

Low Density Sludge Storage In A Flooded Underground Mine

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Abstract

This paper discusses the chemical and physical characteristics of Low Density Sludge (LDS) and its interaction with mine water. A general overview of the physics of the LDS produced at a German fluorite mine is described. The work confirmed the highly hydrous nature of the sludge (11.5 to 17% solids), its rather low sedimentation rate, and its thixotropic viscosity. LDS interaction with mine water has been both tested in the laboratory and modelled with PHREEQC. Mine water quality was modified when in contact with sludge: its total alkalinity and pH increased and its iron concentration and total acidity decreased. On this account we showed that mine water chemistry was improved when in contact with LDS, even though LDS represents less than 1% of total mine water volume. As a consequence, the re-injection of the sludge within the mine is a sustainable tool for the handling of the LDS and the improvement of mine water quality.

Key words: LDS; PHREEQC; mine water chemistry; iron rich sludge; chemical modelling; sludge rheology; thixotropic; Straßberg/Germany; fluorite mine; Harz mountains.

Introduction

Polluted mine water draining from working or abandoned mines might be an environmental risk and therefore needs treatment. One out of two options can be used: active or passive treatment. In the first case large amounts of sludge are produced and its disposal needs space and consumes land in land fills or underground waste repositories. Researchers and consultants worldwide seek for an option to use the sludge or to dispose it with the help of a cheap and environmentally sound technique. This paper describes laboratory investigations and numerical modellings conducted with the low density sludge of a German mine water treatment plant in the Harz Mountains. Those results help to understand the ongoing processes within the flooded mine in which the sludges are disposed of.

“Low Density Sludge” (LDS) is an iron-rich sludge that usually contains 1 to 10% solids. This LDS is a highly hydrous waste product of mine water treatment, which in addition to iron, may contain various proportions of other metals. Modern mine water treatment plants apply a more efficient flocculation processes to achieve densities of 30% or better and thus decrease the waste volume. This “High Density Sludge” (HDS) has a higher metal content than LDS and an improved crystallinity, with a reduced potential for metal leaching (GAN ET AL. 2005; ZINCK 1997). The various metals contained in the sludge originate from the precipitation of metals and ions dissolved in acidic mine water. The process of Acid Mine Drainage (AMD) generation is well understood and shall not be repeated here (STUMM & MORGAN 1981).

In a conventional treatment system (ZINCK 1997; YOUNGER et al. 2002; BROWN et al. 2002; WOLKERSDORFER 2006) alkaline materials are added to raise the pH of the AMD water to levels that cause the solubilised metals to precipitate. A preferred alkaline material is hydrated lime (calcium hydroxide), which is added to the AMD as a slurry. The effluent is then aerated, and flocculants are sometimes added. Treated sludge then settles in a pond, and excess water is decanted from the pond and released to a stream. In general LDS consists of amorphous oxy and hydroxy iron oxides plus excess calcite (CaCO_3 ; KALIN et al. 2006; ZINCK 1997).

Because of widespread occurrence of the sludges, the empirical knowledge of their characteristics and handling has been improved in recent years (GEORGAKI 2003). SEYSSIECQ et al. (2003) also conducted an extensive review of the literature devoted to the rheological characterisation of activated and sewage sludges. They showed an important variability in properties depending upon sludge history and processing and the lack of clearly identifiable composition and structure highlighting our incomplete scientific understanding of the sludges.

Sludges produced by conventional AMD treatment processes require appropriate disposal to prevent the re-release of metals. LDS sludge has sometimes been re-injected in the flooded mines and, due to residual CaCO_3 of the treatment process, is thought to be a possible buffering source for the AMD. It could increase the pH and cause the metals to precipitate directly within the mine. Thus it could

improve the quality of effluent water, solving both mine water acidity and metal concentration problems quoted before.

The aims of this report are to examine the water quality and mine water quality changes during the mixing between sludge and mine water. LDS physical properties and mine water chemistry were therefore measured in the case of the Straßberg Mine, Germany, where LDS is re-injected within the flooded mine since 1992. The key questions of this paper will be: is this handling solution sustainable and can it be generally applied in other mines as well?

Materials and methods

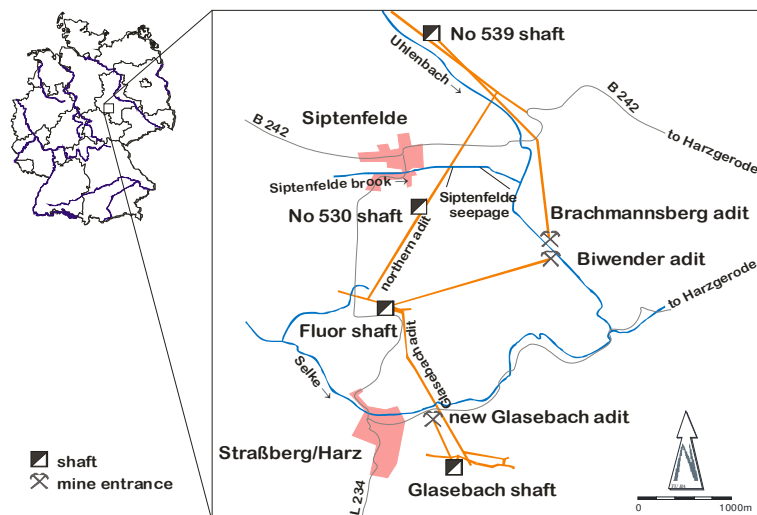
Site details of the Straßberg Mine

The Straßberg Mine is located in the central part of the Harz Mountains, in the German region of Saxony-Anhalt (Fig. 1). The average precipitation was 650 mm/year during the period 1969—1999 (RÜTERKAMP & MESSER 2000), with a continental climate.

