the dominant microorganisms of the studied microceneses are heterotrophic microorganisms capable of producing various hydrolytic enzymes and utilizing various organic substrates. The data obtained by us give an representation of the diversity of bacteria in the soda sludge storage, which is an environment with an extreme anthropogenic load. The smallest biodiversity was found in water samples with a pH of 12.6. Despite less extreme conditions of coastal zone (pH 8), phylogenetic diversity was reduced, which may be due to lower humidity compared to sediments (8% versus 52%). In general, the phylogenetic diversity of microorganisms of soda sludge storage is substantially different from natural biotopes, that may be due to a different elemental composition and higher pH values.

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References
Developing a risk assessment for local groundwater degradation by mine waste storage facilities

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Abstract
A linear and nonlinear statistic approach was chosen to develop a risk assessment predicting the groundwater pollution potential and SO₄ concentrations considering twelve environmental and spatial variables at an industrial and coal mining complex. Linear regression models and nonlinear classification and regression trees indicated that the explanatory variables lnWLDensity and vadose zone were most significant in predicting the potential pollution risk and SO₄ values. Tree models were able to identify additional correlations between SO₄ and distance to pollution, fault and stream as they recognize nonlinear relationships, and were found to be useful visual tools to develop a site-specific risk assessment.

Keywords: sulfate prediction, linear regression, classification and regression trees

Introduction
Mine waste facilities are often substantial sources of diffuse and point pollution which affects the water quality of the surrounding environment (Morin and Hutt, 2001). Groundwater monitoring is limited at these sites due to financial constraints and the possibility of creating unnecessary pathways between the pollution source and the aquifer due to drilling. This results in incomplete data sets and expensive monitoring programs (Babiker et al. 2005). Therefore, risk assessments have become helpful tools and are widely used to delineate areas that are more prone to groundwater pollution due to anthropogenic activities (Babiker et al. 2005; Kazakis and Voudouris 2015). Once vulnerable areas have been identified, they can be targeted with refined monitoring programs and individual remediation or prevention techniques (Babiker et al. 2005).

A widely accepted aquifer vulnerability assessment is the DRASTIC method which has been studied in a combination of various statistical approaches (e.g. Huan et al. 2018; Kazakis and Voudouris 2015; Khosravi et al. 2017). It is a deterministic approach using order and ranking to evaluate multiple options with specific variables that are not measured but classified according to a rank. This method incorporates the major hydrogeological factors affecting and controlling groundwater movement including Depth to water table, net Recharge, Aquifer media, Soil media, Topography, Effect of the vadose zone and hydraulic Conductivity of the aquifer (Aller et al. 1985).

However, the DRATIC method is not suitable to predict aquifer vulnerability for small, relatively homogenous areas as DRASTIC is designed to assess different locations with spatially variable phenomena (Babiker et al. 2005). Therefore, this study considers an alternative approach employing simple linear models and regression and classification trees which can deal with nonlinear relationships and high-order interactions of complex data (De’Ath and Fabricius 2000).

The aquifers of investigation form part of the Karoo Supergroup located in the north-eastern portion of the Karoo Basin, South Africa. At the study site, seepage from different types of discard dumps containing waste rock and by-products from a coal mining and power station facility and mine water storage dams, typically contain elevated sulfate concentrations. High sulfate levels were detected in the local shallow weathered and deeper fractured aquifer near such mine waste storage facilities and local streams.
These sulphate levels exceed both the South African Drinking Water Standard and water use license requirements of 200 and 134 mg/L \( \text{SO}_4 \) respectively.

This study aimed to develop a risk assessment by employing a linear and nonlinear statistic approach to predict a) groundwater pollution risk by \( \text{SO}_4 \) and b) \( \text{SO}_4 \) concentrations in areas without monitoring boreholes based on environmental and spatial variables. This would aid in the decision making of the mining and industrial complex to be able to comply to the water use licence and to protect the local ground- and surface water quality. In addition, the site of investigation was divided into a control and study site involving a fine coal discard dump. A statistic model should determine whether measured elevated \( \text{SO}_4 \) concentrations were a result of seepage from the discard dump or were to be expected in the area even in the absence of the discard dump.

**Methodology**

**Study site**

The industrial and coal mining complex has an approximate size of 209 km\(^2\) and is located in the Mpumalanga Province, South Africa. This area forms part of the northeastern section of the Karoo Basin and is composed of upward-coarsening cycles of siltstone, mudstone, immature sandstone, carbonaceous shale and coal seams of the Permian Vryheid Formation of the Ecca Group (Johnson *et al.* 2006). Locally, the formation was intruded by late Karoo sub-horizontal dolerite sills with a thickness ranging between 30 and 60 m (Hulley 2013). Several faults were mapped in the area during mining activities, which form part of a larger graben structure with a displacement ranging from 22 to 55 m (Hulley 2013; pers. com. Vermeulen 2015).

Two aquifers control the geohydrological setting, an unconfined shallow weathered and deeper semi-confined fractured Ecca aquifer (Grobelaar 2001) with an average yield of 0.6 and 0.2 l/s, respectively (King 2003). Although these aquifers are relatively low yielding, bedding planes and secondary structures such as fractures, fissures and faults may form preferential flow paths that would allow seepage from the mine waste storage facilities to reach the aquifer system.

**Data acquisition**

Data were obtained from boreholes forming part of a continuous monitoring program. Sulfate was treated as the response variable, as it was determined to be the major pollution culprit at the study site. The explanatory variables were based on the DRASTIC model (Aller *et al.* 1985), but parameter \( R \) was excluded, since only one value was assigned to the relatively small study area, making it statistically irrelevant.

In addition, distance to nearest pollution, study dump, pollution excluding study dump, fault, stream and electrical resistivity tomography (ERT) were considered as explanatory variables (Tab.1). For \( \text{SO}_4 \) and depth to water level, the latest value was used. The slope % was calculated for small sections of the study site according to Freeze and Cherry (1979), utilizing the coordinates and elevation of three boreholes at a time. The hydraulic conductivity was obtained from a hydrogeological model constructed for the area (IGS Report No. 01/2018/AA). Distances from boreholes to potential pollution sources were calculated using the middle point of each source. Distances to streams and faults were measured in intervals by constructing buffer zones of 10, 50, 100 and 500 m around the linear features. Observations with missing \( \text{SO}_4 \) data were excluded from the analysis as the remaining information of the dependent variable did not add any value to the statistical model.

**Statistical analysis**

Different statistical model approaches were chosen to explore relationships between the variables and to predict 1) the probability of high (\( \text{SO}_4 > 134 \text{ mg/L} \)) and low risk (\( \text{SO}_4 < 134 \text{ mg/L} \)) of groundwater pollution, and 2) the sulfate concentration in the groundwater based on the given environmental parameters. Seventy percent of the data set was randomly split into a training sample and the remaining 30% were used as control sample to validate the statistical model. Variables \( \text{SO}_4 \), K, WLDepth, DistPol, DistToDump and DistWithout were
transformed to the natural log scale due to high variations in minimum and maximum values. All statistic methods were run with the freely available software R version 3.4.2 (The R Foundation for Statistical Computing 2017).

At first, a logistic regression model was implemented with the dependent variable $SO_4$ posing a high (>134 mg/L) or low risk (<134 mg/L), based on the water quality objectives of the water use license. The control sample set excluded data from artesian boreholes. An iterative approach was applied to find combinations of factors that explain the risk of elevated $SO_4$ ranging from including all to none of the explanatory variables (Tab. 1). The different models were compared by means of the Bayesian Information Criterion (BIC) to try and balance the accuracy of the model fit against the model complexity.

As a next step, a linear regression model was developed to predict future $SO_4$ values using the natural log (due to a wide range of values) and a normal distribution. Similarly, to the logistic regression, an iterative approach was applied using a combination of factors. The models were then fitted against the log of $SO_4$ with a significance level of 0.05 ($P=0.05$) to determine the most applicable model.

Classification and regression trees were applied to fit non-linear models by means of decision trees that try to maximally differentiate the sample with each succeeding split in a branch. Regression and classification trees are useful tools when dealing with nonlinear relationships and high-order interactions of complex data sets (De’Ath and Fabricius 2000). Splitting of tree branches was performed with the aid of the Gini index for the classification tree, and with the ANOVA method (sums of squares) for the regression tree. Other than the previous models, all variables were included to populate the trees. The trees were then pruned utilising the default complexity parameter (CP) method.

As final approach, a robust regression model was utilized to try and predict the natural log of $SO_4$ ($lnSO_4$) based on the observed sulfate measurement of the

| Table 1 Description of the study variables; the type of variable is denoted by N=numeric or C=categorical; materials are denoted by ss=sandstone, BKFL=backfill, mudst=mudstone. |
|------------------|---------------|-------|----------------------------------|
| Variable         | Short name    | Type  | Value (min. and max. range)     |
| $SO_4$ concentration (mg/L) | SO4           | N     | 0.25-31071                      |
| Distance to pollution (m)   | DistPol       | N     | 88-14393                        |
| Distance to study dump (m)   | DistToDump    | N     | 224-2939244                     |
| Distance to closest pollution without study dump (m) | DistWithout | N     | 88-2935399                     |
| Depth to water level (m)    | WLDepth       | N     | 0-108                           |
| Aquifer geology            | Aquifer       | C     | bedded shale/ss/mudst, BKFL, dolerite, dolerite weathered |
| Soil                        | Soil          | C     | absent, BKFL, clay, clay loam, gravel, loam, sand, sandy loam |
| Vadose zone                 | Vadose        | C     | bedded shale/ss/mudst, BKFL, dolerite, dolerite weathered, clay, siltstone |
| Hydraulic conductivity (m/d) | K             | N     | 0.05 (discard dump), 0.14 (weathered aquifer), 14 (conductive area), 85 (fault) |
| Slope %                    | Slope         | N     | 0-3                             |
| Distance to fault (m)       | Fault         | N     | 0-12308                         |
| Distance to stream (m)      | Stream        | N     | 0-4000                          |
| ERT (Ωm)                   | ERT           | N     | 1.8-96                          |
Results and discussion

Predicting sulfate concentrations with linear functions

Results of the logistic regression model indicated that simple models including only the significant variables were preferred. Based on the BIC value (393.26), the second logistic regression model was the most favourable with only the two explanatory variables vadose zone and lnWLDepth being statistically significant (for P<0.05). The resulting linear formula is \( Y = -0.4868 \times \ln WLDepth + 0.0695 \) (add -2.0739 if vadose=clay, 1.4054 if vadose=dolerite and 1.4957 if vadose=dolerite weathered).

Similar to the logistic regression model, the linear regression model considered the two variables vadose zone and lnWLDepth to be statistically most significant. According to the lowest BIC value, the model that could most reliably predict future sulfate concentrations is \( SO_4 \approx e^{-0.458 \times \ln WLDepth + 4.919} \) (but add to 4.919 a) -2.804 if the vadose zone=clay, b) 1.137 if the vadose zone=dolerite, or c) 1.22 if the vadose zone=dolerite weathered). This prediction is based on the control sample given that the water level is below the surface (not artesian).

Considering the control and study area around the discard dump, the model suggested that the study area has a generally higher \( SO_4 \) concentration with an increase factor of 95.5% compared to the predictions of the control area.

For the robust regression model, the same linear model was fitted using a Bayesian framework with a more robust student-t distribution including artesian borehole measurements. The resulting formula for the model with the best fit predicting future sulfate concentrations was \( SO_4 \approx e^{0.334 \times \ln WLDepth} \), adding a) 4.782 to the exponent if the vadose zone is composed of shale, b) 2.007 for clay, c) 5.834 for dolerite or d) 6.045 for weathered dolerite. This model proposed that the study area has a generally higher \( SO_4 \) concentration with an increase factor of 88.3% compared to the predictions of the control area.

All linear model approaches were consistent in that they only considered the two explanatory variables depth to water level (as natural log) and vadose zone as the major environmental factors that control the risk of sulfate pollution at the investigated site. Both linear and robust regression formulas showed similar results for the prediction of future sulfate concentrations in the control area. Furthermore, both models indicated that the observed sulfate concentrations in the study area were much higher than predicted for the control area. This suggests that there are additional environmental factors that were not considered in the model influencing the sulfate concentration in the groundwater. For example, the study site contains a backfilled area, wetlands and some observed groundwater flow paths at depth, possibly due to anthropogenic alterations of the geology caused by undermining which could play a role in the \( SO_4 \) distribution. It was surprising that the distance to the closest pollution point statistically did not have a significant effect on the sulfate concentration in the groundwater, although the sulfate distribution suggested otherwise. Boreholes closest to the tailings dumps and mine water dams had the highest sulfate concentrations. It is therefore recommended to revisit the methodology on how the distance of boreholes to the closest pollution source was calculated.

Risk evaluation and sulfate prediction with nonlinear functions

Nonlinear regression and classification trees were applied to relate \( SO_4 \) concentrations to spatial and physical environmental variables and to predict \( SO_4 \) concentrations as well as the risk of groundwater pollution by \( SO_4 (>134 \text{ mg/L}) \) based on a random training sample. The regression tree was overfitting using all variables, but showed better results considering only the variables lnWLDepth, vadose zone and distance to pollution, fault, and stream (Fig. 1A). According to the splitting of branches, the variable lnWLDepth was most significant to determine the risk of sulfate pollution for both the regression and classification tree, followed by the vadose zone (Fig. 1). This corresponds with the
findings of the linear regression models.

In the regression tree, distance to pollution was also considered as a significant variable, followed by distance to fault and stream (Fig. 1A). Although the regression tree was able to model complex data to determine environmental characteristic associated with $SO_4^-$ groundwater distribution, it showed discrepancies when trying to explain the distance to pollution with $SO_4^-$ concentrations. For example, it could not reasonably explain an elevated $SO_4^-$ concentration at a distance to pollution $\geq 3681$ m compared to a shorter distance to pollution with lower $SO_4^-$ concentration. This contradicts the field observations and could be explained by either additional factors that were not considered in this risk assessment or due to inconsistencies in the data set.

Other than the regression tree, the classification tree also considered the soil type to be a significant branch to distinguish between high and low pollution risks of $SO_4^-$ but did not include distance to stream (Fig. 1B). Like the regression tree, one branch split indicated that a low $SO_4^-$ risk is expected for distances closer to the pollution source compared to distances further away ($>1039$ m) which disagrees with the field observations and could be related to other factors not being considered in the risk assessment. Overall, the regression and classification trees were a useful and visual tool to predict $SO_4^-$ concentrations and potential risk of $SO_4^-$ pollution for unknown areas in the field. Furthermore, this nonlinear approach was able to identify additional relationships between variables which were not addressed with linear functions due to the complexity of the data.

**Conclusions**

Sulfate predictions and groundwater pollution risk were assessed with linear and nonlinear functions to determine the environmental and spatial relationships with $SO_4^-$ at an industrial and mining site. All statistical approaches indicated that the explanatory variables $lnWLDepth$ and vadose zone were most significant in predicting the potential pollution risk and future $SO_4^-$ values. No relationship was found between...
the dependent variable \( \text{SO}_4 \) and the response variables ERT, slope\%, hydraulic conductivity and aquifer geology. This can be explained by a limited ERT data set and a small data range of the remaining response variables. The simple linear and robust regression model showed that the study area around the discard dump had a generally higher \( \text{SO}_4 \) concentration than predicted by the control area with a factor of 95.5 and 88.3\%, respectively. This could be caused by additional environmental factors not being considered for the study site such as a backfilled area, wetlands and groundwater flow paths possibly related to underground mining activities. Compared to the logistic and linear regression analysis, regression and classification trees were able to identify additional relationships between \( \text{SO}_4 \) and distance to pollution, fault and stream as they consider nonlinear relationships and high-order interactions of complex data sets. Regression and classification trees also provided a useful visual tool to predict \( \text{SO}_4 \) for areas not tested at the study site and to evaluate the pollution potential of the aquifer. It is recommended to re-evaluate the method applied to determine the distance of boreholes to closest pollution points as no relationship was determined with the linear regression models, although the field observations suggested otherwise.

