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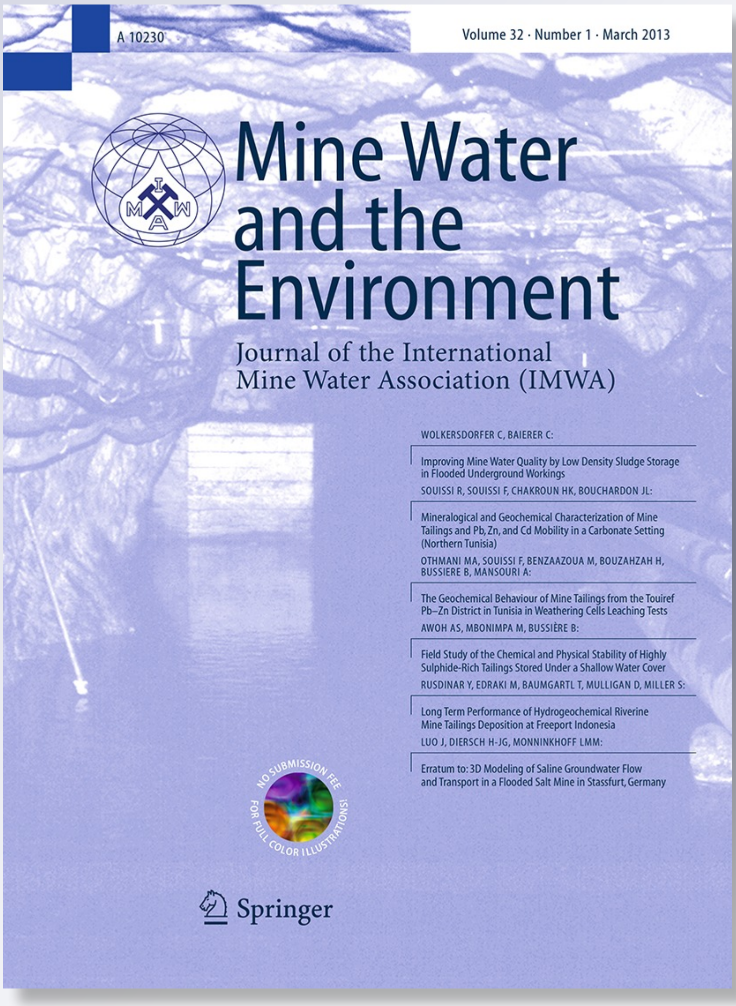

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TECHNICAL ARTICLE

Improving Mine Water Quality by Low Density Sludge Storage in Flooded Underground Workings

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Abstract This paper discusses the chemical and physical characteristics of low density sludge (LDS) and its interaction with mine water in a flooded German underground fluorite mine. The highly hydrous nature of the sludge (11.5–17 % solids), its rather low sedimentation rate, and its thixotropic viscosity were confirmed. The interaction of LDS and mine water was tested in the laboratory in batch experiments and modelled with PHREEQC. Mine water quality improved through contact with the LDS sludge: the total alkalinity and pH of the water increased and its iron concentration and total acidity decreased. Storage of sludge in a flooded mine could be a sustainable tool for both the handling of LDS and improvement of mine water quality, even when the LDS represents less than 1 % of the total mine water volume. No polymer flocculants from the LDS treatment plant were found in the discharged mine water.

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Introduction

Polluted mine water draining from working or abandoned mines, commonly called acid mine drainage or metal leachate (AMD/ML), can cause environmental problems and therefore needs reliable treatment (Brown et al. 2002; Younger et al. 2002; Wolkersdorfer 2008). When active treatment is used, large amounts of sludge are produced and its disposal consumes space in landfills or underground waste repositories. Researchers and consultants worldwide seek ways to use the sludge or to dispose of it using cheap and environmentally sound techniques (e.g. Hedin 2002; Stiles and Ziemkiewicz 1999; Zinck 2006). In this paper, we describe laboratory investigations and numerical modelling conducted with low density sludge (LDS) from a German mine water treatment plant in the Harz Mountains. This plant operated from 1992 to 2008 and has been subsequently replaced by a high density sludge (HDS) plant (pers. comm. Ronny König 2012).