The exploitation of the mine started 600 years ago, first for lead, zinc and silver, finally for fluorite. It is also accompanied by pyrite and marcasite. Oxidation of those later minerals is the initial reaction in the formation of AMD and metalliferous leaching at the site.

In 1989 production was stopped, and the flooding of Straßberg Mine started on May 31st 1991. (BST Mansfeld GmbH & Co KG 2005). The flooding caused a contact between oxygenated water and pyrite, and a first flush reaction: dissolved iron concentrations in the mine water increased from 1—2 mg/L in 1990 to about 40 mg/L in 1994, with a pH of around 5.5. In May 1992, with a sudden death of fishes in the Selke River, mine water treatment became compulsory. In autumn 1992 pumping (total capacity ca. 7 m³/min) of the mine water started in the Main Pit (Fluor Shaft, Fig. 1) of the Straßberg Mine and in the No. 901 shaft. The mine water is treated at the Fluor Shaft and Brachmannsberg sites (Fig 1) by addition of hydrated lime and aeration. A flocculent (polyacrylamid Synthofloc) is added only at the Brachmannsberg site. The water and sludge then settle in ponds (three at the Main Pit site, two at the Brachmannsberg site), and the superficial water is released to a river (tributary of the Selke River and Uhlenbach respectively). After about two months the sludge is gathered and re-injected into the mine.

Figure 1 Schematic map of the Straßberg Mine site.



The repumped sludge is nearly liquid. In 1996 the solid content was evaluated to be about 9.13 g/L, which corresponds to about 1% solid, with a measured pH value of 9 to 11. The same year, the volume re-injected was of about 7,200 m³/month (WEYER 1996). However, less water was progressively used to gather the sludge, and in 2000, the average water volume injected was 1,600 m³/month (König, personal communication). The current solid percentage is thought to be higher. Tracer tests (WOLKERSDORFER & HASCHE 2003; WOLKERSDORFER 2005) have shown that the different location points of the mine are well connected, with a global flow from North to South. The Sludge is re-

injected into the mine at the Westfeld borehole, north-west of the Fluor Shaft. From there the water stream direction is from Westfeld toward Main Pit and Glasebach.

This study focuses on the sludges originating from the Fluor Shaft and Brachmannsberg sites, in particular on their physical properties, and on modelling their interaction with mine water. Water samples of four different sites and sludge samples of two different sites were collected in March 2007. Three water samples were taken underground at the Fluor Shaft main pit, at No. 539 (Brachmannsberg) and at the Glasebach pit. A further water sample was collected from a mine drainage gallery near Alexisbad. This latter water is assumed to have a quite similar chemical composition as the original Straßberg Mine water. Two sludge samples were taken at the Fluor Shaft site in the pond II by Mansfeld GmbH & Co. KG and one sample at the surface of the northern pond at the Brachmannsberg site.

pH, redox potential, mine water temperature, dissolved oxygen, and electric conductivity were measured on site with WTW portable instruments. For redox potential measurements, the results obtained with the Pt–Ag/AgCl InLab501 (ARGENTHAL, 3 mol/L KCl) electrode system were adjusted to a potential relative to that of the standard hydrogen electrode, at 10°C. All samples were filtered through 0.45 µm cellulose acetate filters and for the trace element analyses HNO₃ was added. Total acidity and alkalinity were measured using a Hach digital titrator. Mine water samples were analyzed with a Perkin-Elmer AAS-3300 Spectrometer for total iron, manganese, zinc, aluminium, sodium, potassium, calcium, and magnesium, Perkin-Elmer SIMAA-6000 Spectrometer for silver, cadmium, copper, nickel, and lead, and DIONEX-IC-DX-100 for fluoride, chloride, nitrate, and sulphate. Iron during the batch experiments was detected with a HACH photometer. The percentage of solids was determined through the weight loss from oven drying at 140 °C for 20 hours and then cooled down in a desiccator. Sedimentation rates of the LDS were measured in 1000 mL cone-shape sedimentation funnels (Imhof funnel), graduated every 50 ml between 1000 mL and 500 mL. The sludge in the sample containers was vigorously stirred for some minutes before taking the samples. Rheological parameters were measured with a Haake CR Rheometer VT 500. It is a rotational rheometer, composed of two concentric elements (inner and outer cylinder). The internal cylinder is rotated at a controlled rotation rate in order to shear the sample contained in the gap. Shear stress is determined measuring the resistant torque on one of the two elements.

Mine Water-LDS chemical interaction and geochemical modelling

Two different methods were used to determine the influence of LDS on the mine water quality: batch experiments in the laboratory and modelling with the PHREEQC software.

Eight batch reaction tests were performed with different proportions of mine water and LDS: 0.5%, 1%, 2.5%, 5%, 7.5%, 10%, 25% and 50% LDS. Water from Alexisbad was used, because it was supposed to be closer to the Westfeld chemical water composition than the Brachmannsberg or the Glasebach mine water. Those tests were performed with both Fluor Shaft and the Brachmannsberg LDS, in order to observe possible reaction differences in the chemical and physical behaviour.

A total of three experimental series were conducted, in which water and sludge reacted together for 77 hours, 24 hours and 16.5 hours in an overhead mixer. After each test electrical conductivity, pH, total acidity and alkalinity, ferric, and total iron concentrations were measured.