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FUTURE OF THE CLOSED KIZEL COAL BASIN
Abstract
Processes affecting neutralization of acidic mine drainage (AMD) were evaluated within the overburden fissure-karst limestones. Flow of AMD from flooded mines into overlying carbonate deposits occurs in zone of large faults in the Kospashskoye coalfield of Kizel coal basin. In order to understand the geochemical processes occurring within the limestone aquifer the mine water flows into, the chemical data of effluents emerged from ascending springs were processed by geochemical modeling. To evaluate the degree of possible AMD dilution by neutral-to slightly alkaline ambient groundwater and its affect to acid neutralization, their mixing in different ratio was simulated. Simulation of AMD reaction with calcite has showed possible pH and compositions of neutralised mine water. The results of the modeling were compared with measured chemical data of spring effluents. Calculations of saturation index of the effluents with respect to most common secondary minerals identified the potential form of metals precipitation.
Keywords: AMD, carbonate deposits, neutralization, dilution ratio, saturation index, PHREEQC modeling

Introduction
The formation of acid mine drainage (AMD) is a common problem for coal and sulphide ore mining regions (Cravotta and Trahan 1999, Cravotta and Ward 2008). The AMD typically contains elevated concentrations of dissolved and particulate Fe and dissolved SO$_4$$^{2-}$ produced by the oxidation pyrite (Cravotta and Trahan 1999). The processes of pyrite oxidation and formation of AMD have been extensively studied and described (Singer and Stumm 1970, Evangelou and Zhang 1995, Blowes and Ptacek 2003). However, the quality of the mine drainage depends in large part on the reactions with minerals capable of neutralizing the acidic water (Sherlock et al. 1995). Carbonate rock dissolutions can increase pH and concentrations of alkalinity (HCO$_3^-$, CO$_3^{2-}$, OH$^-$) of mine water (Cravotta and Ward 2008). The neutralized AMD has circum-neutral or alkaline pH values and is usually called neutral mine drainage (NMD) (Banks et al. 2002). Other geochemical reactions that contribute to formation of NMD are: a low content of sulphide minerals, neutralization of acid by naturally highly alkaline groundwater, dissolution basic silicate minerals (Banks et al. 2002), CO$_2$ degassing, precipitation of gypsum, dissolution of metal hydroxides (Fe(OH)$_3$, Al(OH)$_3$) and oxyhydroxides (FeOOH, AlOOH) (Stumm and Morgan 1996; Blowes and Ptatchek 2003). Inversely, precipitation of the (oxy)hydroxides and hydroxysulfates is accompanied by the release of protons H$^+$ (Stumm and Morgan 1996; Blowes and Ptatchek 2003; Bigham et al. 1996). Co-precipitation metals can occur together with the precipitation of hydroxide and hydroxysulfate minerals. Precipitation of the secondary compounds can coat or armor the limestone surfaces, decreasing the rate and extent of limestone dissolution and alkalinity production (Cravotta and Ward 2008).
Understanding the processes that cause changes in chemical composition of mine water is essential for making decisions about remediation activities. This paper considers neutralization of the acid mine water flowing into overburden fissure-karst...
carbonate aquifer. Scientific researches related to the study of hydrogeochemical processes occurring in the carbonate deposits overlying the coal strata and controlling acid neutralization of the mine drainage are almost absent for the study area. In order to evaluate geochemical processes occurring within the carbonate aquifer and its effect on AMD quality, chemical composition of the effluents from two springs was thoroughly studied and processed using methods of hydrochemical modeling.

**Description of Study Area**

The Kospashskoye coalfield is located in the northeast part of Kizel coal basin in Perm Kray, Russia. The main structure of the Kospashskoye coalfield is a synclinal fold, the western flank of which is dislocated by a thrust with an amplitude of up to 600 m (Imaikin and Imaikin 2013). The coal-bearing strata occur within the formations of the Lower and Middle substage of the Visean (С1v1-2). The rocks of the coal strata include pyrite and organic sulphur. An aquifer system of the coal-bearing strata (С1v1-2) comprises sandstone beds separated from each other by layers of argillite and coal. In the area under study, the coal strata are overlaid by carbonate deposits of the Upper Visean substage (C1v3) and the Serpukhovian stage (C1s) that constitute a carbonate fissure–karstic aquifer (Cv1+s). On a flank of the syncline, the Visean coal-bearing strata occupy a higher position relative to the Visean-Serpukhovian deposits in the centre of the structure. In natural undisturbed conditions, the karstic aquifer in the Visean-Serpukhovian rocks is separated from the aquifer of the coal-bearing strata by a layer of low permeable bituminous rocks. In zones of large faults, this aquitard is interrupted and the considered aquifers are hydraulically connected. Due to the hydraulic connection, mine water (AMD) can migrate into the karstic limestone aquifer influencing the groundwater quality in it.

The mines in the Kospashskoye coalfield were operated from 1939 to 1998. The cessation of groundwater pumping after the mines closure has resulted in gradual recovery of the piezometric level and formation of a number of ascending springs with both clean and acidic groundwater. The research focused on two of the springs, which in a previous study (Imaikin and Imaikin 2013) are identified as discharges of groundwater extremely contaminated by AMD. They are located in the valleys of East Kizel and Poludny Kizel rivers where the Visean-Serpukhovian limestone outcrops.

**Materials and methods**

In this investigation, the geochemical data of clean groundwater (Cv1+s, well 5g), springs water (spr. 29 and spr. 31), and mine water from the “Kospashskaya” mine (one of the mines in the Kospashskoye coalfield) for the period of 2011-2013 years were studied and processed. Hydrochemical monitoring in the area of the coalfield have been performed by Inter-industry Scientific Research Institute of Environment of the Fuel and Energy Complex (original abbr. “MNIIEKO TEK”). Chemical analyzes of the water samples were carried out in the analytical laboratory of the Inter-industry Scientific Research Institute of Environment of the Fuel and Energy Complex (original abbr. “MNIIEKO TEK”). Inductively coupled plasma-atomic emission spectroscopy was applied for the water quality control. The mean chemical composition of the considered water samples is presented in Table 1.

In order to determine the saturation state of the uncontaminated groundwater (Cv1+s), springs effluents, and the mine water (AMD) with respect to selected minerals, the saturation index (SI) calculations were made. The results of geochemical calculations are shown in Table 1. To assess the degree of possible dilution of the AMD by uncontaminated groundwater or, conversely, the degree of pollution of the groundwater by the mine water, modeling of their mixing in various proportions was performed. At the next stage, modeling of interaction of the mine water with calcite was carried out. The data obtained as a result of the simulations were compared with the actual data of chemical composition of the springs. All simulations were performed using the PHREEQC geochemical code (Parkhurst and Appelo 2013) with the WATEQ4F thermodynamic database (Ball and Nordstrom 1991). Eh (redox) was not measured in the field. In the processing, the values of redox potential were
found for each analysis using the activities of ammonium (NH$_4^+$) – nitrate (NO$_3^-$) redox couple.

**Results and discussion**

Having evaluated the groundwater quality data (table 1), we found two springs effluents with pH ranging from acidic to circum-neutral. A circum-neutral effluent is not common to be observed among the acidic mine drainages from the pyrite-rich mines of coalfield. The following characteristics of the effluent should be noted: the pH of the effluent in the spring 29 is mostly acidic (4.0 – 6.2), while the effluent in the spring 31 is rather circum-neutral (6-6.6) (for the observed period); all samples from both springs are characterized by elevated concentrations of SO$_4^{2-}$, Fe, Ca$^{2+}$, Mg$^{2+}$ and other metals; the content of Ca$^{2+}$ in the springs water is higher than in the mine water; HCO$_3^-$, lacking in the mine water, are found in the springs effluents in concentrations substantially higher than ones in the clean groundwater.

The increased concentrations of HCO$_3^-$ and Ca$^{2+}$ (in comparison with mine water) can indicate the high rate of calcite dissolution by acidic main drainage. Approximately close concentrations of SO$_4^{2-}$ in samples from the spring 29 and from the Kospashskaya mine suggest that this spring effluents origin from this underground mine. The loading of SO$_4^{2-}$ in the spring 29 is unlikely substantially affected by reactions with the neutral groundwater.

Table 1 Different parameters of Adsorption kinetics of Hg$^{2+}$ onto SH-MWCNTs/MoS$_2$ nanohybrid

<table>
<thead>
<tr>
<th>Parameter or constituent</th>
<th>Well 5g</th>
<th>Spr. 29</th>
<th>Spr. 31</th>
<th>Mine water</th>
</tr>
</thead>
<tbody>
<tr>
<td>t, C°</td>
<td>4.7</td>
<td>7.03</td>
<td>4.6</td>
<td>8.38</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td>5.4</td>
<td>6.3</td>
<td>3.5</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>166.70</td>
<td>320.9*</td>
<td>591.40</td>
<td>0</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>40.00</td>
<td>4863.0</td>
<td>3066.0</td>
<td>4799.0</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.04</td>
<td>1.18</td>
<td>0.60</td>
<td>1.55</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.17</td>
<td>0.14</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>35.70</td>
<td>437.59</td>
<td>536.05</td>
<td>332.23</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>11.47</td>
<td>462.46</td>
<td>341.835</td>
<td>344.76</td>
</tr>
<tr>
<td>Na</td>
<td>2.74</td>
<td>9.36</td>
<td>9.66</td>
<td>7.67</td>
</tr>
<tr>
<td>K</td>
<td>0.31</td>
<td>23.80</td>
<td>16.04</td>
<td>41.15</td>
</tr>
<tr>
<td>Fe$_{tot}$</td>
<td>0.09</td>
<td>1904.5</td>
<td>845.2</td>
<td>2888.6</td>
</tr>
<tr>
<td>Al</td>
<td>0.01</td>
<td>8.59</td>
<td>1.79</td>
<td>76.99</td>
</tr>
<tr>
<td>Mn</td>
<td>0.001</td>
<td>26.993</td>
<td>17.705</td>
<td>37.16</td>
</tr>
<tr>
<td>Si $^\text{logPco}_2$</td>
<td>3.42</td>
<td>7.26</td>
<td>7.49</td>
<td>12.68</td>
</tr>
<tr>
<td>Calcite (CaCO$_3$)</td>
<td>-0.21</td>
<td>-2.68</td>
<td>-0.53</td>
<td>n.d.</td>
</tr>
<tr>
<td>Dolomite (CaMg(CO$_3$)$_2$</td>
<td>-0.89</td>
<td>-5.29</td>
<td>-1.21</td>
<td>n.d.</td>
</tr>
<tr>
<td>Siderite (FeCO$_3$)</td>
<td>-9.13</td>
<td>-0.09</td>
<td>1.44</td>
<td>n.d.</td>
</tr>
<tr>
<td>Rhodochrosite (MnCO$_3$)</td>
<td>-2.34</td>
<td>-1.36</td>
<td>0.49</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ferricydrite [amorphous Fe(OH)$_3$]</td>
<td>2.95</td>
<td>4.13</td>
<td>5.82</td>
<td>1.31</td>
</tr>
<tr>
<td>Goethite (FeOOH)</td>
<td>8.07</td>
<td>9.33</td>
<td>10.93</td>
<td>6.60</td>
</tr>
<tr>
<td>Amorphous Al(OH)$_3$</td>
<td>-1.52</td>
<td>-1.91</td>
<td>0.68</td>
<td>-5.68</td>
</tr>
<tr>
<td>Gibbsite [Al(OH)$_3$]</td>
<td>1.36</td>
<td>0.95</td>
<td>3.57</td>
<td>-2.83</td>
</tr>
<tr>
<td>Diaspore (AlOOH)</td>
<td>2.50</td>
<td>2.09</td>
<td>4.70</td>
<td>-1.68</td>
</tr>
<tr>
<td>Manganite (MnOOH)</td>
<td>2.52</td>
<td>-4.40</td>
<td>-2.34</td>
<td>-7.30</td>
</tr>
<tr>
<td>Gypsum (CaSO$_4$*2H$_2$O)</td>
<td>-2.21</td>
<td>0.13</td>
<td>0.01</td>
<td>-0.29</td>
</tr>
<tr>
<td>Jarosite-K [KFe$_2$(SO$_4$)$_3$*(OH)$_2$]</td>
<td>-4.56</td>
<td>11.73</td>
<td>12.86</td>
<td>6.86</td>
</tr>
<tr>
<td>Jarosite-Na [NaFe$_2$(SO$_4$)$_3$*(OH)$_2$]</td>
<td>-7.57</td>
<td>7.44</td>
<td>8.72</td>
<td>4.03</td>
</tr>
<tr>
<td>Jarosite-H [(H$_2$O)Fe$_2$(SO$_4$)$_3$*(OH)$_2$]</td>
<td>-12.25</td>
<td>5.05</td>
<td>5.00</td>
<td>3.48</td>
</tr>
<tr>
<td>Jurbanite [Al$_2$(SO$_4$)$(OH)^+*SH$_2$O]</td>
<td>-5.21</td>
<td>0.98</td>
<td>1.36</td>
<td>0.40</td>
</tr>
<tr>
<td>Alunite [KAl$_2$(SO$_4$)$(OH)^+*SH$_2$O]</td>
<td>-4.86</td>
<td>6.39</td>
<td>10.61</td>
<td>0.14</td>
</tr>
<tr>
<td>Basauluminine[Al$_2$(SO$_4$)$(OH)^+*SH$_2$O]</td>
<td>0.87</td>
<td>5.46</td>
<td>14.15</td>
<td>-6.74</td>
</tr>
<tr>
<td>log Pco$_2$</td>
<td>-2.65</td>
<td>-0.51</td>
<td>-0.84</td>
<td>n.d.</td>
</tr>
<tr>
<td>n of samples</td>
<td>6</td>
<td>12</td>
<td>10</td>
<td>9</td>
</tr>
</tbody>
</table>

* For Spr. 29, mean value of HCO$_3^-$ was calculated ignoring 4 samples with none HCO$_3^-$.
In the spring 31, concentrations of SO$_4^{2-}$ are notably lower than in the mine water. That may indicate the greater degree of the mine water neutralization by carbonate minerals of host rocks and neutral groundwater of the coal overlying aquifer (that leads to precipitation of secondary compounds). However, high concentrations of HCO$_3^-$ and Ca$^{2+}$ in the spring effluent may contradict the assumption about the significant dilution of the AMD by ambient groundwater.

Thus, the evaluation of the geochemical data enables us to state that the considered springs discharge the mine effluent that has been neutralized in different degrees by reactions with carbonate minerals, while their interaction with uncontaminated neutral groundwater along the mine flow path is not substantial.

Modeling of mine water – groundwater mixing in different ratio has been conducted to predict the possible composition of the solution resulted in case if the mine water inflows to neutral groundwater. Mean composition of the mine water and the groundwater (well 5g) were taken into account in modeling. Changes of pH values and concentration of HCO$_3^-$, Fetot and SO$_4^{2-}$ in the solutions obtained by modeling of the mine water and the groundwater mixing are shown in the plots (Fig. 1 a, b). The plot in Fig. 1a indicates that the pH of the resulting solutions reaches the values closed to ones the springs samples match or are very close to these values in the modeling solutions, at corresponding SI of calcite. The interaction of AMD with calcite leads to decrease of concentrations of SO$_4^{2-}$, as it shown in Fig. 2 c. The contents of SO$_4^{2-}$ in spring 31 are close to the ones in the model solutions. The spread of values in the plots is due to the average composition of mine water was taken for modeling.

The modeling of the mine water interaction with calcite has showed that the composition of springs water is mainly caused by dissolution of calcite. The modeling of AMD mixing with clean groundwater and comparison of the results with real water chemistry of the both springs have not revealed any substantial dilution of the mine water by the groundwater (and, consequently, any substantial influence of neutral groundwater on the AMD composition) along the AMD flow path. The results of the simulations confirm the assumption that the considered springs (29 and 31) are the mine effluents which has been subjected to different degrees of neutralization when seeping through carbonate rocks.

It should be noted that, the latest samples taken from spring 29 in September and October 2013 are characterized by low pH values 4.0 and the absence of HCO$_3^-$ and SO$_4^{2-}$. The decreased pH of water in the spring 29 in 2013 compared with 2011-2012 indicates that the acid neutralizing capacity of carbonate aquifer along the mine water flow path has substantially diminished. It may be caused by coating (armoring) of the limestone surfaces in result of precipitation of Fe(OH)$_3$ and other secondary compounds.