Low density sludge (LDS) is an iron-rich sludge that usually contains 1–10 % solids (Kostenbader and Haines 1970; Zinck 2005). It is a highly hydrous residual of mine water treatment, which in addition to iron, may contain various proportions of other metals (e.g. Mn, Zn, Cr) and semi-metals (e.g. As, Sb) as a result of co-precipitation (Table 1; e.g. Fadda et al. 2002; Zhu et al. 2003). Modern mine water treatment plants use more efficient recirculation and flocculation processes to achieve densities of 30 % or better and thus decrease the sludge volume (Kostenbader

Table 1 Total analyses of a sludge sample in settling pond III (Straßberg LDS treatment site, sample SBG-0707-T3)

Parameter	Concentration (%)	Parameter	Concentration (%)
H	0.35	Cr	0.021
CO_2	34.38	Mn	1.62
C	0.85	Fe_2O_3	7.64
N	0.081	Co	0.007
MgO	0.92	Ni	0.015
Al_2O_3	0.82	Cu	0.010
SiO_2	5.92	Zn	0.057
SO_3	0.19	As	0.12
Cl	0.014	Sr	0.029
K_2O	0.038	Sn	0.001
CaO	46.91	BaO	0.004
TiO_2	0.010	Pb	0.001
V	0.0004	Sum	100.008

and Haines 1970). This HDS has a higher metal and semi-metal content than LDS, improved crystallinity, and consequently, reduced potential for metal leaching (Gan et al. 2005; Zinck 1997).

In a conventional treatment system (Brown et al. 2002; Wolkersdorfer 2008; Younger et al. 2002; Zinck 1997), alkaline material is added to buffer the acidity and raise the pH of the AMD/ML water to levels that cause the solubilised metals to precipitate. A preferred alkaline material is hydrated lime (calcium hydroxide), which is typically added to the AMD/ML as slurry (SENES Consultants Limited 1994). The effluent is then aerated and flocculants are sometimes added to improve the settlement of the iron hydroxide. Treated sludge then settles in a pond or a settler where excess water is decanted and discharged into a receiving water course. In general, LDS consists mainly of amorphous oxy and hydroxy iron oxides plus excess calcite ($CaCO_3$), Figure EA a (included in the electronic version of this paper, which all journal subscribers have free access to) and gypsum (Aubé and Zinck 1999; Kalin et al. 2006; Zinck 1997). SENES Consultants Limited (1994) summarized sludge characteristics and concluded that lime (hydroxide) sludges show a tendency to be gelatinous and voluminous. They have a low density due to their fine amorphous nature and contain chemically bonded water, which makes dewatering and compaction difficult.

Because of their widespread occurrence, empirical knowledge of sludge characteristics and handling has improved in recent years (Georgaki et al. 2004; Zinck et al. 1997). Seyssiecq et al. (2003) conducted an extensive literature review of the rheological characteristics of activated and sewage sludges. They showed a large variability in properties depending on sludge history and processing and the lack of clearly identifiable composition and structure. Their work demonstrated that scientific understanding of sludges is incomplete, despite numerous years of research.

Sludges produced by conventional AMD/ML treatment processes require appropriate disposal to prevent the re-release of metals. LDS sludge has sometimes been injected into flooded underground mines or open pits mines (e.g. Gorshkov and Kharionovsky 1982; SENES Consultants Limited 1994; Zinck 2005) and, due to residual $CaCO_3$, is thought to be a possible buffering source for AMD/ML (Hansen 1998; Table 1; Figure EA a). It can increase the pH and cause metals to precipitate directly within the mine (Klinger et al. 2000). Thus, it can improve effluent water quality. Kostenbader and Haines (1970) stated that "the discharge of excess sludge via a borehole to an area adjacent to the underground mine-water pool proved to be a satisfactory disposal method." No data about potential mine water improvements was reported by them, but they note that "there was no evidence that sludge was either solubilized by contact with the acid water or short-circuited to the AMD pumps." Aubé (2004) and Aubé et al. (2005) investigated the injection of HDS treatment sludge into the abandoned and flooded mine workings of the 1B mine pool on Cape Breton Island/Canada. They concluded that "returning sludge underground ⋯ therefore improves the mine water quality and does not appear to cause long-term stability issues." McDonald et al. (2006) reported that treatment sludges investigated with the SALT (strong acid leach test) method might become chemically unstable at pH values below $\approx$6.5 once all the neutralisation potential has been exhausted. To exclude such redisolution for very acidic mine water conditions, it is advisable to test the sludge–mine water interaction with real sludges and mine water before disposing of treatment sludges into abandoned mine workings.