Forward modelling with the PHREEQC code version 2.0 (PARKHURST & APPELO 1999; MERKEL & PLANER-FRIEDRICH 2002) was used to investigate the influence of re-injected LDS on the mine water chemistry. The thermodynamic database of PHREEQC was enlarged with data from other geochemical codes: MINTEQ and WATEQ4F. The approach is based on a mass-balance concept: initial water composition + reactants = final water composition + products. Knowing the initial water composition and the chemistry of the LDS solid solution, mass-balance expressions for each element in solution are assembled into a linear system of equations.

Inputs to the model were:

- The chemical composition of the original water in Westfeld, arriving upstream of the sludge injection point within the mine (Water No. 1, sampled in 1989),
- The LDS chemistry in the ponds and the chemistry of water in contact with the LDS in the ponds (Water No. 2), and
- The percentage of LDS/Water No. 2 compared to the total mine water volume

Because the Westfeld is currently not accessible for water sampling the numerical model is based on analyses conducted in 1989. The water of this analysis is oxidized and well buffered. To evaluate the initial pH of this water, the sulphate and copper concentrations were used to calculate the amount of dissolved pyrite and chalcopyrite and consequently, the pH

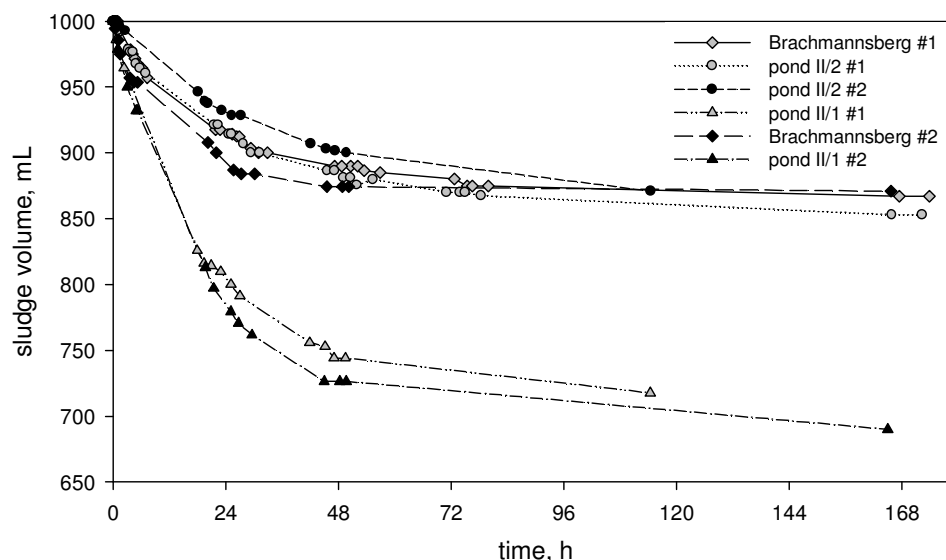
Based on the chemical composition of the sludge (KINDERMANN & KLEMM 1996), we calculated the mineralogical composition of the sludge according to the CIPW norm (WIMMENAUER 1985). This mineralogical composition was then used as a basis for the chemical modelling of the sludge/water interactions. For the given data calcite, magnetite, corundum, hematite, pyrite, and natron were identified. Those are the equilibrium phases for the first part of the simulation with PREEQC. They correspond to the results of other LDS chemical analyses (ZINCK 1997).

In 2000, an average of 1600 m³ of sludge per month was produced and then injected into the mine. The average solid percentage of LDS sludge is 1 to 10%. The total water volume of the mine is of 277 050 m³ (RÜTERKAMP & MESSER 2000). Therefore this LDS-water No. 2 would have a volume that corresponds to only 0.58 % to 5.80 % of total mine water volume (with the initial composition of water No. 1). On this basis between 0.01 and 10% for the modelling of sludge-mine water interactions with PHREEQC were used. The results were then interpreted using a hierarchical cluster analyses in order to compare the mine water composition at the Main Pit (Fluor Shaft) and the water composition after the modelled mixing reactions.

Results and discussion

This part of the study aims to clarify the question if the sludge injected into the mine will stay in place near the injection point or if it will be transported into other parts of the mine by the mine water flow. Therefore the sedimentation rate of the LDS and the viscosity once settled within the mine were detected and investigated.

Figure 2 Sedimentation curves (Imhof cylinder) of the Straßberg Mine sludges.



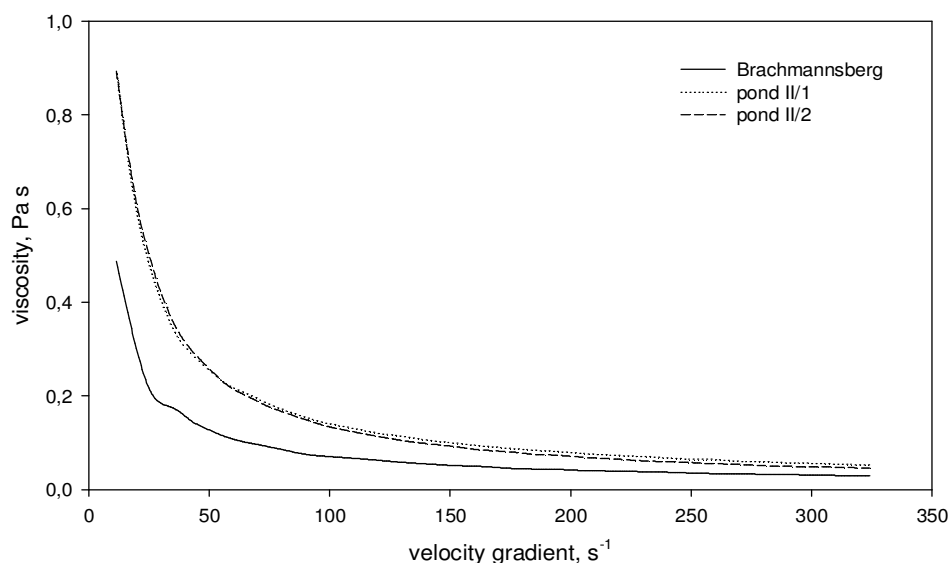
For the three sludge samples mean values of 11.5% (pond II, sample 1), 14.9% (pond II, sample 2) and 17.2% (Brachmannsberg left pond) of solids were determined. The sludge originating from Brachmannsberg, to which flocculants are added, has a higher solid content, as expected. Furthermore, the solid content of the Low Density Sludge is higher than expected and a difference between the two samples collected at the pond No. 2 at the Fluor Shaft exists. This fact might be due to sludge aging. The sedimentation curves show a major sedimentation in the first 48 to 72 hours, followed by a much less significant change thereafter. Only sludge in direct contact with mine water reacts with it. It is therefore an advantage if the LDS stays in suspension in the water as long as possible and does not quickly settle down.