Conclusions

In order to evaluate the processes affecting the neutralization of acid mine drainage when it inflows to karstic carbonate aquifer, modeling of AMD mixing with neutral groundwater, mine water interaction with calcite and SI calculations on the base of the PHREEQC geochemical code were performed. The compositions of the resulting solutions were compared with the actual chemical composition of the springs.
Figure 1 The results of modeling of acid mine water and clean groundwater mixing

Figure 2 Modeling of mine water interaction with calcite

effluents. Comparison of the pH values and HCO$_3^-$ concentrations in the simulated solutions with measured pH and content of the compounds in the springs water has indicated that chemical composition of the springs (29 and 31) effluents forms mostly due to the dissolution of carbonate minerals of the water-bearing rocks by acidic mine water while dilution of the mine water with neutral groundwater of the deposits (Cv1+s) overlying the coal strata is not significant.

Calculated saturation indexes of water from the springs indicate the potential for precipitation of Fe, Al hydroxides and hydroxysulfates. Saturation indexes of water samples from the spring 29 with respect to ALOH3 are mostly negative (ranges from -7.60 to 0.69), while they are predominantly positive in spring 31 (ranges from -0.49 to 1.28). The SI values of siderite and rhodochrosite are positive in all water samples from the spring 31 and range from negative to positive in the
samples from spring 29.

It is particularly remarkable that, the water temperature in the spring 29 (mean 7.03°C) is close to the temperature of the mine waters (mean 8.38°C), while the water temperature in the spring 31 (mean 4.6°C) corresponds to temperature of groundwater of the upper Visean aquifer.

The chemical compositions, saturation state, and the temperature of the springs effluents allow saying that the residence time of the mine water, discharged by the spring 29, within the carbonate flow path is less than those of the mine water discharged by the spring 31. The decrease of pH values in the spring 29 in 2013 in comparison with 2011-2012 is obviously connected with diminish of acid neutralizing capacity of carbonate rocks caused by coating of the limestone surfaces in result of precipitation of secondary compounds along the mine water flow path.

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Alteration Of Physico Chemical And Morphological Characteristics Of Sod-podzolic Soils In Technogenically-affected Landscapes Of Moscow Brown Coal Basin

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Abstract
Long-term coal mining in the Moscow basin has led to changes in soil properties of landscapes. Spoil heaps of sulphide-bearing overburden rocks and subsidence over the mined space are formed at abandoned mine fields. Acid mine drainage (AMD) of sulfuric acid, Al and Fe sulfate as well as pyritized material, entering from eroded spoil heaps, results in morphological changes in soil properties. This study aimed at evaluation of physico chemical transformation of soil properties, which is adjacent to spoil heaps. Natural soils are sod-podzolic soils. On foreslopes around spoil heaps technogenically transformed soils are common. Technogenically transformed soils are characterized by acidic reaction with a high content of Fe and Al sulfate as well as a considerable amount of exchange and total titratable acidity in soil solid phases and soil solutions, respectively. It is revealed that contaminated sod-podzolic soils, in relation to natural soils, has a specific morphologic features: intensification of eluvial process (bleaching of soil mass) along with intensive accumulation of iron (nodules and patches of Fe oxides and hydroxides) and organic matter of coal origin. Sod-podzolic-gley soils with transformed water regime are formed in mine subsidence.

Keywords: brown sulfur coals, spoil heaps, acid mine drainage, mine subsidence, technogenically transformed soils

Introduction
Coal mining causes substantial environmental alterations of landscapes (terrain, soils and ground waters) (Nordstrom and Alpers 1999). In sulfur brown coal mining areas of Moscow basin, soils are affected by acid mine drainage (AMD), solid sulfide-bearing mine wastes and carbonaceous particles. Solid mine wastes of Moscow basin, which comprise of overburden and host rocks, are stored in conical spoil heaps (40-60 m in height) near mine sites (Solntseva et al. 1992). At present, coal mining is terminated. Abandoned spoil heaps in Moscow basin have not been recultivated and erode intensively due to physico chemical properties of waste rocks. As a result, mine wastes enter the environment.

The toxicity of waste materials for biota is determined by the high amounts of iron sulfides (mostly pyrite and marcasite). Very high total content of sulfur (up to 5%) is connected to marine origin of brown coals in the Moscow basin. Pyrite is subjected to continuous weathering and oxidation in spoil heaps (Lottermoser 2010). Active oxidation of sulfides in waste dumps results in the producing of toxic sulfuric acid and iron sulfate (Nordstrom and Alpers 1999). Aluminosilicates in clay minerals (predominantly kaolinite and illite) of spoil heaps are in contact with acidic pyrite oxidation waters that creates toxic Al sulfate (Younger 2004; Silva et al. 2011). Weathering of spoil heaps led to formation of deluvial and proluvial waste dump tailings of technogenic materials on soil surface. Solid-phase products of chemical weathering and mechanical dispersion of spoil heaps, transported by drainage waters, formed technogenic deposits on the soil surface.

Other environmental concern is the formation of dips and subsidence areas over the mined space due to the dewatering of
abandoned coal mines. It results in alteration of the soil water regime (Younger 2004; Wang et al. 2017).

The aim of the study was to examine the post-mining transformation of physico-chemical and morphological soil properties under the effect of supply of technogenic material from the spoil heaps and changes of the terrain in abandoned sulfur coal mining areas.

**Study area**

Sampling site was located in the Cherepet brown coal deposit of Moscow basin (the Tula Region, Russia). We investigated Glubokovskaya-4 (36°32′17″E, 54°10′43″N) abandoned spoil heap and adjacent areas (fig. 1). According to Geology of coal and oil shales of the USSR (1962), carboniferous strata of Moscow basin belong to the Visean stage of the Lower Carbon. Waste dumps of Cherepet deposit comprise of iron sulfide-bearing carbonaceous black greasy clays with kaolincic clays, brown coal layers, loams, sandy loams and quartz sands, as well as pyrite crystals (Solntseva et al. 1992). There may be CaCO$_3$ (calcite) and FeCO$_3$ (siderite) impurities in clays. At the reference site natural soils are sod-podzolic soils, mainly weakly podzolic (Albeluvisols in WRB 2014 (IUSS Working Group WRB 2015)), sandy-loamy on moraine loams. Sod-podzolic-gley soils prevailed in depressions. The vegetation of the site is represented by mixed forests with birch, aspen and pine.

**Methods**

Descriptions and soil sampling were carried out at sites with technogenic transformation (soil profiles SUV 2 to SUV 6) and at relatively natural site (soil profile SUV 1). Waste material was sampled at foothill of the spoil heap (SWD point). AMD was sampled from technogenic reservoir at foothill of the spoil heap (SPW point) (fig. 1). Samples of AMD, soils, waste materials and displaced solutions from soils and waste materials were investigated. Fresh soil samples, taken from each genetic horizon and overburden sediments, were used for soil solutions displacement.

Soil solutions were displaced by ethanol (Ishcherekov-Komarova method, Russia) (Snakin et al. 2001). The composition of soil solutions was measured by ion chromatography. The content of Fe$^{2+}$ and Fe$^{3+}$ ions in soil solutions was determined by spectral photometry. The content of H$^+$ and Al$^{3+}$ ions in soil solutions (the sum of H$^+$ and Al$^{3+}$ is equal to titratable acidity) was determined by titration to pH 8.2 using a 0.01 M NaOH solution. The pH value was measured by the potentiometric method using Expert 001 ionometer (Econics Expert,
Russia). Electrical conductivity (EC) was measured using conductometer SevenEasy S30 (Mettler Toledo, Switzerland).

Exchangeable cations (H\(^+\), Al\(^{3+}\), Ca\(^{2+}\), Mg\(^{2+}\)) were released upon exchange by 1 M KCl solution at a soil to solution ratio of 1:2.5. Total alkalinity in the aqueous extract was determined by acid-base titration using a 0.01 M H\(_2\)SO\(_4\) solution to pH 4.4. The content of Ca\(^{2+}\) and Mg\(^{2+}\) was determined by titration using a 0.05 M EDTA solution (Vorobyova 2006). The total content of organic carbon was determined by dichromate oxidation.

Results and Discussion

Technogenic deposit (TD) on the soil surface, composed of the waste dump material, had a highly acidic reaction (pH=3.4-3.9) as well as high content of organic carbon of coal origin (up to 18.1%). Aluminum sulfates prevailed among readily soluble salts. The share of Ca\(^{2+}\) and Mg\(^{2+}\) was also considerable (tab. 1). Clay material of the deposits was very fine, dirty brown in color, with inclusions of silty detrital carbonaceous particles. Dump tailings were covered by white saline crusts composed of Fe and Al-hydrated sulphates. There was no vegetation on the surface of TD.

Technogenic waterlogged reservoir (SPW), filled with highly acidic filtrated waters (pH = 2.7-3.0), had reddish-yellow colour with elevated concentrations of Fe, Al and sulfate (tab. 1), that is typical for coal mining areas (Martin et al. 2008). EC value was about 2920 µS/cm.

At the reference site, natural sod-podzolic soils were characterized by low carbon content (up to 1.5%) and had a weak-acid reaction (pH 5.5-6.3). EC value of soil solutions did not exceed 320 µS/cm. Soils had a homogenous distribution and low content of salts throughout the profile (SUV 1). A predominant cation in the readily soluble salts was Ca\(^{2+}\) (tab. 2). The composition of the anionic part was sulfate-bicarbonate (SUV 1). Exchangeable Ca\(^{2+}\) prevailed in natural soils (tab. 3).

Soils with technogenic transformation were overlapped by technogenic deposits up to several dozen centimeters in thickness. Buried part of soil profile had the specific chemical and morphological properties (Solntseva et al. 1992). The contaminated soils, affected by technogenic fluxes, were characterized by a strong acidic reaction (pH=3.5-4.5). EC of soil solutions was extremely high (from 940 to 5680 µS/cm). Technogenic fluxes from waste dumps contain fine dispersed fractions of coal material. As a result, organic carbon of coal origin was accumulated in the upper horizons of technogenic soils. Concentrations of organic carbon (up to 10%) exceeded background values by 2.5-5.6 times. The specific feature of the newly formed salt composition in polluted sod-podzolic soils (SUV 4) was the presence of aluminum sulfates in soil solution in very high amounts, especially in the layer of 32-60 cm in EL and BEL horizons. The horizons were bleached (tab. 2) and had homogeneous light-grey colour that might be associated with partial acid hydrolysis of the primary silicates (mainly feldspars and phyllosilicates) (Martin et al. 2008). Sod-podzolic soils at the reference site had no water-soluble aluminum sulfates. There were less Fe\(^{3+}\) and Fe\(^{2+}\) ions in solutions, because of their precipitation in BTg horizon, mainly in amorphous or poorly crystallized forms (Simon et al. 2001).

Increasing of the concentration of H\(^+\) and Al\(^{3+}\) ions in the liquid phase of contaminated soils decreased the amount of exchangeable Ca\(^{2+}\) and Mg\(^{2+}\) in soil ion-exchange complex by 2.5 times due to the substitution of Ca\(^{2+}\)

Table 1: Chemical properties (pH value, composition of readily soluble salts, titratable acidity, water-soluble Fe) of waste dumps (displaced solutions) and AMD

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>pH</th>
<th>HCO(_3)</th>
<th>Cl</th>
<th>SO(_4)(^{2-})</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>K(^+)</th>
<th>Na(^+)</th>
<th>H(^+)</th>
<th>Al(^{3+})</th>
<th>Fe(^{3+})</th>
<th>Fe(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWD(^1)</td>
<td>2.9</td>
<td>0.1</td>
<td>1.0</td>
<td>65.3</td>
<td>25.0</td>
<td>16.1</td>
<td>0.2</td>
<td>1.0</td>
<td>0.4</td>
<td>3.4</td>
<td>18.0</td>
<td>4.8</td>
</tr>
<tr>
<td>SPW(^2)</td>
<td>3</td>
<td>ND(^3)</td>
<td>0.2</td>
<td>28.9</td>
<td>14.0</td>
<td>2.1</td>
<td>ND</td>
<td>0.1</td>
<td>9.7</td>
<td>21.6</td>
<td>22.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\(^1\)SWD technogenic material of waste dumps \(^2\)SPW filtrated waters and acid mine drainage \(^3\)ND not detected
### Table 2 Chemical properties (pH value, composition of readily soluble salts, titratable acidity) of displaced solutions from soils and deposits of waste material

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Horizon</th>
<th>Depth, cm</th>
<th>pH</th>
<th>composition of readily soluble salts (mmol/dm³)</th>
<th>titratable acidity (mmol/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCO₃⁻</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>SUV 1, reference site</td>
<td>AY 0-13</td>
<td>6.0</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>EL 13-18</td>
<td>6.3</td>
<td>0.4</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>BEL 18-45</td>
<td>6.2</td>
<td>1.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>BT₁ 45-90</td>
<td>5.5</td>
<td>0.7</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>BT₂ 90-110</td>
<td>5.9</td>
<td>0.6</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>WTD 0-15</td>
<td>3.8</td>
<td>0.1</td>
<td>0.1</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>TD¹ 15-32</td>
<td>3.7</td>
<td>0.1</td>
<td>0.1</td>
<td>252.1</td>
</tr>
<tr>
<td>SUV 4, technogenically-affected site</td>
<td>EL 32-54</td>
<td>3.8</td>
<td>0.1</td>
<td>0.1</td>
<td>200.9</td>
</tr>
<tr>
<td></td>
<td>BEL 54-60</td>
<td>3.5</td>
<td>0.1</td>
<td>0.2</td>
<td>201.0</td>
</tr>
<tr>
<td></td>
<td>BT 60-110</td>
<td>3.4</td>
<td>0.1</td>
<td>0.2</td>
<td>221.8</td>
</tr>
<tr>
<td></td>
<td>TD 0-23</td>
<td>4.1</td>
<td>0.1</td>
<td>ND²</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>EL 23-34</td>
<td>4.5</td>
<td>0.3</td>
<td>ND</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>BTg1 34-51</td>
<td>4.3</td>
<td>0.3</td>
<td>0.2</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>BTg2 51-95</td>
<td>4.1</td>
<td>0.2</td>
<td>0.3</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>BTg2 95-110</td>
<td>4.2</td>
<td>0.3</td>
<td>0.2</td>
<td>20.5</td>
</tr>
</tbody>
</table>

¹TD technogenic deposit, ²ND not detected

### Table 3 Concentrations of exchangeable cations in natural and technogenically transformed soils

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Horizon</th>
<th>Depth, cm</th>
<th>pH_{H₂O}</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>H⁺ (cmol·kg⁻¹)</th>
<th>Al³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AY 0-13</td>
<td>3.3</td>
<td>4.1</td>
<td>1.3</td>
<td>0.1</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EL 13-18</td>
<td>3.7</td>
<td>4.6</td>
<td>1.9</td>
<td>0.1</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BEL 18-45</td>
<td>3.8</td>
<td>5.3</td>
<td>1.8</td>
<td>ND</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BT₁ 45-90</td>
<td>3.9</td>
<td>6.5</td>
<td>2.5</td>
<td>0.1</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BT₂ 90-110</td>
<td>4.0</td>
<td>6.9</td>
<td>2.9</td>
<td>0.1</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>WTD 0-15</td>
<td>3.5</td>
<td>2.1</td>
<td>0.9</td>
<td>0.2</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TD¹ 15-32</td>
<td>4.1</td>
<td>1.3</td>
<td>0.5</td>
<td>ND</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EL 32-54</td>
<td>4.1</td>
<td>1.5</td>
<td>0.5</td>
<td>ND</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BEL 54-60</td>
<td>3.7</td>
<td>5.8</td>
<td>2.3</td>
<td>0.1</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BT 60-110</td>
<td>3.7</td>
<td>7.4</td>
<td>4.8</td>
<td>0.1</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TD 0-23</td>
<td>4.0</td>
<td>2.5</td>
<td>1.1</td>
<td>0.1</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EL 23-34</td>
<td>4.0</td>
<td>1.0</td>
<td>0.6</td>
<td>0.1</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BElg 34-51</td>
<td>3.7</td>
<td>3.8</td>
<td>2.1</td>
<td>0.1</td>
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</tr>
<tr>
<td></td>
<td>BTg₁ 51-95</td>
<td>3.8</td>
<td>4.5</td>
<td>3.1</td>
<td>ND</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BTg₂ 95-110</td>
<td>3.7</td>
<td>4.6</td>
<td>3.3</td>
<td>0.1</td>
<td>4.9</td>
<td></td>
</tr>
</tbody>
</table>

¹TD technogenic deposit, ²ND not detected
and Mg$^{2+}$ by H$^+$, and at low pH values by Al$^{3+}$ (Snakin et al. 2001; Androkhanov et al. 2004). Al$^{3+}$ was predominant in the ion-exchange complex of soils in the amount of up to 70-80% of the total exchange cations. The share of exchangeable H$^+$ was also substantial (tab. 3). The content of exchangeable Mg$^{2+}$ exceeded concentrations in natural soil.