We examined the water quality changes that occur during the interaction between sludge and mine water. The physical properties of the LDS and the mine water chemistry were measured in the Straßberg Mine, Germany, where LDS was injected into the flooded mine between 1992 and 2008. In addition, infrared (IR) spectroscopy was used to determine if polymer flocculants in the injected sludge might be resuspended and transported to the discharging shafts. The key questions were: is this handling technique of LDS sustainable and which general recommendations can be drawn for applying this process in other mines?

Materials and Methods

Site Details of the Straßberg Mine

The Straßberg Mine, which consists of three interconnected mines (from north to south: Brachmansberg, Straßberg, Glasebach), is located in the central part of the Harz Mountains, in the German state of Saxony-Anhalt (Fig. 1). Mineral exploitation started in 1691 at the Glasebach Pit and in 1860 at the Straßberg Pit (Liessmann 2010). Both were originally mined for silver, lead, and zinc. In 1780, the Brachmannsberg Pit was opened to mine fluorspar and thereupon, the other two pits were mined for flourspar as well. In addition to those metals and minerals, the ore veins contain considerable amounts of pyrite and marcasite (Kuschka and Franzke 1974), which were also mined for vitriol production in the 18th century (Liessmann 2010). Oxidation of the latter minerals is the initial reaction in the formation of AMD/ML.

In 1989, production stopped; the flooding of the Straßberg Mine started on May 31st 1991 (pers. comm. BST Mansfeld 1999). In total, the flooded mine's catchment area comprises 54 km^2 and the mean flow is 7.5 m^3 min^{-1}, with a maximum of 17.7 m^3 min^{-1} during snowmelt. Average precipitation was 660 mm/year during the period 1969–1999 (Rüterkamp and Meßer 2000), with a continental climate.

The flooding caused contact between oxygenated water and pyrite and dissolution of metal sulfate salts that had precipitated within the mine; subsequently, dissolved iron concentrations in the mine water increased from 1–2 mg L^{-1} in 1990 to about 40 mg L^{-1} in 1994, with a pH of around 5.5. In May 1992, sudden death of fish in the Selke River made mine water treatment compulsory. Consequently, in autumn 1992, pumping (total capacity ca. 7 m^3 min^{-1}) of the mine water started in the Main Pit (Fluor Shaft, Fig. 1) of the Straßberg Mine and in the No. 901 shaft (ca. 300 m east of the Flour Shaft). To optimise water treatment, the mine operator constructed three new discharge adits between 1995 and 1998 into the Brachmansberg, Straßberg, and Glasebach mines at an elevation of 357.5 m above sea level. The 3-adit system became fully operative in fall 1998 and currently discharges between 0.02 and 10.6 m^3 min^{-1} of mine water to be treated.

From 1992 until 2008, when a new mine water treatment plant in the Uhlenbach valley came into operation, the mine water was treated by aeration and the addition of hydrated lime at two different locations: the Fluor Shaft and the Brachmannsberg site (Fig. 1). A flocculent (Synthofloc polyacrylamid) was only added at the Brachmannsberg site. Both the water and sludge were then discharged into settlement ponds (three at the Main Pit site, two at the Brachmannsberg site), and the superficial water was released to receiving water courses: a tributary of the Selke River and the Uhlenbach, respectively. After about 2 months, the settling ponds had filled up with sludge, which was collected by road tankers (Figure EA b) and injected into the mine, which has a volume of 282.800 m^3 of non-backfilled storage capacity, 98 % of which was flooded (Leonhardt 1994).

In 1996, about 7,200 m^3/month of nearly liquid sludge was being injected into the mine (Figure EA b); the solid content was determined to be about 1 % solids (9.13 g L^{-1}), with a measured pH of 9–11 (Weyer 1996). However, less water was progressively pumped with the sludge, so that in 2000, the average volume injected was 1,600 m^3/month (pers. comm. Ronny König 2008). Tracer tests (Wolkersdorfer and Hasche 2001, 2004) showed that the mine water of the three different parts of the mine forms a hydraulically well-connected mine pool, with an overall flow from north to south. Currently, the sludge of the new treatment plant is injected into the mine at the Westfeld boreholes (B1/01 3F West and B2/01 3F Ost) as well as the No. 530 shaft, north-northwest of the Fluor Shaft by means of a pipe system. From there, the mine water flows south towards the Fluor Shaft (Main pit) and the Glasebach Pits.