The loss of volume due to sedimentation is 12.9 (± 0.6) % for the sludge in pond II and 31 (± 0.5) % at the Brachmannsberg site (Fig. 2). There is a different behaviour between the samples from the pond II. This matches the solid contents results, which indicated higher water content in sample 1 of pond II. The sludge within one pond can therefore have a quite different water percentage, suggesting that the chemistry of its interstitial water could also vary. For all three samples, though different in their detailed behaviour, the sedimentation properties are rather similar. Therefore it can be stated that the time needed by the LDS to settle is relatively long and could possibly allow a transport of a part of the LDS within the galleries by the mine water flow. The currents within the mine are supposed to be higher and less laminar in galleries than in the mine workings. A slow injection of the sludge in galleries would therefore be a good solution to help it to be diffused and not to settle too quickly. For all samples the apparent viscosity decreases as the shear rate (velocity gradient) increases (Fig. 3). Such a fluid corresponds mainly to thixotropic behaviour, as observed on the schematic flow curves for model time-independent materials by SEYSSIECQ et al. (2003). For all three a power function exactly fits the results ($r^2 = 0.998$ —1.000). Other than in the settlement experiment, the rheological behaviour of the two samples of pond II is very similar. Compared to the Brachmannsberg settling pond, their viscosity is higher.

The sludge injected into the mine is diluted with water and should have, as a consequence, a lower viscosity, not exactly known, but still higher than water viscosity (10^{-3} Pa·s at 10°C). However water is expelled during and after settlement, and the viscosity of the LDS once settled is therefore supposed to be the one measured here. Yet, the question is if the LDS sludge will stay settled or be eroded and transported by the mine water.

Tracer tests within the mine resulted in mean effective velocities of 0.01 to 0.14 m/min (95% confidence interval; WOLKERSDORFER & HASCHÉ 2003). If we compare it to the results of Figure 3 and consider the length of mine galleries, we would find a velocity gradient inferior to 10. We can not read on the graphic Figure 3 the corresponding viscosity value, because the viscosity is not directly proportional to the velocity gradient, as it would be the case with a Newtonian fluid. This means that the curve cannot be linearly extrapolated to obtain a precise viscosity value corresponding to the velocity gradient within the mine (inferior to 10). However, we can notice that this viscosity would be high. We tried to evaluate this value using the equation of the regression curve of the pond II sample 2 sludge: $\eta = 9.0492 \times \delta^{0.9157}$, with η the viscosity in Pa s, and δ the velocity gradient in s^{-1} . On a 2000 meter gallery, at the velocity of 0.14 m/min and a laminar flow, this would be equal to a viscosity of about 2450 Pa s. This is an indicative value, as no uncertainty range can be evaluated.

Figure 3 Viscosity curves of LDS samples originating from pond No. 2 and from Brachmannsberg northern pond.



The measured flow rates within the Straßberg Mine are too low compared to this high viscosity value and would therefore not be sufficient enough to physically erode the LDS once settled. This is also true for other mines, as no natural flow within the galleries will be great enough to reach a 100 s^{-1} velocity gradient or more.

Mine water chemistry

As can be seen from the results of the chemical analyses (Tab. 1), the waters of the different sites of Straßberg Mine differ in their chemical composition. The total iron concentration at the Main Pit, where the water is pumped, is 10.7 mg/L , with a pH of about 6.5 but a relatively high acidity (total acidity K_B higher than the total alkalinity K_S). This corresponds to the results regularly measured in the mine.

These waters have a high sulphate, calcium and iron concentration, but also a relative higher concentration in metals. We can also notice that the water at the Main Pit and at Glasebach contains a high HCO_3^- concentration. This HCO_3^- has its origin in the LDS re-injected into the mine. As highlighted by the tracer tests, the global circulation of water is from North to South. The LDS in suspension or the water that reacted with the sludge is transported to the Glasebach site but also to the Main Pit site, as the pumps there create an artificial flow in this direction.

Table 1 Physical and chemical parameters of Straßberg and Alexisbad waters. Wat. Temp.: water temperature; Cond.: electrical conductivity; K_B : total acidity; K_S : total alkalinity; n.d.: not determined.