The soils in a subsidence area (SUV 6) had excessive moisture, lower pH and lower content of salts in soil solution due to the additional lateral intrasoil runoff of water. Hydromorphic gley and gleyic soils with secondary gley genesis were formed in subsidence areas (fig. 2).

Various morphological alterations were revealed in the sod-podzolic soils influenced by technogenic fluxes of phytotoxic rocks. Filling of pore space with finely dispersed material led to compaction of soil mass and formation of horizons with extremely high bulk density, and low porosity and a substantial amount of technogenic carbonic admixtures (fig. 2). The microaggregation of the contaminated soils was law. Granular and cloggy aggregates were replaced by cloddy, lumpy, and nutty ones.

Due to AMD effects that had destroyed fine clay minerals, numerous clarified areas were formed, composed of quartz and feldspar. Throughout the profile, there were signs of gleying (grayish and smoke blue shades) and ferrugination (ochreous and rusty-brown iron patches, nodules and crusts of Fe oxides and hydroxides) on faces of structural units (Solntseva and Rubilina 1987). In soil genetic horizons specific cutans with the high content of coal particles were formed (fig. 2).

**Conclusions**

Long-term introduction of sulfide-bearing technogenic material to the environment led to substantial geochemical transformation of sod-podzolic soils. The main changes in morphology of sod-podzolic soils were the intensive ferrugunation of the buried soil profile and the intensification of the eluvial process (formation of carbonaceous films). Chemical properties and morphological features of technogenically altered soils and natural soils differed considerably. Key geochemical processes at mine sites in sod-podzolic soils were: (1) acidification and Fe-
Al-SO₄ salinization of soil profile along with the increasing of H⁺ and Al³⁺ ions content; (2) cation exchange, leading to replacement of Ca²⁺ and Mg²⁺ ions by Al³⁺ and H⁺ ions, perhaps, and by Fe²⁺ in soil ion-exchange complex; (3) mineral transformations. Thus, sod-podzolic with technogenic transformation at post sulphur coal mining sites were similar to northern podzolic soils in terms of intensive acid hydrolysis of the layer silicates. The results of this investigation could be used to implement a complex remediation measures in Moscow coal basin, as well as prognosis on the negative effect of mine wastes on soil salinity status.

Acknowledgements
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Using the industrial wastes for remediation of sites affected by acid mine water dumping

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Abstract
Kizelovsky coal basin is located in the Urals in the Perm region. Coal mining was carried out during 200 years. The high water content of coal mines and substantial sulfur content in the rocks of coal-bearing strata affected the worsening of the environmental situation. As a result of sulfur oxidation in mine workings, acid mine waters (pH≈2-3) with a high content of $\text{SO}_4^{2-}$, $\text{Fe}^{3+}$, $\text{Fe}^{2+}$, $\text{Al}^{3+}$ and potentially toxic metals are formed. Parts of the former mine water discharge are polluted. They are not overgrown with vegetation even since 25 years after the closure of mines. Method of these sites reclamation with using alkaline waste of soda production and activated sludge of biological treatment facilities as reagents have been developed and tested by the authors.

Keywords: coal basin, acid mine waters, spillway, disturbed lands, technogenic soils, neutralization of soils, reclamation

Introduction
The oldest in the Urals Kizelovsky coal basin is located in the Perm region. It is stretched in the meridional direction, and has a length of more than 100 km and a width of 15-20 km.

The history of coal mining begins at the end of the XVIII century. In the first decades, coal mining was performed in small volumes to meet the demand of local enterprises. The increase of coal mining began after the Mining railway construction in 1879. Further, a substantial increase of coal mining happened during the first five years of the USSR (since 1928) and, especially during the Great Patriotic war, when Donbass was captured by the Nazis, and the country needed coal to win. In the first post-war decades, production volumes also grew, but then because of difficult geological, hydrogeological and mining conditions, the growth stopped, and then lowering of production followed. In the 1990s coal mining in the Kizel basin had to be unprofitable and all mines of Kizel mine association were closed until 2000.

The environmental problems of the territory were not solved by the closure of mines. On the tributaries of the Kama and Chusovaya rivers extremely high levels of water pollution and sediments are constantly recorded. Currently, the main sources of pollution are acid mine waters, which spontaneously flow to the surface (Imaykin 2014). Together with them, more than 90% of the total amount of pollutants enter the rivers. Rivers pollution happens due to the effluents of 53 rock dumps of coal mines with an area of more than 300 ha.

Source of environmental pollution are areas of former mine water discharge (Imaykin and Imaykin 2018). During the coal mines working acidic water with high mineralization was pumped to the surface and dumped into ravines. The soil and vegetation layer is absent here. The upper part of the section is represented by man-made soils with pH≈3 and high content of water-soluble sulphates, iron, aluminum and potentially toxic metals. There is no spontaneous overgrowth of these areas, although mine water has not been discharged for 17-25 years. Removal of chemical elements from these areas with water flows leads to pollution of surface and groundwater, and of adjacent areas, and causes degradation of existing ecosystems.

Methods and results
The exploration of Shirokovskaya coal mine acid water former discharge area. The mine was commissioned in 1945 and closed in April 1997.
In the flooding of mine groundwater in coal-bearing strata, confined to Sandstone packs, played the main role. Much less fissure-karst waters of the viséan aquifer took part. In the period from 1977 to 1996, the highest inflow of water into the mine was 2.7 thousand m$^3$/h, the average annual – about 1.0 thousand m$^3$/h (Krasavin 2005).

Mine’s drainage was equipped with a wooden box from the dump site to the river Poludennyi Kizel. Over time, the box became unusable, and mine water flowed directly on the earth’s surface, resulting the formation of the largest area of disturbed land (fig. 1). A detailed survey of the object showed that the site is extended in the North-West direction from the mine site to the river Poludennyi Kizel. The length of the plot is about 2 km, width-100 m and more.

At the “Shirokovskaya” mine during one of the periods of its work there was a mine waters neutralization with lime. As a result, a substantial amount of finely dispersed iron hydroxides was accumulated at the discharge site. Currently, from the surface of the site there lies a layer of man-made soils with a capacity up to 1 m, represented by finely dispersed iron hydroxides with fragments of mine dumps rocks. There are technogenically metamorphosed loams below.

To study the properties and composition of man-made deposits and modified loams, 36 soil samples on six transverse profiles, evenly spaced throughout the site were taken. Analysis of the water extract showed that the soils from the contaminated area have an acidic reaction of the environment. The hydrogen index of soils profile water extraction, closest to the source of pollution (mine) is 2.3-2.6. With the distance from the industrial site, it increases slightly and on the profile, which is located near the Poludennyi Kizel river, it is 2.7-3.0. The content of water-soluble salts near the source of pollution is about 3 g/kg. On the profiles, which are located near Poludenny Kizel river it is reduced to 1-1.5 g/kg.

According to the microelement gross analysis, there is an increased content of pollutants, particular to the Kizel coal basin. In technogenic soils, the highest concentrations for Cu, Zn, Pb and Mo are observed, their content is several times higher than the background. Changed and underlying loams are also polluted. There is a migration of elements from the surface hydroxide-ferruginous layer of technogenic soils to the underlying loams and their accumulation in

Figure 1 An area of the former acid water discharge of mine “Shirokovskaya”.
the clay substrate. Loams are good sorbents and accumulators of pollutants.

To determine the changeability of man-made soils material composition in the section of the pit there were selected 5 samples layer by layer and their x-ray phase analysis. The section of man-made soils in zone of acid mine drains influence is stratified. The upper horizon is composed of x-ray amorphous iron hydroxide and goethite technogenic sediments. Loams, lyied under it, metamorphised with the formation of newly formed minerals goethite and jarosite in them.

In the space snapshot an area of the former discharge of “Shirokovskaya” mine is clearly visible due to the lack of soil cover, and also due to the high content of iron hydroxides, which give the surface a bright brown color (fig. 2).

Comparison of the site boundaries in the modern space snapshot with the plan, drawn in the period after the closure of the mine, showed that there is no spontaneous overgrowth of disturbed lands, although 22 years have passed after the closure of mine. This area requires environmental measures, including the neutralization of acidic soils and remediation.

A new method of acidic soil reclamation using industrial waste. The authors have developed an effective and economical method of acid mine water discharge sites recultivation. Industrial wastes of local enterprises were chosen as reagents and additives. To reduce the acidity of the soil areas of the former mine spillway, the waste of Open Joint Stock Company (OJSC) "Bereznikovskyi soda plant" was used as a reagent. As an organic fertilizer, which contains elements necessary for the plants development, the active sludge of OJSC “Metafrax” was applied (Blinov et al. 2008).

Waste of soda production belong to the 5th class of danger. They are more than 90% composed of finely dispersed calcium carbonate. The pH value of the extraction is 9. The content of water-soluble chlorides, sulfates and sodium in waste of this layer has low values. The content of trace elements does not exceed the MPC for the gross content in soils. There are no harmful organic impurities in the soda waste. The volume of waste, which is ready for use as a reagent for reclamation of disturbed lands without any preparation exceeds 1 million m³.

Acidic soil neutralization method for reclamation of disturbed land was used in Korea (Jae et al. 2006). Achieved positive effect from the use of waste for the formation of vegetation on the surface.

Studies of activated sludge showed high quality when used for remediation. It represents a hygroscopic (humidity 49-54%) mixture of mineral (53-78%) and organic
(22-47%) substances with a sufficiently high content of total nitrogen – up to 3.6% and phosphorus – up to 4.8 %. The pH value of the extract is 4.5–6.0. The concentration of potentially toxic metals does not exceed the MPC (Maximum Permitted Concentrations) for soils in residential areas and non-agricultural ecosystems. The content of radionuclides is normal.

As a result of laboratory experiments, the optimal amount of waste soda production introduction and activated sludge for the reclamation of acidic soils were determined. The optimal amount is about 20 kg per 1 m². The required amount of soda production added waste was determining from the condition of bringing the man-made pH soils to the background values of ≈ 6.0. The required amount of activated sludge was determined by the best development of plants, used for reclamation.

Experiments were carried out on the site of the former discharge of acidic water on the “Shirokovskaya” mine. On the area of 150 m², experimental sites with three variants of experiment conditions were laid – the lack, the optimal amount and the excess of the introduced reagent amount.

To create a stable blackening of the surface of man-made soils, the selection of grass mixtures, taking into account the edaphic conditions and biophysiological features of plants, was carried out. The composition of grass mixtures included turf-forming species (cereals) in combination with soil-improving siderophilic (bean) species.

After reclamation, the chemical properties of soils have improved. General chemical and microelement analysis of water extraction, microelement analysis of soils showed that the content of pollutants meet the criteria for soils in residential areas.

As a result of the full-scale experiment, a stable vegetation cover was formed (fig. 3). The rate of phytoproduction in the first year of observation was 3.5 to 9.7 centner/ha in the second year – 4.2-14.0 centner/ha of dry weight. It corresponds to the background productivity of zonal dry pastures - 10 centner/ha of dry mass. The assessment of vegetation cover state is given as prosperous, because in the composition of vegetation in the optimal proportion for the sod formation, legumes and cereals are presented.

Microelement analysis showed that the
concentrations of chemical elements in the phytomass of the experimental sites do not have an environmental danger. Their content in most of cases do not go beyond the natural background frames and do not exceed the maximum allowable levels. A slight excess of Cr, V, Ti and Sr has a tendency to decrease on the 2nd year of observations (Krasilnikova and Blinov 2016).

**Conclusions**

Successful large-scale pilot industrial tests of the method on the area of 0.25 ha were carried out. Effectiveness and efficiency of the offered method is confirmed by an independent examination with the participation of regional and Federal representatives. Due to the use of industrial waste, the cost of environmental protection measures is reduced 4 times compared with lime use. The authors obtained a patent for the invention «Method of disturbed lands reclamation» (Blinov at al. 2008).

The introduction of the method will ensure the effective restoration of biological productivity of disturbed lands and eliminate the negative consequences of the exhausted mines production activities on land resources. With distinct adaptation, the method can be used for reclamation of disturbed lands, mine dumps and sludge storage on enterprises which produce and process minerals, containing sulfide, sulfur, and also industrial sites of sulfuric acid production enterprises.

**References**


The General Concept of Kizel Coal Basin Remediation

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Abstract
Acid rock drainage (ARD) is a worldwide environmental problem. Development of ARD is especially characteristic of coal fields. We studied the effect of ARD on the environment in Kizel coal basin, Russia.

Kizel coal basin (KCB) is located on the east part of Perm region, Russia, within the West Urals folding zone adjacent to the pre-Ural boundary deflection. Exploitation of basin started in 1796. Folded geological structure of the basin and intensive karst processes within carbonate rocks determine a big amount of water inflow in mines. There is an elevated content of sulphur in basin’s coal also. These factors determine the generation of large volume of acid mine water and drainage from waste piles. Cessation of mines in 1990s led to the raising of watertable level, mine flooding and starting of acid mine water (pH 2-3) discharge on surface. Over 35 million cubic meters of waste rocks were accumulated in more than 100 waste piles after the cessation, which provide generation of enormous amount of acid rock drainage water. As a result these processes have led to the deforestation of large area, river water contamination with metals and metalloids, and accumulation of yellowboy precipitate covering river beds. Thus, over than 500 kilometres of river streams was degraded. The yellowboy precipitate contains high content of such components as Fe, Al, Mn, Cu and other chemical elements. So, this precipitate is considered as the secondary source of pollution.

Investigations of the environmental problems of the basin began in 1980s. Some treatment methods were proposed: the passive treatment based on geochemical barriers installed at the floor of waste pile, and the active mine water treatment constructions. At present we study the possibility of using various methods of the environment remediation in KCB. It is planned to use both active and passive treatments: injection of alkaline reagents into mine voids, sealing and recultivation of waste piles and some other techniques to neutralize acid discharges. We also plan to use GIS-modeling to choose the proper placement of treatment systems.

Keywords: Coal basin, acid rock drainage, remediation, active treatment, passive treatment

Introduction
The development of coal deposits is one of the leading mining industries. The share of coal is about 25% of the global energy balance (Gonzalez-Toril et al. 2003; Maksimovich, Khayrulina 2011; Maksimovich et al. 2018).

However, the process of coal mining leads to various environmental problems, such as:

- the formation of acid mine water (AMW). AMW is formed as a result of the interaction of ground- and rainwater with sulfur-containing coal-bearing rocks, leading to the increasing of water acidity and the formation of water which had the excess of sulfate ions and metal ions (Fe, Al, Cu, Mn, etc.) in thousands times of MPC;
- the accumulation of waste rock in the form of waste piles and sludges, emerging drains from which contain a large amount of pollutants;
- the violation of the natural hydrogeological conditions of the territories;
- the deforestation of land surface.

All these problems are characteristics of the liquidated Kizel coal basin (KCB), Russia.
Object and geological settings

Kizel coal basin is located in Perm region within the West Urals folding zone adjacent to the pre-Ural boundary deflection and occupied the area of about 1500 km². Rocks of the basin are represented by sandstones, mudstones, siltstones, shales, limestones, dolomites, marls, coals, and others. Carbonate rocks are intensely karsted, especially in the upper part of geologic cross-section. Coal of the basin exhibits elevated content of sulfur (mainly as a pyrite) – 5.8% (Maksimovich et al. 2018).