Polyacrylamide-based Polymer Flocculants

One of two polyacrylamide based polymer flocculants was used during the LDS mine water treatment process: Synthofloc 82.32 (a powder) or Sachtofloc 46.12 (a liquid). Those flocculants, with molecular weights of 9 to 12 million (pers. comm. Stefan Vollmuth 2004) have a structural composition of $[CH_2CHCONH_2]n^-$ and, as can be seen from the chemical formula, are negatively charged. They form large heavy molecules with the positively charged iron-hydroxide sludge and thereby decrease the sludge settling time. Based on the literature (Chen et al. 1994; Jungreis 1981; Lentz et al. 1996; Leung et al. 1987), IR spectroscopy should be able to detect the polymer at these concentrations despite the low expected concentrations (pers. comm. Stefan Vollmuth 2004). Characteristic groups that can be identified by IR spectroscopy are the functional H_2N^-, CH^-, CO^-, and CH_2^- groups, which cause peaks at wave numbers 3,435 ± 10^{-1}, 2,915 ± 10, 1,640 ± 10 and 2,910 ± 10 cm^{-1}. The typical wave numbers for acrylamide are 3,350, 3,102, 1,673, 1,613, 1,281, 1,137, 990, 962 and 510 cm^{-1}, but only the wave number 2,920 ± 10 cm^{-1} is unique for acrylamide, as the others can also be due to other mine water or sludge components (e.g. carbonate, nitrate, sulfate, phosphate, silicate, water, or hydroxide).

Samples

Three water samples were collected underground at the Fluor Shaft (Main Pit), at the No. 539 shaft (Brachmannsberg Pit), and at the Glasebach shaft (Glasebach Pit). An additional water sample was collected from a mine

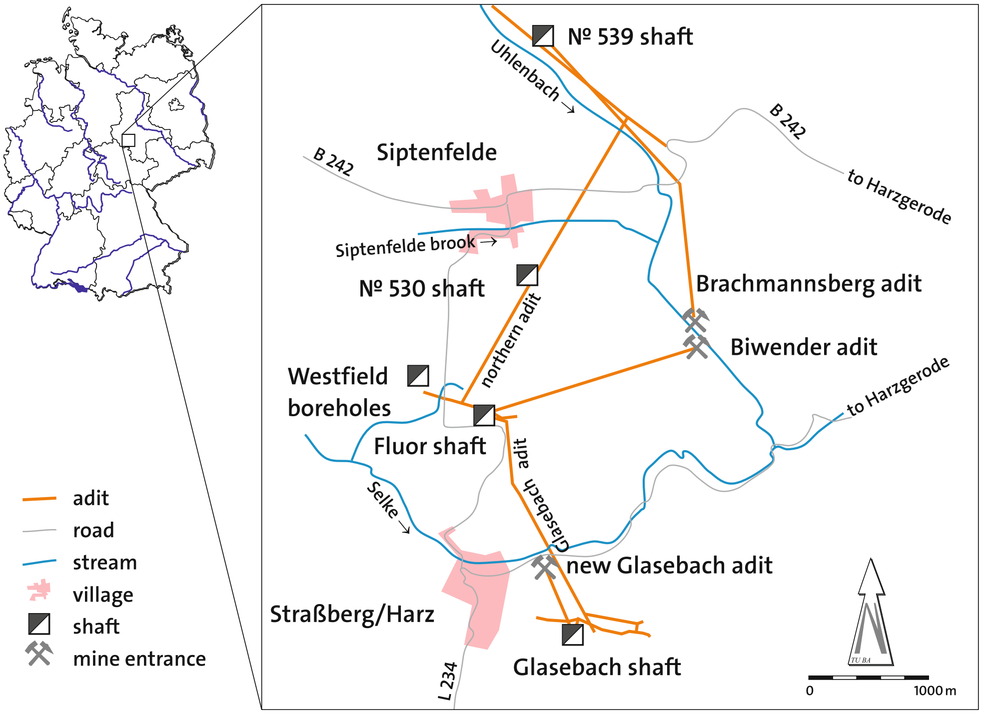


Fig. 1 Schematic map of the Straßberg Mine site including the three new dewatering adits and the northern and Glasebach adits connecting the three mine sites