Site	Fluorschaft (Main Pit)	Brachmannsberg (539 Shaft)	Alexisbad	Glasebach
Wat.Temp. (°C)	10.1	10.4	8.5	n.d.
Cond. ($\mu\text{S/cm}$)	822	542	607	n.d.
pH	6.53	6.52	5.54	n.d.
RedOx (mV)	256	137	369	n.d.
O_2 (mg/L)	0.13	0.18	10.48	n.d.
Total Fe (mg/L)	10.655 ± 1.92	13.71 ± 1.86	0.245 ± 0.16	0.25 ± 0.15
Mn (mg/L)	5.135 ± 1.00	0.987 ± 0.20	2.686 ± 0.20	7.03 ± 0.97
Zn (mg/L)	0.295 ± 0.06	0.05 ± 0.03	1.93 ± 0.31	0.115 ± 0.05
Al (mg/L)	1.12	0.6	1.75	0.15
K (mg/L)	2.696 ± 0.35	2.168 ± 0.35	1.62 ± 0.38	7.24 ± 1.92
Mg (mg/L)	23.3 ± 1.63	18.2 ± 1.58	16.25 ± 1.59	24.3 ± 1.64
Cl (mg/L)	23.66 ± 1.36	32.32 ± 1.42	43.31 ± 0.97	29.67 ± 1.38
NO_3 (mg/L)	<0.74	<0.74	2.96 ± 0.08	2.26 ± 0.07
SO_4 (mg/L)	305.33 ± 2.12	146.61 ± 2.12	218.44 ± 2.12	211.92 ± 2.12
F (mg/L)	4.65 ± 0.18	2.21 ± 0.17	1.75 ± 0.18	2.75 ± 0.17
Ca (mg/L)	106.26 ± 7.99	41.5 ± 3.94	55.88 ± 3.97	105.94 ± 7.99
Na (mg/L)	16.80 ± 2.62	22.66 ± 2.55	20.12 ± 2.55	15.88 ± 2.65
Cu ($\mu\text{g/L}$)	8.65 ± 0.058	7.62 ± 0.051	115.65 ± 0.770	31.81 ± 0.212
Ni ($\mu\text{g/L}$)	83.157 ± 0.251	11.936 ± 0.036	48.342 ± 0.146	27.957 ± 0.085
Pb ($\mu\text{g/L}$)	0.416 ± 0.001	1.684 ± 0.006	2.841 ± 0.010	$1;021 \pm 0.004$
Cd ($\mu\text{g/L}$)	3.630 ± 0.259	0.349 ± 0.016	2.771 ± 0.173	3.522 ± 0.247
As ($\mu\text{g/L}$)	100.486 ± 0.455	131.895 ± 0.608	22.632 ± 0.098	3.392 ± 0.015
K_B (mmol/L)	11.92 ± 0.12	11.84 ± 0.12	13.76 ± 0.14	5.78 ± 0.06
K_S (mmol/L)	2.14 ± 0.02	1.15 ± 0.01	0.340 ± 0.003	3.38 ± 0.03
HCO_3 (mg/L)	130.33 ± 1.30	70.17 ± 0.70	20.75 ± 0.21	206.35 ± 2.06

Figure 4 Total alkalinity curve of the batch experiments between Alexisbad water and the two different types of LDS.

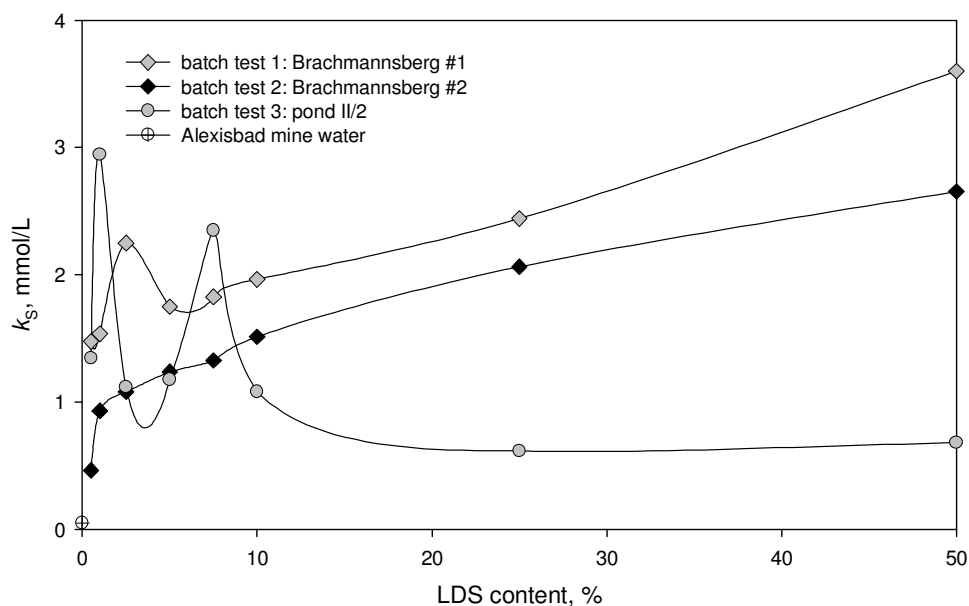
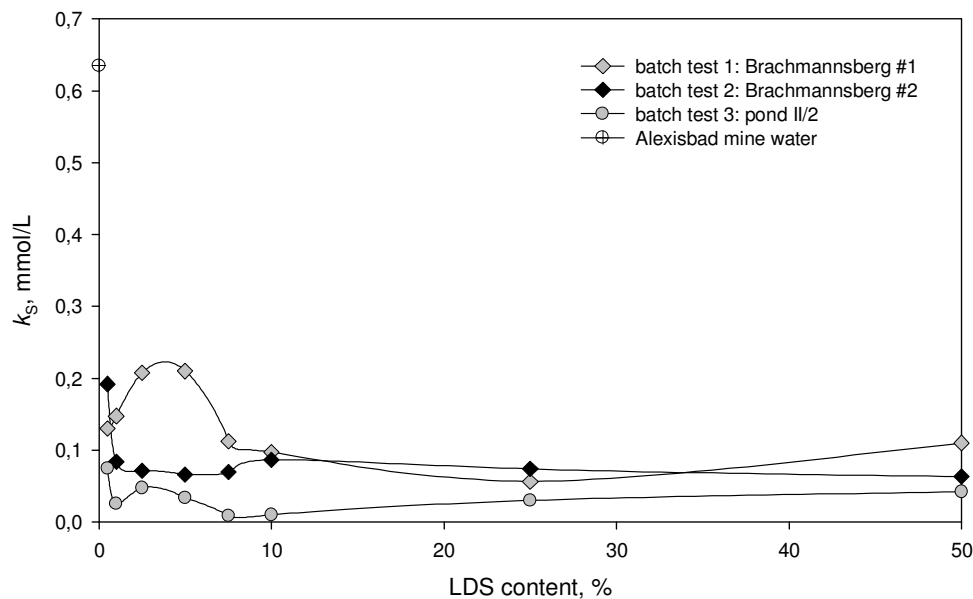