The increased amount of precipitation falls on the territory of KCB – up to 900 mm annually – is the result of the barrier effect of the Ural Mountains. At the same time the average annual amount of precipitation in the region is 600-700 mm (Pyankov, Shikhov 2014).

The complicated geological structure and hydrogeological conditions, intensive karst processes and abundant rainfalls ensured extremely high water content of the basin’s coal-bearing stratum. The water inflow into the basin’s mines reached 2500 m³ h⁻¹. Every 4 tons of mined coal demanded the pumping of about 7 m³ of mine water out (Maksimovich 1997).

During the basin exploitation, the mine water containing large amount of sulfur, iron, aluminum, manganese compounds, etc., were discharged into the drainage system without any treatment. The constant and intensive inflow of mine water to rivers led to the fact that the chemical composition of river water tended to approach one of mine water. The river water had a hydrocarbonate-calcium composition and a total salinity of 90–150 mg dm⁻³. Downstream after the confluence with mine waters, they acquired a sulphate composition and characterised with extremely high concentrations of Fe, Al, Mn, and salinity ranged from 640 to 6000 mg dm⁻³. The pH value of river water decreased from 6.5-7.0 to 2.5-2.9 under the influence of mine water (Maksimovich et al. 2017).

Environmental situation at present

Cessation of mines in the 1990s led to a gradual restoration of the groundwater level and the formation of mine water discharges through various adits, wells, boreholes, etc. Currently, there are about 18 discharges of mine water to the surface on the territory of KCB (table 1).

Acid drainage from waste piles. Waste piles have a substantial effect on the environment.

Table 1 Mine water discharges in the territory of KCB

<table>
<thead>
<tr>
<th>Mine</th>
<th>Mine water discharge source</th>
<th>Average pH</th>
<th>Average acidity, mg dm⁻³</th>
<th>Average discharge, m³ year⁻¹</th>
<th>Average acid load, tons year⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lenin</td>
<td>Main and auxiliary shafts</td>
<td>3.9</td>
<td>7386</td>
<td>137623</td>
<td>1016</td>
</tr>
<tr>
<td></td>
<td>Sloping shaft 8</td>
<td>3.4</td>
<td>4640</td>
<td>3024205</td>
<td>14033</td>
</tr>
<tr>
<td>Volodarsky</td>
<td>Adit</td>
<td>2.5</td>
<td>1328</td>
<td>155155</td>
<td>206</td>
</tr>
<tr>
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<td>Adit</td>
<td>3.1</td>
<td>4052</td>
<td>157785</td>
<td>639</td>
</tr>
<tr>
<td>Us’va-3</td>
<td>Adit</td>
<td>3.0</td>
<td>345</td>
<td>902879</td>
<td>312</td>
</tr>
<tr>
<td>Chkalov</td>
<td>Kamenka adit</td>
<td>2.9</td>
<td>444</td>
<td>362401</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>Claudinskaya adit</td>
<td>3.0</td>
<td>608</td>
<td>277000</td>
<td>168</td>
</tr>
<tr>
<td>Nagornaya</td>
<td>Sloping shaft</td>
<td>3.7</td>
<td>1387</td>
<td>657436</td>
<td>912</td>
</tr>
<tr>
<td></td>
<td>Adit</td>
<td>2.9</td>
<td>344</td>
<td>374037</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 years of October</td>
<td>Hole 17</td>
<td>3.4</td>
<td>699</td>
<td>4777368</td>
<td>3338</td>
</tr>
<tr>
<td></td>
<td>Holes 56-62</td>
<td>3.2</td>
<td>566</td>
<td>88535</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Well 13</td>
<td>4.9</td>
<td>486</td>
<td>87600</td>
<td>43</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1st May</td>
<td>Adit</td>
<td>2.6</td>
<td>542</td>
<td>571531</td>
<td>310</td>
</tr>
<tr>
<td>Kalinin</td>
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<td>4865</td>
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<td>Shumikhinskaya</td>
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<td>111</td>
<td>87600</td>
<td>10</td>
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<tr>
<td>Taethnaya</td>
<td>Northern adit</td>
<td>3.2</td>
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<td>11370</td>
</tr>
<tr>
<td>Kospashskaya</td>
<td>Hole 2-bis</td>
<td>3.5</td>
<td>4659</td>
<td>1814523</td>
<td>8454</td>
</tr>
<tr>
<td>Belyi Spoy</td>
<td>Hole 63</td>
<td>3.3</td>
<td>771</td>
<td>555753</td>
<td>428</td>
</tr>
</tbody>
</table>

Total: 22779712 57743
Total number of waste piles in KCB is more than 100 (fig. 1). Excavation of rocks from the mines and storing them in the piles resulted in oxidation of sulfur-contained minerals and heat generation together with spontaneous combustion of piles. As a result of burning, a large amounts of hydrogen sulfide and carbon dioxide were released into the atmosphere (Maksimovich & Khayrulina 2011). Rainfall and groundwater interacting with the piles’ rocks are saturated with various macro- and microcomponents, acquire the mineralization of up to 50 g dm$^{-3}$, and contaminate groundwater and surface water in the zone of influence of the coal basin.

**River water contamination.** Mine water discharges contaminate the catchment areas of 4 large rivers of the Perm region. The total length of polluted watercourses is over 500 km. The substantial amounts of technogenic yellowboy precipitate, contained high concentrations of mobilized contaminants, have been accumulated in rivers and floodplains (Maksimovich 2011; Maksimovich, Khayrulina 2011; Maksimovich, Berezina 2018). The dynamic of yellowboy accumulation is shown on fig. 3.

### Planned treatment measures

In 2018 and the beginning of 2019, we developed the schedule of measures to minimize and eliminate the negative effect of KCB contamination sources on the environment, based on laboratory experiments and field works.

**AMD treatment.** Hydrogeological GIS-modeling was used to determine the proper location of the first-step treatment measures. It allowed to evaluate the hypothetical efficiency of these measures applying also (Table 2).

**Waste piles treatment.** We plan to cover piles with alkaline waste products. Laboratory experiments revealed the high efficiency of

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**Figure 1** Waste pile of Kospashskaya mine

**Figure 3** Accumulation of yellowboy in the rivers of KCB (with forecast up to 2030)
Table 2 The first-step treatment measures in the territory of KCB

<table>
<thead>
<tr>
<th>Mine</th>
<th>Mine water discharge source</th>
<th>Average discharge, m³/year</th>
<th>Treatment measure</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lenin</td>
<td>Main and auxiliary shafts</td>
<td>137623</td>
<td>Tamponage</td>
<td>Liquidation</td>
</tr>
<tr>
<td>Voledarsky</td>
<td>Adit</td>
<td>155155</td>
<td>Tamponage</td>
<td>Liquidation</td>
</tr>
<tr>
<td>Krupskoy</td>
<td>Adit</td>
<td>157785</td>
<td>Diversion of surface water</td>
<td>Decrease on 80%</td>
</tr>
<tr>
<td>Us'va-3</td>
<td>Adit</td>
<td>902879</td>
<td>Diversion of surface water</td>
<td>Decrease on 60%</td>
</tr>
<tr>
<td>Chkalov</td>
<td>Kamenka adit</td>
<td>362401</td>
<td>Injection of alkaline reagents</td>
<td>Decrease on 30%</td>
</tr>
<tr>
<td></td>
<td>Claudinskaya adit</td>
<td>277000</td>
<td>Injection of alkaline reagents</td>
<td>Decrease on 50%</td>
</tr>
<tr>
<td>Nagornaya</td>
<td>Sloping shaft</td>
<td>657436</td>
<td>Diversion of surface water</td>
<td>Liquidation</td>
</tr>
<tr>
<td>40 years of October</td>
<td>Holes 56-62</td>
<td>88535</td>
<td>Tamponage</td>
<td>Liquidation</td>
</tr>
<tr>
<td></td>
<td>Well 13</td>
<td>87600</td>
<td>Tamponage</td>
<td>Liquidation</td>
</tr>
<tr>
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<td>Adit</td>
<td>571531</td>
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<td>Liquidation</td>
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<td>Diversion of surface water</td>
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<td>Taezhnaya</td>
<td>Northern adit</td>
<td>5426038</td>
<td>Diversion of surface water</td>
<td>Decrease on 40%</td>
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<tr>
<td>Belyy Spoy</td>
<td>Hole 63</td>
<td>555753</td>
<td>Diversion of surface water</td>
<td>Decrease on 50%</td>
</tr>
</tbody>
</table>

Figure 4 pH of water draining covered (1) and uncovered (2) waste pile

Figure 5 Chemical characteristics of river water after overlaying yellowboy with limestone rocks
using them to neutralize water draining piles’ rocks (Sedinin 2018 a ,b) (fig. 4).

Yellowboy treatment. We plan to use limestone rocks to overlay yellowboy covering riverbeds. Laboratory experiments revealed that 0.5 cm thickness cover of limestone over yellowboy is sufficiently effective to keep neutral pH of river water during 310 days at least (fig. 5).

Conclusion
Hydrogeological GIS-modelling revealed that the first step treatment measures could lead to 40% decrease of negative effect of ARD in KCB. To achieve complete remediation of KCB territory, we plan to use active and passive treatment systems. GIS-modelling was applied to choose proper displacement of them.

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MODERN EDUCATION FOR GEOLOGICAL SPECIALITIES
Abstract
Massive Open Online Courses (MOOCs) have been applied at the university level in various forms worldwide. However, not enough attention has been paid to this educational resource in the area of teaching English for Specific Purposes (ESP) for students of the earth science. The paper considers the methodological and educational potential of the MOOCs for students of geological disciplines and offers innovative ways of integrating this pedagogical resource in the ESP programs. The use of such free resources proves to be a certain advantage for Russian lecturers and their students since it provides an opportunity to search for and select new up-to-date materials. It discusses a possibility to create own MOOCs that are best suited for educational purposes locally and internationally.

Keywords: massive open online courses, integration, geoscience students, English for Specific Purposes

Introduction
Massive Open Online Courses (MOOCs) have been applied at the university level in various forms worldwide since 2008. However, not enough attention has been paid to this type of educational resources in Russian higher schools of learning, especially in the area of teaching ESP (English for Specific Purposes) to students of the earth science.

A comparative analysis of a number of textbooks used by English teachers from Russia revealed that they are largely oriented towards translation of theoretical materials rather than real life communication in a professional field. For example, in the ESP textbook for students of mining and geological specialties, the focus is on reading and translation of original literature on mining, annotation and abstracting articles on mining topics (Delieva et al. 2015). English for Petroleum Geo-students Teaching manual is aimed at forming skills in reading authentic literature on petroleum geology and discussing the relative topics using colloquial and terminological lexis. (Soukhanova 2009; Zhuravleva 2011; Kitkova and Safyannikova 2006). Thus by the end of the ESP course geo sicence students are supposed to master the terminological vocabulary, reading and understanding texts on geology and acquire basic skills in speaking on geo scientific and technical topics.

Another drawback of the conventional approach is a lack of interdisciplinary interaction between related sciences, namely geology, hydrology, ecology, biology, chemistry and physics, social sciences and environmental issues. Thus, new types of teaching materials for educating Bachelor, Master and postgraduate students are necessary to develop.

At the same time, we argue that there should be a balance between language learning and the content. MOOCs are designed for developing both language skills and expanding the learners’ knowledge in a particular subject area. Here we use the term CLIL (Content and Language Integrated Learning) as an HE (Higher Education) approach in which some form of specific and academic language support is offered to students in order to facilitate their learning of the content through the English language. Whereas materials provided by online courses can be still teacher-centered or content-based, we consider MOOCs to be truly learner-centered in our case since students have a privilege to choose what courses they prefer to study as future professionals.
In this paper we consider a project of integrating MOOCs as an innovative educational ESP tool based on the learner-centered approach, cognitivism and connectivism in the digital era. The learner-centered or student-centered approach includes methods of teaching that shift the focus of instruction from the teacher to the student. The students and the teachers become partners in the learning/teaching process. The primary goal of the teacher is to facilitate students’ learning and comprehension of the subject material. We fully agree with Nunan’s view on learner-centeredness, who says that “it is a matter of educating learners so that they can gradually assume greater responsibility for their own learning.” (Nunan 2012).

Some other features according to this approach are as follows: 1) Students work harder than teachers. Students do a lot of tasks on their own outside the classroom. 2) Students apply new learning to real-life, authentic experiences. Classes focus more on skills that you can use in real-life. Classes that don't have real-life application hardly ever motivate students to engage in meaningful learning. 3) Students use personalized technology to produce. Students learn by doing. So technology, especially mobile phones and tablets which are easier to handle and use than computers can really boost engagement and motivation. If you want your students to create, one of the cheapest and engaging ways is using the resources available on the Internet (Richard 2017).

One of the ways to implement the use of the true learner-centeredness can be done through using online resources, namely, massive open online courses (MOOCs) in and outside the classroom. We looked into the methodological potential of the MOOCs offered by the FutureLearn platform and the Coursera’s portal: “Geohealth: Improving Public Health through Geographic Information”, “Introduction to Waters”, “Introduction to Sustainability, Water, Civilization, and Nature: Addressing Water Challenges of the 21st Century” and others. These MOOCs are strongly oriented towards video presentation, participation and collaboration. The use of such free resources undoubtedly gives certain advantages for lecturers and their students, as it provides great opportunities to searching and selecting the materials that are best suited for educational purposes.

We implemented this project by offering the students the above-mentioned topics for self study and partly through doing it in a computer class. For monitoring the students’ work they were asked to send the screen shots of their comments for further analysis and discussion in class. Upon the completion of a certain topic the students were given several questions for feedback to reflect on the course.

**Methodology**

Massive Open Online Courses (MOOCs) burst upon the higher education scene in 2008 and since then there has been ongoing heated discussion about their place in and effect on higher education. We propose to approach MOOCs, not as a replacement of traditional in-class instruction, but rather to selectively integrate those courses which are in line with the academic courses of home institutions which are not organisers of any MOOCs.

The term MOOC stands for Massive Open Online Course. Massive refers to scale giving opportunity for connections among participants, Open doesn't mean just free but refers to open access, open syllabi and self-directed learning outcomes, Online points to making materials available on internet in abundance, and Course referring to structure of the online course.

A MOOC consists of short lecture videos, learning tasks for individual or group work, quizzes, peer-graded assignments, discussion forums. The first Massive Open Online Course (MOOC) was conducted by George Siemens and Stephen Downes in 2008. MOOCs are characterized by the absence of formal requirements for enrolment and free participation, by the content being delivered entirely online in an asynchronous manner, by not requiring a link with universities and the lack of penalty for evasion.

By definition, MOOCs are offered in virtual environments, with online registration and use of videos, blogs, etc. and may or may not be linked to universities. The “M” refers to “Massive”, which means that thousands of people can simultaneously take courses
One of the biggest advantages of a MOOC is personalised learning which means putting the student in the center of education. It involves extending the educational concepts of differentiation (teaching tailored to the learning preferences of different learners) and individualisation (teaching paced to the learning needs of different learners) to connect to the learner’s interest and experiences and meet the needs, abilities and interests of every student through tailoring curriculum and learning activities to the individual. The ultimate aim of a personalised learning environment is to create an educational system that responds directly to the diverse needs of individuals rather than imposing a ‘one size fits all’ model on students (Bates 2014).

MOOCs can be considered by some ESP teachers as online ESP language courses and EAP courses since they teach not only the subject area, but also English. It is important that a foreign language MOOC also includes the four major benefits of online language learning for learners: (a) flexibility, (b) personalization, (c) autonomy, and (d) automation (Blake and Guillen 2014).

Flexibility is a key characteristics of a MOOC because students can choose their level of participation in an “a la carte” manner without fees and any prerequisites other than internet access and interest, no predefined expectations for participation including no formal accreditation” (Cooper and Sahami 2013). An opportunity to select a course makes it truly learner-centered.