drainage gallery near Alexisbad ("Schwefel-Stollen"), approximately 7 km northeast of Straßberg. This water is assumed to be chemically similar to the Straßberg Mine water before the flooding process started (Table 2). Two 20 L sludge samples were collected from Pond II at the Fluor Shaft site (Figure EA b) and one from the surface of the Northern Pond at the Brachmannsberg site.

The pH, redox potential, mine water temperature, dissolved oxygen, and electrical conductivity were measured on site with WTW portable instruments (Figure EA c). For redox potential measurements, the results obtained with a Pt–Ag/AgCl InLab501 (ARGENTHAL, 3 mol L^{-1} KCl) electrode system were adjusted to the standard hydrogen electrode at 10 °C. All samples were filtered through 0.45 μm cellulose acetate filters and HNO_3 was added for the trace element analyses. Total acidity and alkalinity were measured on site using a Hach digital titrator and a WTW pH meter. Mine water samples were analysed at the hydrogeological laboratory at the Ludwig Maximilians Universität München. A Perkin-Elmer AAS-3300 spectrometer was used for total iron, manganese, zinc, aluminium, sodium, potassium, calcium, and magnesium, a Perkin-Elmer SIMAA-6000 spectrometer was used for silver, cadmium, copper, nickel, and lead, and a DIONEX-IC-DX-100 was used for fluoride, chloride, nitrate, and sulphate. Iron was detected during the batch experiments with a HACH photometer. The percentage of solids in the sludge was determined by the weight loss from oven drying at 140 °C for 20 h; the samples cooled down in a desiccator. Sedimentation rates of the LDS were measured in 1000 mL cone-shape sedimentation (Imhoff) funnels, graduated every 50 mL between 1000 and 500 mL. The sludge in the sample containers was vigorously stirred for some minutes before taking the samples. Rheological parameters (e.g. viscosity) were measured with a Haake VT 500 (CR) rheometer. This rotational rheometer is composed of two concentric (inner and outer) cylinders. The internal cylinder is rotated at a controlled rotation rate in order to shear the sample contained in the gap. Shear stress is determined by measuring the resistant torque on one of the two elements. During the whole experiment, the temperature was maintained at 10.1 °C, which was the temperature measured on site at the Straßberg mine.

Three additional sludge samples and two samples of the two polymer flocculants were analysed by IR spectroscopy and for carbon, nitrogen, and sulphur at the Technische Universität Bergakademie Freiberg (Table 3). Sludge samples (small sludge particles floating on top of the water, Figure EA c), were collected in the No. Ü539 shaft and the Flour Shaft, where most of the mine water discharges into one of the three drainage galleries as well as at settling pond III at the former Straßberg treatment plant site (Figure EA d). Normally, no sludge is discharging at the shafts, but in the past, sludge could occasionally be observed.

Table 2 Physical and chemical parameters of Straßberg and Alexisbad mine waters. Parameters with empty lines were not analysed