Figure 5: Total acidity curve of the mix of the Alexisbad water with the two different types of LDS.



Water-sludge mixing simulation: evolution of water chemistry

The aim of these experiments was to quantify the influence of the LDS sludge on the chemistry of mine water (Figures 4, 5, and 6). The chemistry of the Alexisbad water sample has changed between sampling and the laboratory experiments. The large water volume needed for the experiments (50 L) made it impossible to keep the water at a cool temperature in a fridge. Alkalinity value was 0.340 ± 0.003 mmol/L at sampling, and 0.0475 ± 0.0005 mmol/L at the start of the experiments. Acidity was 13.76 ± 0.14 mmol/L and 0.635 ± 0.006 mmol/L, respectively. Moreover, the pH value of Alexisbad

water was 5.54 during sampling and 4.15 at the start of the laboratory experiment clearly indicating the pH decrease as a result of iron hydrolyses.

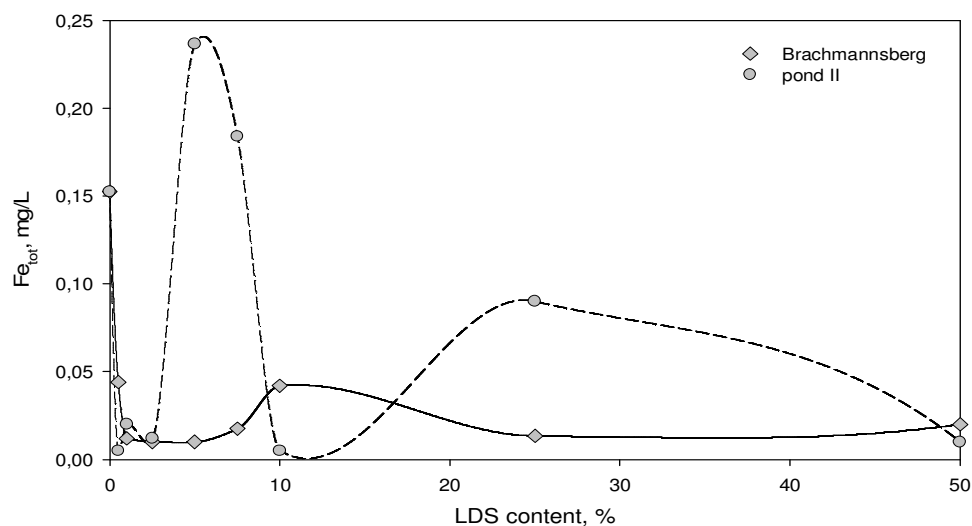
The results of the batch experiments (Figure 4) show that a mixture of the acidic water and the LDS causes an increase of total alkalinity. It also causes a decrease of total acidity (Fig. 5). This is also true if LDS is set to only 0.5 % of the total solution. The pH measured in the batch samples was 7.07 to 8.05. This pH increase, compared to the mine water, is due to the residual carbonate in the LDS and those pH-values are high enough to cause iron and aluminium oxides to precipitates. Iron hydroxides have precipitated before the batch experiments. Thus, the dissolved ferric and total iron concentrations have decreased within the mine water in comparison to the results of Tab. 1. The values for Alexisbad mine water at the beginning of the batch experiments were 0.01 mg/L ferric iron and 0.15 mg/L total iron (all Fe-values ± 0.006 mg/L).

After the batch experiment with Fluor Shaft (No. 3) and Brachmannsberg (No. 2) LDS, the ferric iron concentrations within the water were mainly below 0.01 mg/L (detection limit). The only results above 0.01 mg/L were 0.02 mg/L ferric iron for batch experiment No. 3 with 5% LDS, and 0.01 mg/L ferric iron for batch experiment No. 3 with 25% LDS. Considering the precision error and low concentration, we conclude that the ferric iron concentration in the mine water has generally decreased as a result of the LDS addition.