**Integrating MOOCS in the English language classroom for the Science Students**

We can integrate a MOOC in the English language classroom in several ways. We will demonstrate this using the online platform Futurelearn as an example.

First, this resource is good for both individual and group work and can be considered learner-centered since it focuses on the students’ professional interests.

It offers a great variety of courses for geoscience students to suit different tastes and interests. In the category “Nature and Environment” students have a choice to select from a variety of topics: Concepts in Sustainable Development: An Introduction to the Key Issues, Environmental Challenges: Human Impact in the Natural Environment, Environmental Challenges: Scarcity and Conflict in the Natural Environment, The Earth in My Pocket: an Introduction to Geology and several others.

The last course prepared by Open University offers an introduction to geological processes and invites the students to make a journey of discovery, digging out the geology of the world around us and to find out some amazing things about the Earth. The students...
Learn about different types of rock, before finding and identifying some rocks near them, at the rock cycle and plate tectonics, the link between volcanoes and your mobile phone, or why tiny marine wildlife is at the core of the plastics industry. The students can explore basic geological processes, focusing on how, where and why different rocks and natural resources form across the Earth. Also, they look at some of the environmental and sustainability considerations that geologists need to take into account when extracting and processing these resources.

The course consists of 4 weeks, students are invited to spend three hours a week to complete it.

Since our students have different levels of proficiency in English, they have an opportunity to do the course in their own pace which is a tremendous advantage. One of the benefits is that the students are not forced to complete the whole course if they feel unable to do it. We encourage them to do as much as possible taking into account their individual abilities and competencies.

By doing this we maintain their motivation to learn both their subject and professional English.

This course is conducted by Anne Jay, a lecturer in the School of Environment, Earth and Ecosystem Sciences at the Open University. She researches the geologic structures called large igneous provinces. The second instructor is professor Marcus Badger, a lecturer in Earth Sciences at the Open University. His scientific interests include organic molecules preserved in rocks to study the past 66 million years of the Earth's carbon cycle and climate.

Since the developers of such courses are specialists in their field, the students trust the information provided by the course to develop their specialism knowledge.

Findings and results

In a broader sense, such MOOCs can be considered as “live” textbooks both for the students and professors.

MOOCs could also be successfully done in groups in the form of a flipped classroom where “the extra class hours could be utilised positively for more interaction and in depth discussion of relevant topics.” (Fagen 2012).

This implies that teachers should participate in the ‘flipped classroom’ approach as learners so that they genuinely facilitate enriched learning in the classroom.

Moreover, we strongly believe that MOOCs can be collaboratively developed by an interdisciplinary team of Russian educators from the geosciences and ESP teachers and educators, on the one hand, and a partner university colleagues who can develop a comprehensive comparative analysis of real world issues and practices, on the other hand. We suggest that such online courses will be beneficial for all the participants involved.

One more important distinction of MOOCs from regular courses is the opportunity for students to collectively discuss its topic on an online forum under the teacher’s supervision. This could be the major advantage for geoscience students of Perm State University as well as most Russian institutions of higher education, since they do not usually have seminars on the geological and related subjects and thus tend to adopt available geological information ‘as is’, without proper critical re-evaluation. In other words, online forums of MOOCs can add an important component to the educational process allowing students to develop strong professional thinking and gain deeper understanding of the subjects.

Additionally, the fact that geoscientific related MOOCs are held in the English language can possibly increase the level of engagement of students into the discussion. Discussions are arranged once a week in a traditional classroom to monitor the students’ performance where they report on what they have read about and what new things they have learned and as a means of developing the learners’ speaking skills. The teacher can also prepare a number of questions to ask the students to assess the knowledge they have gained. Upon the completion of a course we organize a roundtable discussion that covers the major topics of the MOOC.

Another form of the speaking skills development is organizing a conference where students make presentations on the analysis of the information learned. Traditionally, we invite specialists-experts to participate in the conference.
One of the ways of assessing the students’ progress in the English language skills for specific purposes is the learners’ feedback analysis where they are offered the answer some questions about what they particularly liked in the course, what they did not like, what difficulties they faced, what language skills they were able to improve, what they learned about the subject area and whether they would like to study new courses. They were instructed to give full answers to the questions.

The results of the feedback analysis show that their reading, writing and listening skills have considerably improved and special vocabulary has been expanded. Overall, the students’ feedback was positive.

Conclusions
These modern models of e-learning seem to be promising. They are freely distributed, user-friendly and utilize the existing approaches to the topics and problems studied. These resources, however, should be a part of a blended course whereby both conventional and innovative methods are combined. It is explained by a limited number of hours taught, the curriculum and the Russian state educational standards.

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Training of Specialists and Masters on Geology in the Field of Placers, Technogenic Deposits and Research the Microstructures of Substance in Perm University

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Abstract
Placers and man-made (technogenic) deposits are an important resource for mining in the world. The geological department of the University of Perm has being training of specialists, bachelors, masters and PhDs in placer and technogenic deposit geology since 1961. A scientific school has been formed to study the structure and composition of alluvium deposit and placers. Specialized concentrating complexes and techniques have been developed that allow for prospecting and exploration for placers of gold, platinum, diamonds, zirconium-titanium minerals. Much attention is paid to the study of the geology of technogenic-mineral formations.

The consolidation of knowledge and practical work skills occurs during the period of specialized training practice in the search and exploration of minerals. The practice takes place on alluvial deposits and man-made objects of the Western Urals, the Krasnoyarsk Territory, Khakassia and Tuva. While studying, students write scientific articles and take part at scientific conferences. The materials of educational and industrial practices are the basis for the implementation of term, graduate and thesis bachelors and specialists, master's theses. Over the past 10 years, more than 150 graduates have been trained for industrial, scientific, and research organizations.

Keywords: Training, specialists and masters on geology, field of placers, technogenic deposits, Nano-sculpture the surface of gold.

Introduction
Placers and man-made (technogenic) deposits are an important resource for mining in the world. Placers are among the deposits mastered by mankind since ancient times. These attract attraction primarily due to the ease of their development, simplicity and low cost of extracting useful minerals from them. Placers and now continue to play an important role as sources of many types of mineral raw materials - gold, platinum, diamonds, cassiterite, zirconium-titanium minerals, amber and other minerals. Technogenic placers remain in the form of dumps and landfills after the development of natural alluvial deposits and are also an important source of mineral raw materials in the world.

Therefore, the training of qualified specialists in the field of geology of placers, technogenic deposits and microstructure research of substances is an important task. The Geology Department of the Perm University has being training of specialists, bachelors, masters and PhDs in placer and technogenic deposit geology since 1961. A scientific school has been formed to study the structure and composition of alluvium deposits and placers. The main topics are fine grains of minerals of useful. Perm University twice (2005, 2015) held international meetings at which reports on placer geology were discussed.

In the study of placers, we use standard and innovative approaches. Specialized concentrating complexes and techniques have been developed for prospecting and exploration of gold, platinum, diamonds and zirconium-titanium minerals placers. Much attention is paid to the study of technogenic-mineral complexes. During the course the students firstly obtain basic
geological knowledge. Then they study the special courses Geology of placers, "Alluvial lithogenesis", "Panning method", "Geology of technogenic deposits", "Fine valuable minerals", "Mineral processing (geological approach)". Published textbooks, manuals and monographs are used in the educational process (Lunev and Naumova, 2005, 2011; Osovetsky, 2009, 2012, 2013; Osovetsky and Naumova, 2014; Naumov, 2011). Special courses are given by professors of Perm University, as well as visiting professors from other universities, scientific and industrial organizations. Academician N.A. Shilo, Doctor of Geology, Professor N.G. Patyk-Kara, Doctor of Geology, Professor A.V. Korobitsyn, Doctor of Geology, Professor Yu.V. Shumilov, Doctor of Geology, Professor A.G. Barannikov, Doctor of Geology, Professor A.V.Lalomov at various times have been working at the Department of Mineral Exploration and Prospecting at the Perm University. Canadian placer geologists W. LeBarge and Alejandra Duk-Rodkin lectured to undergraduate and graduate students.

Field studies
Specialists in the geology of placers in the world use standard concentrating complexes and technologies for prospecting and exploration of gold, platinum, diamond and zirconium-titanium placers. The peculiarity of our approach is that the Perm University has developed a unique enrichment plant "Small Valuable Minerals". This is a combination of processing equipment: screen (sieve), screw separator and screw gateway. This installation is compact and easy to use. It showed good results in the enrichment of placers deposits.

The consolidation of knowledge and practical work skills occurs during the period of specialized training practice on the prospecting and exploration of minerals. The practice takes place on alluvial deposits and man-made objects of the Western Urals, at enterprises and deposits of the Krasnoyarsk Territory, Khakassia and Tuva with participation of the students of Oxford University (UK) and China Petroleum University (China, Qingdao).

Specialized geological practice of the students is carried out in accordance with the curriculum approved by the Educational-Methodical Council of the Geological Department of Perm State National Research University. The practice is organized in order to consolidate the theoretical knowledge of students on the courses: "Petrography", "Mineralogy", "Structural Geology". The form of practice is geological excursion. The main tasks of the practice are developing the skills of field geological research, collecting sampels of rocks, ores and fossilized remains of ancient flora and fauna, materials for students research, replenishing educational geological collections.

The practice areas are the geologically well-studied placers of the Eastern Sayan, the eastern slope of the Kuznetsk Alatau, the Minusinsk Intermountain Trough, and the Tuva Basin. Students independently conduct field testing of gold placers on the "Small Valuable Minerals" installation. The objects of excursions are mineral deposits of more than 10 geological and industrial types, Paleozoic and Mesozoic stratotypical cuts, standards of ore-bearing igneous complexes, geological sights and natural monuments of world and federal rank. All objects of practice are well naked.

The organizational forms of practice are bus and walking tours. The organization of life are accommodation in tent camps and meals in the field. The time and the main places of practice coincide with the time and places of practice for geological students from leading universities in Siberia: Tomsk Polytechnic University, Novosibirsk, Siberian and Tomsk State Universities. Students and teachers have the opportunity to meet, establish business contacts and make friends with colleagues. Duration of practice is 13 days. Excellent climate, good nudity, diversity of geological structures are very useful for educational geological practice of geological students.

During the internship, students visit unique deposits at the Kuznets k Alatau (Kommunarovskoe gold ore, Sorskoye copper-molybdenum, and Teysk skarn-magnetite); in the Minusinsk depression (bentonite, coal); in the Western Sayan (Kibik-Kordonskoe marble, Abaza iron ore); in the Tuva intermountain trough (chrysotile asbestos Ak-Dovurak, coal). At
some deposits (gold Tardan, gold placers of the Bai-Syut River, Saraly) and in the river valleys (Yenisei, Abakan, Kea-Khem, Bia-Khem, their tributaries), students conduct field testing, assess the gold-bearing nature and man-made formations. They get practical skills in using pans (prospector’s tray) and spiral concentrators. Students use the enrichment plant «Small Valuable Minerals » for enriching samples and trapping fine gold.

**Laboratory research**

At the laboratory stage, students process samples and carry out particle size, mineralogical and petrographic analyzes.

Samples taken in the field are studied according to the following scheme:

1) drying; 2) magnetic and electromagnetic separation; 3) isolation of the heavy fraction (minerals with specific gravity over 2.9 g/cm³); 4) research under a binocular microscope of minerals and gold. They detect gold sizes, determine the coefficients of flatness, sphericity, roundness and describe gold morphology.

Modern scientific equipments are used for research such as a compact powder diffractometer D2 Phazer (Bruker) for X-ray diffraction analysis, a JSM-6390LV microscope (Jeol) and EDS energy dispersive spectrometer (OxfordInstruments) for electron microscopy and microprobe analysis; a JSM-7500F microscope (Jeol) for high-resolution electron microscopy; an X-ray fluorescence spectrometer S8 Tiger (Bruker) for an X-ray fluorescence analysis, an thermal analyzer of the synchronous thermal analysis STA 409 Luxx with detectors for thermogravimetric

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**Figure 1** Gold from man-made dumps (Kytylym placer, Sverdlovsk region), general view of grains. Scale line is 100 mkm

**Figure 2** New formations on the surface of gold. Increase (number of times) - 12000

**Figure 3** New formations on the surface of gold (nanofilm). Scale line is 100 nm

**Figure 4** New formations on the surface of gold (nanopores). Scale line is 100 nm
analysis, an atomic absorption spectrometer MGA-915 (Lumex) for atomic absorption analysis. Granulometric analysis of terrigenous rocks, petrographic and mineralogical studies, including those on Nikon Eklipsis 100 Pol microscopes (Nikon) are used too. Some results of these studies are shown in Fig. 1-7. The practical experience gained while working with gold on modern equipment is used by students in their professional activities. Special training and obtaining certificates of users on software systems, such as Micromine and others are applied for specialized research and synthesis of materials.

When working at one of the deposits of the Yenisei Ridge, students mined and transferred more than 70 grams of gold to the enterprise. During training students have been participating at scientific conferences of different levels: «Minerageny of ancient and modern oceans» (Miass), «Geology of the Western Urals», «Geology in the Developing World», «Readings in Memory of N.P. Chirvinsky» (Perm), Lomonosov readings (Moscow) and others with publishing the results of research. Usually students have from 1 to 4 publications.

Conclusions
The Department of Prospecting and Exploration of Minerals of Perm State University obtained the state accreditation...
of the educational master program on the geological profile «Geology of gold deposits and fine valuable minerals». This program is unique. Masters of such profile are trained only at Perm University and nowhere else. Master’s training is planned for both Russian and foreign specialists.

While studying, students write scientific articles and take part at scientific conferences. The materials of educational and industrial practices are the basis for the implementation of term, graduate and thesis bachelors and specialists, master’s theses. Over the past 10 years, more than 150 graduates have been trained for industrial, scientific, and research organizations. Improving the quality of geological education in the future can be achieved by increasing the volume of field practices, as well as the development of existing courses and the addition of new special courses on detailed studies of the substance.

Geological education at Perm University prepares specialists who are able to solve different scientific and production problems of scientific and technical research at the modern level.

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International Collaboration in Geo Science Education via Project Based Learning

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Abstract
Future Russian Geo science students are somewhat isolated from the global professional community since university students lack real-world experience as well as the use of the English language in their professional field. The International Project Based Learning Model (IPBLM) is offered to improve the Geo science students' 21st century competences by applying a variety of innovative educational tools with a specific focus on online and offline group discussions and videoconferencing with chosen partner universities. The research analyses recent “real-world” collaborative projects on Geo-ecological issues and environmental matters, such as water conservation and human/environmental interactions.

Keywords: Geoscience students, Project Based Learning, CALL, international collaboration

Introduction
Rather than focus on International collaboration, several Russian universities maintained conventional designs. These conventional designs were focused on producing specialists for local labor markets. This practice isolated Russian Geo science students from their colleagues in the global community. This isolation was aggravated by the fact that university students tended to lack real-world experiences. Some students also lacked opportunities to use the English language when communicating with their peers. Most Russian universities, including Perm State University (PSU), maintained this single-disciplinary orientation approach, which was said to “focus only on a set of trees within a great forest” (Jacob, 2015, p. 2).

The new Russian National Curriculum does not embrace training professionals in competency regarding foreign languages (Federal National Standards, «ФГОС 3+++»). This practice deprives future Russian Geo scientists of global professional communication. Due to this new curriculum, Russian Geo science students have less opportunity to participate at international conferences, mutual research projects and other important academic events. This leads to Russian Geo science students to lag in their disciplines. The current ESP class curriculum is also restricted to only learning words, word combinations and collecting a glossary of terms related to different word concentrations. This current paradigm is ineffective without the practice of real-world communication within international collaboration. This research provides an overview of the initial stage of introducing the International Project Based Learning Model for Geo Science students underpinning the best teaching practices.