Site	No. 539 Shaft (Brachmannsberg Pit)	Fluor Shaft (Straßberg Pit)	Glasebach Shaft (Glasebach Pit)	Alexisbad Adit[d] (*Schwefel-Stollen*)	Westfield[e] (Straßberg Pit)
Water Temp. (°C)	10.4	10.1	11.7[a]	8.5	10.1
Elec. cond. (μS/cm)	542	822	1094[a]	607	
pH	6.52	6.53	6.73	5.54	2.6[f]
RedOx (mV)	137	256	194[a]	369	
O_2 (mg L^{-1})	0.18	0.13	n.d.[c]	10.48	
Total Fe (mg L^{-1})	13.7 ± 1.9	10.7 ± 1.9	0.3 ± 0.2	0.2 ± 0.2	2.23
Mn (mg L^{-1})	1.0 ± 0.2	5.1 ± 1.0	7.0 ± 1.0	2.7 ± 0.2	1.43
Zn (mg L^{-1})	0.1 ± 0.03	0.3 ± 0.1	0.1 ± 0.05	1.9 ± 0.3	0.17
Al (mg L^{-1})	0.6	1.1	0.2	1.8	
K (mg L^{-1})	2.2 ± 0.4	2.7 ± 0.4	7.2 ± 1.9	1.6 ± 0.4	2
Mg, mg L^{-1}	18.2 ± 1.6	23.3 ± 1.6	24.3 ± 1.6	16.3 ± 1.6	14.74
HCO_3 (mg L^{-1})	70.2 ± 0.7	130.3 ± 1.3	206.4 ± 2.1	20.7 ± 0.2	74.05
Cl (mg L^{-1})	32.3 ± 1.4	23.7 ± 1.4	29.7 ± 1.4	43.3 ± 1.0	16.33
NO_3 (mg L^{-1})	<0.74	<0.74	2.3 ± 0.1	3.0 ± 0.1	
SO_4 (mg L^{-1})	146.6 ± 2.1	305.3 ± 2.1	211.9 ± 2.1	218.4 ± 2.1	153
PO_4 (mg L^{-1})					0.17
F (mg L^{-1})	2.2 ± 0.2	4.7 ± 0.2	2.8 ± 0.2	1.8 ± 0.1	3.40
Ca (mg L^{-1})	41.5 ± 3.9	106.3 ± 8.0	105.9 ± 8.0	55.9 ± 4.0	68.61
Na (mg L^{-1})	22.7 ± 2.6	16.8 ± 2.6	15.9 ± 2.7	20.1 ± 2.6	11.30
Cu (μg L^{-1})	7.6 ± 0.1	8.7 ± 0.1	31.8 ± 0.2	115.7 ± 0.8	110
Ni (μg L^{-1})	11.9 ± 0.04	83.2 ± 0.3	28.0 ± 0.1	48.3 ± 0.1	
Pb (μg L^{-1})	1.7 ± 0.006	0.4 ± 0.001	1.0 ± 0.004	2.8 ± 0.010	
Cd (μg L^{-1}	0.3 ± 0.02	3.6 ± 0.3	3.5 ± 0.2	2.8 ± 0.2	17
As (μg L^{-1})	131.9 ± 0.6	100.5 ± 0.5	3.4 ± 0.02	22.6 ± 0.1	
k_B (mmol L^{-1})	11.8 ± 0.1	11.9 ± 0.1	5.8 ± 0.1	13.8 ± 0.1	
k_A (mmol L^{-1})	1.2 ± 0.01	2.1 ± 0.02	3.4 ± 0.03	0.3 ± 0.003	

Elec. cond. electrical conductivity, k_B base capacity (total acidity), k_A acid capacity (total alkalinity), *n.d.* not detected

[a] Data from earlier measurements in 2000, $n = 7$

[b] Data from earlier measurements between 1999 and 2004, $n = 273$

[c] Water is mechanically oxidised with Fuchs oxidisers

[d] More details about this adit (also called *Schwefel-Stollen*) in Dobler (1999)

[e] 1989 Mine water sampled in the Westfield (BST Mansfeld GmbH, pers. comm.)

[f] Estimated from sulphate and copper concentrations

Mine Water-LDS Chemical Interaction and Geochemical Modelling

Two different methods were used to determine the influence of LDS on mine water quality: batch experiments in the laboratory and modelling with the PHREEQC software (Parkhurst and Appelo 1999).

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. Mine water from the Alexisbad Schwefel-Stollen ("sulphur adit") was used, because it was believed to be chemically closer to the Westfeld water composition than the Brachmannsberg or the Glasebach mine water and had not been in contact with LDS. In order to observe potential differences in the chemical and physical behaviour of the sludges, all tests were performed with LDS from both the Fluor Shaft and the Brachmannsberg settling ponds. A total of three experimental series were conducted, in which water and sludge reacted together in an overhead mixer: 77 h and 24 h for the reaction with Brachmannsberg-LDS and 16.5 h for the reaction with pond II-LDS. After each test, electrical conductivity, pH, base capacity (k_B), acid capacity (k_A), ferrous iron, and total iron concentrations were measured.