Concerning total iron concentrations (Fig. 6), the results are different for the two batch experiments. In experiment No. 2, with only 0.5 % LDS, the total iron drops down to 0.04 mg/L (-73 %). With a higher LDS percentage, the total iron concentration remains at this value or decreases. The results are different in experiment No. 3. With 0.5, 1, 2.5, 10 and 50 % LDS, the total iron concentration is below 0.02 mg/L (-87 %), but between 2.5 and 10 % LDS, the total iron concentration is up to 60 % higher (0.24 mg/L) than in the Alexisbad water. However, we must keep in mind that the potential LDS percentage as regard of the overall mine water volume is supposedly under 1 %, in the Straßberg mine case, but in other mines as well. The latter result is in good accordance with the slightly increased k_B -values of this experiment.

Thus, owing to these results, a mixing between mine water and LDS causes a decrease of total acidity and of iron concentrations, and an increase of pH and total alkalinity. Consequently, the mine water quality has improved by the addition of the LDS.

Figure 6 Fe_{tot} concentrations in the batch experiments of Alexisbad water with the LDS of pond II and Brachmannsberg.



Modelling with PHREEQC

The batch tests described before clearly show that the LDS improves the mine water quality. However, the LDS percentages used for the batch experiments were too high in comparison to the real situation in the mine. The modelling with PRHEEQC can be a good solution to model exchanges with low LDS

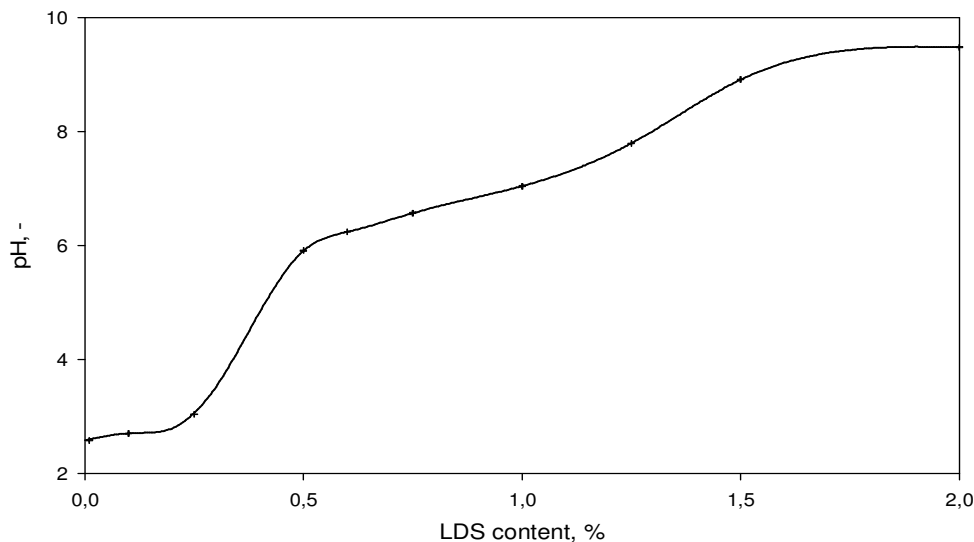
percentages. A further point to check with the modelling results and the hierarchical cluster analyses is to evaluate the best relation between LDS and mine water for a water chemistry close to the one measured in the Main Pit.

The PHREEQC modelling resulted in a pH of 10.1 for pure water reacting with the minerals found as the bulk composition of the LDS (water No. 2) and it is in good accordance with the pH of 9.9 measured in the ponds (KINDERMANN & KLEMM 1996). As can be seen in the figure 7, the higher the LDS percentage, the more the pH increases. Owing to these results, a LDS percentage higher than 0.2 % is required so that the chemicals contained in the sludge (mainly excess calcite) could efficiently start to buffer the mine water. Between 0.5 and 1 % sludge, the pH of the modelled mine water is between 6 and 7. At LDS percentages above 2% the pH increases to that one measured in the settling ponds. The pH measured in the Main Pit on March 12th was 6.53. Considering only the pH values, the volume of LDS within the mine water is therefore between 0.5 and 1%, corresponding to the PHREEQC results.

These results show that except for the conservative parameters Na and SO₄, the ion concentrations decrease as the LDS percentage increases. The differences values between the modelled composition and the Main Pit water can be explained with the equilibrium phases as a substitute for the real mineralogical composition of the LDS. Those were found by using the CIPW-norm calculations based on the total ion analyses of the LDS (KINDERMANN 1996). Cu is not taken into account in the CIPW-norm, therefore we added Cu-pyrite as an equilibrium phase in the PHREEQC input file.

In order to determine which LDS percentage obtained with PHREEQC (Tab. 2) would enable a water composition close to the mine water composition measured at the Main Pit (Fluor Shaft), we used a hierarchical cluster analysis and displayed the results in a dendrogram (Fig. 9). By doing so similarities between the results can be graphically displayed. Based on those results an LDS percentage of 0.75 in the mine water results in a water composition which equals that of the mine pit water.

Figure 7 water pH curve obtained by modelling with PHREEQC.



Conclusion

This work has shown that the injection of low density sludge from a mine water treatment plant into a flooded underground mine improves the quality of the mine water draining from the pit. Batch experiments and a chemical thermodynamic model have shown that small quantities between 0.5 and 1 % of the carbonate rich sludge in the mine water increase the pH and due to buffering reactions decrease the problematic metals in the mine water. The chemical analyses of the batch experiments clearly showed that the metals are not re-mobilized after the sludge is re-injected into the mine. Furthermore, using rheological investigations of the real sludge, we showed that the mine water's velocity is too slow to mobilize the sludge once it has been settled, yet, the velocity is high enough to

distribute the injected sludge through the mine before it settles. From a remobilization point of view the sludge with flocculants has an advantage over the sludge without flocculants.

Though the high density sludge treatment process is advantageous where the sludge shall be stored in waste or sludge disposal sites, low density sludge is advantageous if pumped back into the flooded mine.