Research Questions
There is strong demand for Russian Geo science students to participate in “real-world experiences.” Russian Geo science students need to learn via interdisciplinary approaches, approaches that are widely accepted within other academic institutions.
One commonly used teaching strategy is Project-Based Learning (PjBL) (Stozhko, et al. 2015). Introducing content from both global and interdisciplinary perspectives, require “a radical restructuring of the whole learning process.” (Stozhko, et al. 2015, p. 5) The present research will focus on only the initial research in the field of teaching ESP through PjBL. The questions selected for this stage in the research are as follows:

1) Can the PjBL help students enhance their communicative skills in listening, speaking and writing? 2) Can PjBL increase motivation towards a more profound learning of English and ESP in particular? 3) Can PjBL motivate students to broaden and deepen their knowledge of globalization, as well as disciplines related to the topic of the project?

The questions stated above are the result of evidence cited from numerous publications. PjBL is widely cited in Barak and Dori’s (2005) work, which compared two groups of chemistry students. Group A took a course using traditional methods while Group B – an IT-based PjBL course, achieved better results in terms of understanding chemical concepts and theories.

The steps in the PjBL approach are as follows: 1) In PjBL the student role changes from “learning by listening to learning by doing” (Stauffacher et al., 2006: 255). 2) Learning by doing must be applied to subjects that are of interest to the students, connecting knowledge to everyday life through ‘real-world’ tasks (de Graaf & Kolmos, 2009; Thomas, 2000; Bell, 2010; Hanney & Savin-Baden, 2010). 3) Being a learner-centered approach, PjBL requires the shift of the role of teacher from “sage-on-the-stage” to “guide-on-the-side” (Nation, 2006: 109), or “from a distributor of knowledge to a process manager” Stauffacher et al. (2006: 255). 4) The enhancement of students’ collaborative skills can be regarded as one of the outcomes of the application of PjBL. As Hanney and Savin-Baden explain: “Student activity revolves around a complex series of interactions between team members over time and draws on a range of key transferable skills such as communication, planning and team working” (2013). Collaboration can contribute to the active construction of meaning, through idea generating (divergent thinking), idea linking (convergent thinking), and idea structuring (categorization and classification) (Harasim, 1990: 5) The interdisciplinary nature of the PjBL approach has been specified in different studies (Danford, 2006; Lehmann, 2008; de Graaf & Kolmos, 2009; Otake et al., 2009; Hanney & Savin-Baden, 2013, Polyakova et al. 2013 etc). 6) The end-product (a “quality product”) of the project (Danford 2006:12) can be categorized into three types: the research project (traditional academic output such as a dissertation, literature review or research report); the construction project (the design and production of a technical product or artefact) and the professional work context project based on international collaboration with external actors.

The peculiarities of the applied PjBL sessions at PSU are as follows: 1) the working language is English, which is not the Russian native language and therefore considered foreign for DSU students. 2) a variety of topics in general Geo science projects include biological, sociological, cultural, legal and political issues. The international nature of the cooperation between PSU and partner universities leads to the use of information technologies (IT). Thus, our course can be IT-based as well as PjBL. It is common knowledge that PjBL in many cases can incorporate modern technologies of online interaction.

**Methodology**

The International PjBL Model (IPBLM) is implemented within Computer Assisted Language Learning (CALL) and the Computer-Mediated Communication (CMC) approach. The CALL represents a side of e-learning where computer technology is used in the context of language learning. (Yuan, 2007: 416). The CALL environment is widely used to refer to the area of technology and second language teaching and learning (Chapelle, 2001: 3). This approach is naturally integrated into the CMC paradigm, whereby the focus is on changing both the quality and quantity of communication by allowing time for critical reflection and greater involvement in discussion than is allowed in the traditional
classroom (Berge, 1995; Fishman, 1997; Wells, 1992).

One effective component, of CMC, is video-conferencing. Recently, the term “telebridging” has been used for this new technology (only about fifteen years old). Telebridging allows for interactive meetings between individuals or groups of people located in two – or more – different locations. By “interactive” it is meant that participants in a video-conferencing session can see and hear each other. In addition, the participants can share information using different types of visual aids. Much of the research literature suggested that the synchronous conferencing tool is cost-effective as well as affordable. All studies, however, indicated that interactivity is the key of synchronous conferencing (Greenberg, 2004). The advantages of using synchronous conferencing included use as a collaboration tool for team projects or team teaching (Alexander et al., 1999; Coventry, 1994; Townsend et al., 2001). Telebridging can provide active support, including prompt feedback (Alexander et al., 1999; Chan et al., 2000; Pittman, 2003). Telebridging made it possible for distant people to access experts (Alexander et al., 1999; Pittman, 2003). Telebridging can save travel time and travel cost (Chan et al., 2000; Coventry, 1994; Wilkinson & Hemby, 2000), and it can increase interactive communication with engaging discussion while enhancing social presence (Chan et al., 2000; Coventry, 1994; Pittman, 2003; Smyth, 2005).

The term “telebridging” was introduced in 2011 as a name for a special internet-based international project regarding student and professor collaborations with partner-universities (Mishlanova, Polyakova 2011). Telebridging is an authentic peer-to-peer collaboration that takes place in virtual environment (Gritsenko E.A., Polyakova S.V., Frolovich E.M. 2013; Polyakova, Gritsenko, Losavio M. & Connor D. 2014, etc.)

The project enhanced connectivity and socio-emotional commitment to the learning process by involving Geo science students of Russian and international universities to be active participants in the learning process. Overall, students achieved greater cognitive development working together, rather than working individually. This, in turn, helped students develop their XXI century skills (Unlocking a world of potential 2015).

The Project Based Learning telebridging has been successfully implemented with students in both the Humanities and the Sciences. The project has successfully connected students at PSU and partner universities in the USA (Losavio and Polyakova 2011; Remizova et al. 2013).

2019 Geoscience Project Rationale

This academic year signaled the launch of the new IPjBL telebridges “Environmental Issues of the World”, “Flint Water Crisis: Water Conservation and Human/Environmental Interaction” “Learning Science in Non-Traditional Places” (Ecological Tourism in the USA), “Legal Regulations of Environmental Safety.” These projects were specifically designed for Geo science students at Perm State University, DSU State Uniersity (MS, the USA) and the University of Louisville (KY, the USA).

This research employed a three-stage module pre-conference, during-conference, and post-conference. The specifics of the project were represented by a series of online meetings, centered on a variety of Geo-ecological issues. Some of the topics that were studied and presented, during the online conferences in the second semester, were “Ecotourism”, “Kizel Coal Basin”, “the Permian Period”, “the Kama River Basin”, “The Chusovaya and the Vishera”, “The Disappearing Rivers”, “the Kungur Cave.” It is important to note that the preparation stage was of crucial importance for the successful implementation of the tasks set for the two parties. For the first video session, Professor J. Lane and his students provided the Russian participants with materials for the video conference (the article, video presentation based on the article by J. Lane and J. Stoltman, 2016). The Russian students were able to read the information in advance.

The during-conference stage included discussion of the information presented by the American students. One of the topics was the British Petroleum Oil Explosion in the Gulf of Mexico and its aftermath. In his
five-minute presentation, Brandon (the DSU student) described a deadly explosion that occurred on the oil drilling rig Deepwater Horizon, operating in the Gulf of Mexico. The student shared his personal experience of the accident. The professor explained how the spill had affected tourism, fishing and other industries throughout the US states in the gulf coast, as well as its harmful effect on the wildlife in that area.

The second presentation was devoted to the geographical situation of the State of Mississippi, its climate, biodiversity, cultural and social background. The presenting group compared the climographs of Orenburg Region and the State of Mississippi.

The Russian students prepared several well detailed questions. The Russian students primarily asked questions about the disaster management in the states of Louisiana, Florida, Alabama and Mississippi. In addition, the Russian students asked general cultural questions about the American south and about specific historical places such as Po Monkey's Juke Joint.

The post-conference stage included the students' assessment of the telebridging project. The American and Russian participants (n=26) completed two assessment instruments that were developed by the Delphi Teaching and Learning Center of the University of Louisville. (Losavio, Polyakova, 2011: 348). These instruments, the Ideas to Action “Student Evaluation Form” and “Student Reflection Form,” asked the students to reflect on their attitudes towards the international teleconference project experience and what they gained from it.

For example, the participating students were asked their opinions on whether the participation in the project helped them either connect what they had learned in class to real life situations or contributed to knowledge in the discipline studied. The participating students then evaluated how the teleconference helped them with content application, critical thinking and self-development. Analysis of the students' answers illustrated that both groups found substantial benefit in both the project activities and in the teleconference itself.

Most American and Russian participants agreed, or strongly agreed (18 students), that their interaction in the teleconference helped them to apply the skills and knowledge they gained from their major courses. Both groups of students improved their understanding in other course materials and activities. In addition, both groups of students realized how critical thinking can be used in everyday life. This experience enhanced student ability in communicating real-world ideas and interdisciplinary content. The students also indicated that this project improved their ability to analyze ideas and examine issues from multiple points of view.

The students' assessment instrument also included issues related to critical thinking such as a. Clearly identified the key issue, topic, or situation for the experiences b. Accurately interpreted relevant information c. Developed well-reasoned, specific conclusions and problems d. Considered assumptions, implications and consequences of alternative points of view and e. Precisely communicated the experience to others. Most students indicated point “d” as being relevant to their critical thinking development.

Some American students responded with the following comments on their telebridging experiences: *It helped me learn new things from new people; It has helped me see different teaching methods; I want to view different perspectives now; being a geography major, it had information for me to take in and apply in situations; It had given me the knowledge that I didn't have before; It gave me a Russian point of view on Russia; It has helped me to understand what people from another country think about the USA; I learn more from Russians.*

The Russian students provided the following responses: *It helped me to understand the differences in American and British English; I learned a lot about Mississippi; I know about the crappie fish; The conference is so educating and cool; I have knowledge about many geographical and cultural places.*

Both Russian and American students stated that it was a great experience and that they would love to do it again: “*It was perfect/I loved it*”. One of the American students indicated that it should be included in future classes. This gives students a great chance to connect with students all over the
world. The other wrote that it should be a yearly experience for everyone.

Among other post conference reflections the students emphasised that it was fascinating to learn from other cultures and that it was cross-cultural engagement; It was the first time I connected with an international class; I think it is important to connect with people all over the world; It was interesting to see how students in non-western universities learn etc.

Conclusions and Recommendations

The telebridge project increased interest in cross cultural communication while establishing long-term, professionally oriented, IT communication between American and Russian students and professors. This project also demonstrated how telebridge and cross-cultural discussions may help students better understand their own language and culture as well as the ambiguities within their own language and culture.

Another outcome was that the telebridge had a substantial effect on both Russian and American Geo science students. In addition, Russian biology students increased their motivation in learning English as their language for professional and international communication.

Based on our educational experience of applying the IPBL with other academic institutions, the model brings together faculty and students to explore opportunities of collaborative and problem-solving. IPBL has been applied in the areas of geology, ecology and related sciences. IPBL has also been shown to promote the expansion of relationships between universities and communities.

In addition to international collaboration, the IPBL model includes critical thinking, problem solving and self-management skills. These skills can be implemented through online as well as offline group discussions, workshops, virtual museums and exhibitors, round-tables and conferences. IPBL is especially proficient within the international collaboration of several Geo ecological issues and environmental matters, such as water contamination and public health, raising environmental awareness, water management, mine water treatment and many others. Through these activities’ students increased their awareness regarding differences and similarities in other countries. Thus, the key element for creating “real-world” learning was to establish and promote contacts with partner-universities and international associations that deal with geoscience.

This project facilitated the exchange of ideas regarding new and innovative opportunities, knowledge and skills for students, researchers and faculty from different Geo science disciplines. The collaboration maximized inter-university and community engagement by Geo science students and their counter-parts. A considerable benefit of this international project was that all the Russian participants had the opportunity to communicate in English, which is not their mother tongue. In addition, all the American students increased their understanding of our diverse global community.

In conclusion, the telebridge as an educational technology has enormous educational potential for the development of professional cross-cultural competence of future specialists. The telebridge project promotes the use of learner-centered approach to teaching English for Special Purposes in the IT environment.

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Storytelling Via Digital Media As A Success Factor In Education For Geological Specialties

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Abstract
Telling stories seems to be as old as human language itself and is common in every culture. This provides the framework for the marketing method storytelling that can be used as a didactic instrument to teach complex knowledge through its varied and entertaining effect. Combined with the use of digital and social media, the increase in knowledge, motivation and acquisition of competence can also be increased in the teaching of geological specialties.

Keywords: Storytelling, digital media, education

Presentation of the problem and thematic introduction
For the successful future of the global raw materials and energy industry a sufficient number of skilled workers with suitable skills and social acceptance for the necessary projects (such as opencast mines, underground mines and processing plants) are required. This means that children and young people as the “decision-makers of tomorrow” but also as potential future students need to develop an interest in the subject areas. In order to enable them to do this, it is essential to provide them with sufficient knowledge. However, teachers are increasingly complaining that the pupils hardly perceive their direct surroundings and environment, that they lack a direct encounter with nature and are increasingly alienated from it (Gerl et al. 2018). Moreover, the curricula of most German federal states do not include any educational measures regarding the benefit or necessity of mining sites (Kleeberg and Drebenstedt 2018). As a result, there is a huge need for action in communicating these topics and scientists argue that education can make a decisive contribution (Krombaß 2007).

Students from geological disciplines or attendees of advanced training courses in these disciplines must also be activated in order to maintain their interest and thus their intrinsic motivation to acquire further knowledge as well as to work in this field.

Public acceptance plays a decisive role here. Only if research and mining projects as well as the dismantling of such projects do not encounter protests by the population these projects can be implemented successfully. Otherwise, protests often lead to severe delays and thus to high costs for the stakeholders. On the other hand, public acceptance for geology, mining and related topics leads to a situation in which professional activity in this sector is regarded as desirable by pupils suited for engineering studies.

In order to meet this diverse field of tension, the Storytelling method should be used in a variety of settings. If people are to be convinced to do something, stories can make an essential contribution (Adamczyk 2015). They are the key to successful communication because they allow facts to be linked with emotions (Adamczyk 2015). This makes the messages embedded in the stories appear stronger (Adamczyk 2015). Although the communication of plain facts offers the alleged advantage of objectivity, it leads to impersonality which is why abstract information may and should be translated into convincing images with the help of storytelling and supplemented by a personal component (Small et al. 2007).

Furthermore, digital media and multimedialisation (also) have changed...
teaching and learning considerably in recent years (Otto and Becker 2016). New methods are increasingly creating opportunities for different target groups to absorb information and thus learn, regardless of time and place (de Kraker and Corvers 2014; Otto 2014; Wilson et al. 2011).

**Presentation of the methodology and selected practical examples**

Telling stories has always been an essential part of human communication; it is one of mankind's oldest methods of communication and seems as old as human communication itself (Hennig et al. 2017; Schneider and Köhler 2017; Herbst 2014; Becker and Otto 2016). Listening to stories is learned from an early age and is an indisputable part of human life (Herskovitz and Crystal 2010). Stories are of elemental importance to all nations, cultures and societies and according to Schmieja (2014) have "the ability to transcend cultural, gender and age barriers."

(Schmieja 2014, according to Denning 2011)

The application of storytelling as a didactic tool in schools and other educational settings to teach complex knowledge in a varied and entertaining way can be dated back to the early 1990s (Otto and Becker 2016). In the academic field, storytelling is used in particular when complex problems are to be made handy for knowledge transfer (Floßmann 2014; Schekatz-Schopmeier 2010). Storytelling is a process in which narrating and listening are inseparably linked (Frenzel et al. 2006). In this form of communication, the narrator summarises the complex knowledge in a story and shares it with a person or group (Fisher 1987).

Storytelling means

"to use stories purposefully, consciously and skilfully in order to make important information easier to understand, to support the learning and thinking of the listeners in the long term, to spread ideas, to promote intellectual participation and thus to add a new quality to communication." (Frenzel, Müller, Sottong 2006)

Thus, it is a tool that allows placing experiences in a general context and passing them on in such a way that listeners can empathise with them (Adamczyk 2015).