Table 2 Mine water composition obtained from modelling with PHREEQC for increasing LDS sludge percentage (a), and measured at the Main Pit (Fluor Shaft) (b).

(a) Water composition modelled with PHREEQC (main ions: mg/L)

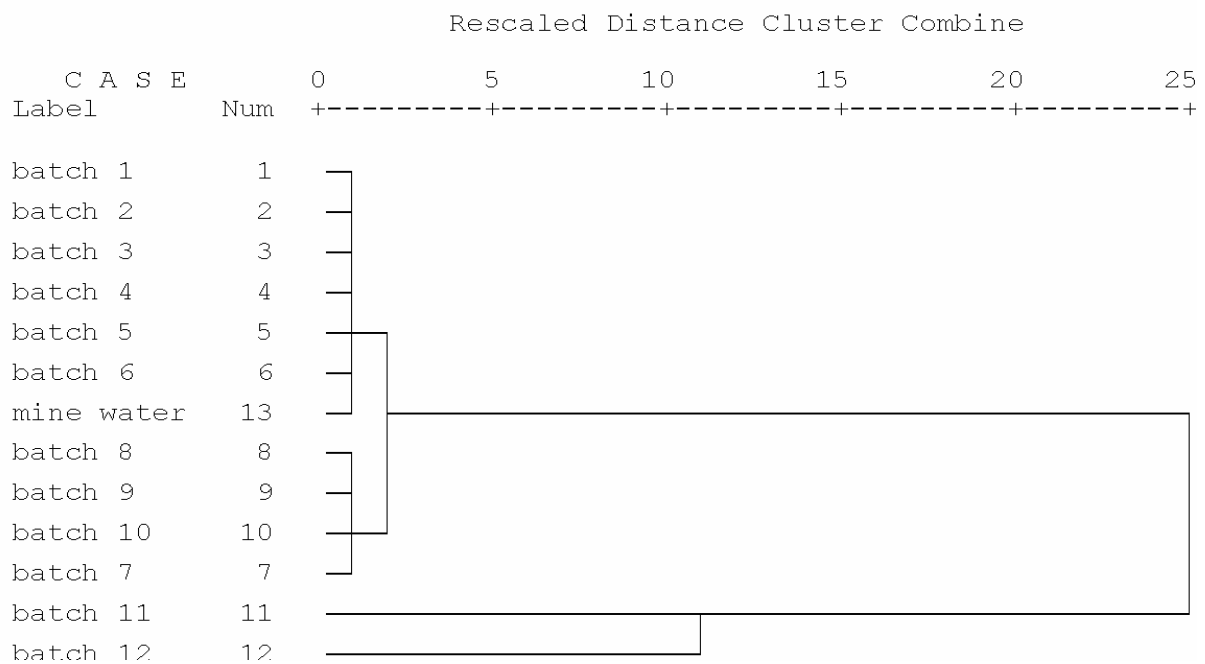
Batch No.	LDS, %	HCO ₃	Ca	Cl	Cu	F	Fe	K	Mg	Mn	Na	SO ₄	pH
1	0.01	0.01	68.6	16.3	0.11	3.4	2.23	2.0	14.7	1.4	11.3	117	2.58
2	0.1	0.02	68.6	16.3	0.11	3.4	2.23	2.0	14.7	1.4	29.2	120	2.70
3	0.25	0.07	68.5	16.3	0.11	3.4	2.22	2.0	14.7	1.4	56.2	125	3.04
4	0.5	53.9	68.3	16.2	0.11	3.4	2.22	2.0	14.7	1.4	101	129	5.91
5	0.6	101	68.3	16.2	0.11	3.4	2.22	2.0	14.6	1.4	119	129	6.24
6	0.75	179	68.2	16.2	0.11	3.4	2.21	2.0	14.6	1.4	146	130	6.57
7	1	288	68.1	16.1	0.11	3.4	2.21	2.0	14.6	1.4	191	130	7.04
8	1.25	399	67.9	16.1	0.11	3.4	2.20	2.0	14.5	1.4	235	130	7.79
9	1.5	447	67.8	16.1	0.11	3.3	2.19	2.0	14.5	1.4	280	131	8.91
10	2	491	67.5	16.0	0.11	3.3	2.18	2.0	14.4	1.4	369	133	9.48
11	5	733	65.9	15.4	0.10	3.2	2.10	1.9	13.9	1.3	902	131	10.05
12	10	1122	63.2	14.5	0.10	3.0	1.98	1.8	13.1	1.3	1778	119	10.17

(b) Water composition at the main Pit (Fluor Shaft)

HCO ₃	Ca	Cl	Cu	F	Fe	K	Mg	Mn	Na	SO ₄	pH
130	106	23.7	4.65	4.7	10.66	2.7	23.3	5.1	16.8	305	6.53

Figure 9 Results of the hierarchical cluster analyses with all parameters of Tab. 2 shown as a dendrogram.

Dendrogram using Average Linkage (Between Groups)



We also demonstrated that only 0.2 % of the Straßberg LDS is needed to start buffering the mine water and increase the pH. It has also been shown that LDS injected into the mine water, decreases the ions concentration dissolved in the mine waters. The results developed for this study used the Straßberg mine LDS composition. However the same components (excess calcite, iron oxides and hydroxides, sulphate), are found in other low density sludges. Moreover we used the water from two different mines, but the conclusion on total alkalinity, total acidity, and dissolved iron concentration were the same. The methodology and the general tendency developed for the study of Straßberg mine LDS and its interaction with mine water can therefore be applied to other mines as well.

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