The essential elements of a story include message, conflict, characters and action that binds them together (Fuchs 2009). The message that is at the heart of a story refers to the values that are to be conveyed (Adamczyk 2015). This central theme is carried by the protagonist (main character), who must generate emotions within the listener so the story appears as intended (Adamczyk 2015). If the four elements of a story are successfully designed to address the recipient, storytelling can achieve a lot. With this method not only facts but also knowledge can be passed on but it enables the presentation of contexts, provides orientation and can convey visions (Thier 2017; Frenzel et al. 2006). Among other things, metaphorical narration and the possibility of actively involving listeners are used to reinforce the remembrance of content and core messages (Becker and Otto 2016; Schneider and Köhler 2017). Neuroscientific research also shows that storytelling can transmit emotions; the listener feels similar to the narrator/protagonist of the story (Stephens et al. 2010). Furthermore, the possible entertainment value of storytelling is very high and the narrator can make use of a certain amount of artistic freedom (Beer 2017). Because of these exemplary advantages, storytelling is nowadays used in various areas such as knowledge management, public relations, value communication, market research and personnel development (Frenzel et al. 2006; Herbst 2014; Thier 2017).

Storytelling today can be described as a classic concept of passing on knowledge (Otto and Becker 2016). Digital storytelling, on the other hand, is a relatively new method (Robin and McNeil 2012). Digital storytelling "combines the narrative transmission of knowledge with new forms of digitisation such as mobile videos [...] [the] goal is the production, presentation and exchange of digital stories" (Otto and Becker 2016).

One project that considered the process of digital storytelling (see figure 1) was "Living with Climate Change - a Digital Story" (2013-2014) (Becker and Otto 2016; Otto 2016). The learning objective was to enable students from Germany and Tunisia to understand "climate change across disciplinary perspectives
and cultural boundaries” (Otto and Becker 2016). The project phase, which lasted about three months, included workshops, a virtual learning phase and an individual reflection (Otto and Becker 2016; Otto 2016). The task of the students was to “create a story about the effects of climate change in both countries” (Otto and Becker 2016) For this purpose, the participants were given insights into how the respective country is dealing with climate change and exchanged views with activists and scientists on site (Otto and Becker 2016). With the help of digital storytelling it was possible to pursue a learning-centered approach, i.e. to place the students at the centre of the learning process (Otto and Becker 2016). The lecturers came to the conclusion that digital storytelling is “a promising didactic method for student interaction and learning success” (Otto and Becker 2016). Otto and Becker (2016) state that the students had understood climate change to be an “interdisciplinary multi-level problem” (Otto and Becker 2016). Approximately half of the participants stated that the use of the method required the ability to “communicate climate science facts and thus put theoretical knowledge into practice” (Becker and Otto 2016), and intercultural competence as well as the critical reflection of cultural models were promoted (Becker and Otto 2016).

However, social media was not used in the first example “Living with Climate Change - a Digital Story”. Yet these are an elementary part of social life nowadays (Fieseler et al. 2010, according to Meckel 2008). In Germany, 97.6% of 14 to 19-year-olds are online every day with an average daily usage of 4:34 hours (Koch and Frees 2017). Over 62.7% of this time is used for social media such as Facebook, Instagram and YouTube (DAK-Gesundheit 2018). Social media is particularly interesting for young people and has a major effect on their everyday lives. The project “SOCIAL NATURE” was designed to generate interest in geological specialties and to increase knowledge (Walter 2019). Students of a 9th and 10th grade in Saxony (Germany) were trained through excursions, diverse teaching units, various didactic methods and a personalized social media storytelling approach. The whitethroat “Dan” was accompanied as a testimonial using pictures, videos (Walter 2018) and a large number of social media posts (Walter 2019a) for almost a year. The content was created for social media using the view of the whitethroat. The storyteller decides on the perspective from which the event is presented and how the audience experiences it (Adamczyk 2015). The content produced was based on the participants’ research, on-site impressions gained at the mining site, interviews with experts and lectures in an informative and entertaining way. The participants were deeply sensitised and motivated by the research at the mining site because they got involved jointly and put themselves in the bird’s perspective. As a result of the project, the level of knowledge among the participants in the fields of raw materials/energy, biodiversity/environment and digital/social media has increased verifiably in accordance with the increasing overall interest in these topics. The gross reach of the project through website, social media accounts and publications totalled to over 10,000 contacts (Walter 2019).
Comprehensive insights

The presentation of the projects exemplifies the broad spectrum of possibilities in the education of pupils and students in geological specialties. The transfer of knowledge should begin in kindergarten and continue through schools and universities up to adult education. Thus knowledge and interest of the participants increases and thereby enhances the public acceptance for the sectors and their projects. Storytelling is a suitable method for (further) education in this context.

The added didactic value of digital storytelling in terms of enhanced competence acquisition is a high motivation to learn and increased commitment has been confirmed in various studies (Robin 2006; Dogan and Robin 2008). In digital storytelling, researchers like Otto and Becker (2016) refer to the acquisition of competence and according to Robin (2006), problem-solving, interpersonal and technological competence can be increased (Robin 2006).

Due to the strong involvement of the participants as storytellers, the method of (digital) storytelling is suitable for illustrating complex problems in a learner-centred way and thereby promoting networked learning (Otto and Becker 2016). But as with all stories, only the really good ones are told to others (Fuchs 2009).

Outlook on further developments

One possibility to further increase learning success and competence acquisition is the use of augmented reality storytelling although the exact benefit of this approach must be evaluated. As explained above, stories can be produced and consumed by modern media technology regardless of time and place (Zünd 2016). The advantage of Augmented Reality in this case is the high degree of immersion and interaction (Zünd 2016). This can but does not necessarily have to be combined with gamification. Typical elements of a game are transposed into a context that is not familiar with the game in order to enrich the elements of the storytelling (Fondon 2018). The intrinsic desires of the users can be addressed through appealingly designed games and thus increase their motivation to learn through playing (Fondon 2018). Another area that will only be briefly mentioned here is the use of storytelling in journalistic reporting. The extent to which storytelling can be used to communicate complex topics such as climate change, recultivation, etc. in a more appealing way is of high general relevance (Schaefer 2016).

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Abstract
The international teleconference project is an effective method of the team based learning model in English for Specific Purposes (ESP) as well as the CLIL context. This research offers an international educational model of the proposal titled “Environmental Issues of the World.” The proposed three-staged project was centered around multinational, multidimensional frameworks and related disciplines. The stages were: Pre-teleconference (2 months), a series of teleconference (4 events) and Post-teleconference (1-3 months). Through these steps students developed cognitive, communicative and professional competences with all parties concerned. Three uniquely qualified groups of Russian and American students and professors were involved in the project: Geoscience, English Language Teaching specialists and Linguistics.

Keywords: Geoscience students, Environmental Issues, Teleconference Project, Interdisciplinary, ESP, international collaboration

Introduction
Environmental issues, for bachelor students, are of high importance in Russian federal educational standards. For example, education of geoscience students at the bachelor level, includes such cultural competence as raising student’s awareness of (1) the natural environment; (2) society; (3) other people and themselves; (4) the motivation to be guided by this obligation in their professional activities; and (5) the ability to use/apply knowledge in the field. These concepts were based on scientific approaches that helped shape students’ (1) attitudes, concerning humans relationship with the environment and (2) life safety issues and the ability to use scientific knowledge in their social and professional activities (Federal State Educational Standard of Higher Education, 2014).

The purpose of the project was to raise environmental awareness (the ability and willingness to understand the role of environmental protection and environmental management for the development and preservation of civilizations, the challenges of sustainable development, individuals in their relationship with the social system and the natural environment and the risks associated with human activities) for Russian and American students in the discipline of Geoscience. This research was also pertinent to students in related disciplines. The growth of ESP terminology, as well as the raising of General English skills, were the key issues in English language curriculum.

These goals can be achieved through the implementation of international teleconference projects in a Russian University and foreign partner universities as part of the English language curriculum (Mishlanova and Polyakova 2011).

Project Methodology
Being unique every international project involves different methods of data collection and analysis. The researchers decided to apply a Learner-Centered Approach (Nunan 1998) as well as the Content and Language Integrated Learning Approach (CLIL), in
order to achieve the goal of utilizing real world materials through launching an international teleconference project «Environmental Issues of the World» in teaching ESP to Geoscience Students.

The researchers were inspired by the tendency of modern world teaching; in an effort to apply real-world approaches into the classroom (Alstrad-Davies, 2014). The researchers argued that real-world examples helped students raise their motivation to increase their language command. In addition, the researchers argued that real-life examples elevated student concern for the environment.

In the current research, the real word is signifyed by a lively, virtual communication, for both students and teachers. This research took place in Russia with peers from the USA during a unique series of online meetings during the Spring 2019 semester.

The Participants

The participants were students and professors in Geoscience education, from Perm State University as well as other universities in the United States. In addition, Linguistics and English Language Teaching specialists participated from PSU.

The Russian Geoscience students (both undergraduates and graduates) learned new terminology in ESP classes, lectures and seminars. The students discussed specialist topics with professors of Geology, Ecology, Geography, Geochemistry and other subjects.

The US Geoscience students (both undergraduates and graduates) prepared presentations on the environmental issues in the USA.

The linguist students familiarized themselves with the terminology and definitions of a particular subject area in the EAP translation studies. They also observed the teleconferences for their future ESP teaching practices.

English Language Teaching specialists developed ESP materials in collaboration with Russian and American professors from partner-universities.

Later, a group of geoscience and law students joined the project in both countries respectively. The focus of their research was on ecological issues (water quality), environmental justice, and legal regulations of water pollution in Russia and the USA.

The project real world materials

The consultants and scientists provided the participants with relevant articles and textbooks centered on geoscience topics. The Russian students discussed the urgent environmental issues of the Perm Region as well as other locations (The Kizel Coal Basin, the Territory of Verhnekamskoye Potash Deposit, the Vishera River Basin) (Khayrulina 2014; Maksimovich and Khayrulina 2011). One of the key materials was a textbook on geochemical barriers and environmental protection, created by N. Makzimovich and E. Khayrulina. The students found interesting information regarding the environmental consequences of placer mining in various areas of Perm Krai, the effect of sludge settling on the landscape and the pollution of the Pashiika River as well as other Geo science issues (Maksimovich and Khayrulina 2011).

The students from the United States, selected a number of topics, ranging from salinization of fresh water in the northeastern United States (Kaushal et al. 2005) to the Flint Water Crisis in the State of Michigan (Glenza 2018) to environmental justice issues and guided environmental educational tourism in the State of Michigan (Lane, Stoltman 2016).

Some of the articles were centered on water issues in Germany, Australia, and Canada (Salama et al. 1999; Matheson et al. 2018; Gibbs et al. 2017). Choosing the articles, and other materials, the researchers tried to elevate the students awareness on global perspectives as well as raise concerns about Geoscience issues.

In the process of reflecting on this topic, students gathered additional information about abandoned mines and quarries in the United Stated and in Russia. This work was particularly relevant to the Perm region, since there are a number of abandoned mines and quarries. The researchers based a discussion centered on the article “Abandoned Mine and Quarry Accidents Claim Several Lives per Year” by Hobart M. King as an English
language original source (King H.M.). The students created short presentations, of their own. These presentation outlined the problems of the abandoned mines, quarries and even settlements as well as towns in Perm region such as Severnaya mine (Kisel area), Shirokovskiy (Gubaha district), Shumikhinski (Gremiachinski district) and Gubaha.

The outcome of this step was the creation of a glossary of geoscience terms by the geoscience and linguistics students. To gain the understanding of term “formation” they students analyzed the glossaries of geoscience terms, which were compiled by Australian Science Museum specialists.

About 300 words directly correlated to the geoscience topics that were identified by the PSU students and used in the consequent steps of the project. Some of the terms included: consistent backfill, efficient waste management, environmental impact, introduction of modern processing technology, mine openings and residues, ore reserves potash fertilizer production, salt content, pollution, underground water, mining, salinization and others. In addition, a QUIZLET platform was created in order to enhance teaching phonetics, spelling, semantization, exercises, tests, learning games for geoscience field.

The project structure

The project was comprised in three stages: (1) Pre-teleconference (3 months), (2) Teleconference (4 teleconferences in January-March, 2 hours each) and (3) Post-teleconference (1 months) stages. The conference took place during the 2018-2019 academic year in Perm State University, Central Michigan University (Michigan), Delta State University (Mississippi) and the University of Louisville (Kentucky).

1. Pre-teleconference stage

At this stage, students acquired all the necessary skills for further professional communication since collaborative real world materials were developed here.

During the first step, of the Pre-conference stage, the students examined the materials mentioned above.

The second step of the Pre-conference stage was designed to assist the geoscience students at PSU in preparing presentations on the chosen topics for the teleconference. Some of the students concentrated on the topics discussed in the articles, while the others came up with their own ideas. The topics included in this stage were: “The Kizel Coal Basin”, “Permian Geological Period”, “The Rivers of Perm Krai”, “The Balatovo Park”, “The Kungur Cave” and others.

American partner-universities formed their own groups of creative and interested students. These students proposed discussions on major Geoscience issues, such as; water crises in the USA – the Flint Water Crisis and its aftermath, The BP Oil Spill, in the Gulf of Mexico, and its effect on the environment of several states, Human/Environmental Interactions, Water & Its Relationship to People.

2. Teleconference stage

This stage consisted of four videoconferences which were devoted to different ecological matters: “Learning Science in Non-Traditional Places” (Ecological Tourism in the USA); “Flint Water Crisis; Human/Environmental Interaction in the USA”, “Environmental Issues in Perm Region”, “Legal Regulations and Environmental Safety”.

The one-hour Skype conferences were held from January to March, 2019 (Spring semester 2019). During the Skype meetings, the students created presentations, discussed issues that were directly related to underground water pollution, the quality of water in their regions, accessibility of drinking water, river cleaning camps, environmental justice etc. The Skype discussion setting was friendly and relaxed. Apart from the water issues the students initiated discussion of their everyday life and cultural heritage. It is worth mentioning that the second and the telebridges were with the same DSU group, which made the communication much easier and open.

3. Post teleconference stage

The post-telebridge stage included gathering American and Russian students’ feedback on the telebridge activities as well as discussions related to what the
students had learned from the teleconference experience. It included the students' assessment of the telebridging project. The American and Russian participants completed two assessment instruments that were developed by the Delphi Teaching and Learning Center of the University of Louisville. These instruments, “Ideas to Action” (1) “Student Evaluation Form” and (2) “Student Reflection Form,” asked the students to reflect on their attitudes towards the international teleconference project experience and what they gained from it.

Generally, the students were very positive about their experiences and expressed their willingness to participate in the future telebridges.

**Conclusion**

Although there has been tremendous development in the English language teaching approach, and ease of information accessibility, over the global network, Russian Geoscience students still have a modest level of English language competence.

Due to the intercultural project “Environmental Issues of the World” Russian and American students were exposed to multicultural scientific and professional environments, therefore overcoming academic isolation.

The international project was up for discussion and could cover diverse topics such as salinization in the Ural Mountain region, potash fertilizer production, etc.

As a result of this learner-centered approach and the CLIL approach, the level of involvement, professional understanding, skill development and terminology competence increased dramatically. Participation in the project allowed Geoscience students, as well as students from other disciplines, to see how the same ecological phenomenon, subject, problem or situation were perceived and acted upon by representatives of other cultures. Consequently, students could contribute to academic and professional work following graduation and appreciate mutual engagement in resolving geoscience issues.

The advancement of educational technology can pave new avenues in communications between cultures, disciplines and academic environments. All students and universities involved in this project were able to take advantage of these innovations in a way that was mutually beneficial to all.

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These Proceedings of the International Mine Water 2019 Conference in Perm, Russia include the peer-reviewed papers of the vibrant community of scholars, practitioners, experts in mine water management, mine water treatment and environmental restoration on the global and local levels. Ten tracks of the Conference, ranging from mine water geochemistry and mine water hydrogeology to environmental monitoring and the future of the closed Kizel coal basin, are reflected in the conference theme “Mine Water: Technological and Ecological Challenges”. Over 200 participants from 42 countries come together to discuss the most burning issues of finding new solutions and bringing cutting-edge technologies into mine water treatment and preventing damage to the unique environments and ecosystems in different corners of the world. The Proceedings offer an outstanding opportunity to acquire the most advanced methods derived from interdisciplinary research and expertise in the field of mine water worldwide.