Forward modelling to investigate the influence of the injected LDS on the mine water chemistry was conducted

Table 3 CNS analytic of sludges from the LDS mine water treatment plant and from small patches of floating sludges in two of the three shafts

Sample number	Location	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)
SBG-0707-T3[a]	Settling pond III	9.97	0.34	0.08	0.08
SBG-0707-Ü539[b]	Shaft No. 539 (Brachmannsberg Pit)	6.35	2.78	0.97	1.90
SBG-0707-HS[b]	Main Shaft (Straßberg Pit)	1.48	2.51	0.18	0.40

[a] Sample from the LDS mine water treatment plant

[b] Samples from small patches of floating sludges

with PHREEQC version 2.0 using the MINTEQ and WATEQ4F databases (Parkhurst and Appelo 1999; Merkel et al. 2005). Inputs to the model were:

- the chemical composition of pre-flooding water in the Westfeld, theoretically arriving upstream of the sludge injection point within the mine (Water No. 1, sampled in 1989, before the mine flooded),
- 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 not accessible for water sampling, the numerical model is based on water samples taken and analysed in 1989. According to the chemical results, this water is oxidized and well buffered. Since its initial pH was not measured at sampling, the sulphate and copper concentrations were used to calculate the pH and the amount of dissolved pyrite and chalcopyrite.

Based on the chemical composition of the sludge (Kindermann and Klemm 1996; Table 2), we calculated the mineralogical composition of the sludge according to the CIPW norm (Wimmenauer 1985; Table 1). This mineralogical composition was then used as the basis for the chemical modelling of the sludge/water interactions. For the given data, calcite, magnetite, corundum, hematite, pyrite, and natron were identified and used as the equilibrium phases for the PHREEQC simulation. These results are very similar to other chemical LDS analyses (Zinck 1997).

Between 1996 and 2000, an average monthly sludge volume of 7,200–1,600 m^3 with a solids content of 1–10 % accumulated in the settling ponds and was injected into the mine. According to Rüterkamp and Meßer (2000), the total water volume of the mine is 277.100 m^3. Therefore, the No. 2 LDS-water would have a volume that corresponds to 2.6–0.6 % of the total mine water volume (with the initial composition of water No. 1). On this basis, we used sludge-water ratios between 0.01 and 10 % for the modelling of the sludge–mine water interactions. Finally, the results were interpreted using a hierarchical cluster analysis in order to compare the mine water composition at the Main Pit (Fluor Shaft) with the water composition of the modelled reactions.

Results and Discussion

Sludge Settling Characteristics

The sedimentation rate of the LDS and its viscosity (once settled) within the mine were measured to determine if the sludge will stay near the injection point into the mine or whether it will be transported into other parts of the mine by the water flow. For the three sludge samples investigated in this step, mean solids concentrations of 11.5 % (pond II, sample 1), 14.9 % (pond II, sample 2) and 17.2 % (Brachmannsberg left pond) were determined. As expected, the sludge originating from the Brachmannsberg treatment site, to which flocculants are added, had a higher solids content. Furthermore, the solids content of the LDS was higher than the expected 10 % and a difference existed between the two samples collected at the pond II at the Fluor Shaft. This might be due to sludge aging. All sedimentation curves showed major sedimentation within the first 48–72 h, followed by a significantly lesser change thereafter (Fig. 2). Because sludge only reacts when in direct contact with mine water, it is advantageous if the LDS in the mine water stays in suspension as long as possible.

The loss of volume during sedimentation is 12.9 ± 0.6 % for the sludge in pond II/2 and Brachmannsberg site and 31 ± 0.5 % for that of pond II/1 (Fig. 2). This different behaviour of the two samples from pond II corresponds with the solid contents results, indicating higher water content in sample II/1.

The sedimentation properties for all three samples, though different in their detailed behaviour, are rather similar. Therefore, it can be concluded that the settling time needed by the LDS is relatively long and possibly allows partial transport through the galleries by the flowing mine water. The currents within the mine are supposed to be higher and non-laminar in galleries compared to the mine workings. Consequently, injection of the sludge into galleries would encourage its dispersion throughout the mine workings.

For all samples, the apparent viscosity decreases as the shear rate (velocity gradient) increases (Fig. 3). Such a fluid behaviour corresponds to thixotropic characteristics,

Fig. 2 Sedimentation curves (Imhoff funnels) of the three different Straßberg Mine sludges used for the bench scale tests. Two sedimentation curves with two different samples were assessed for all sludges

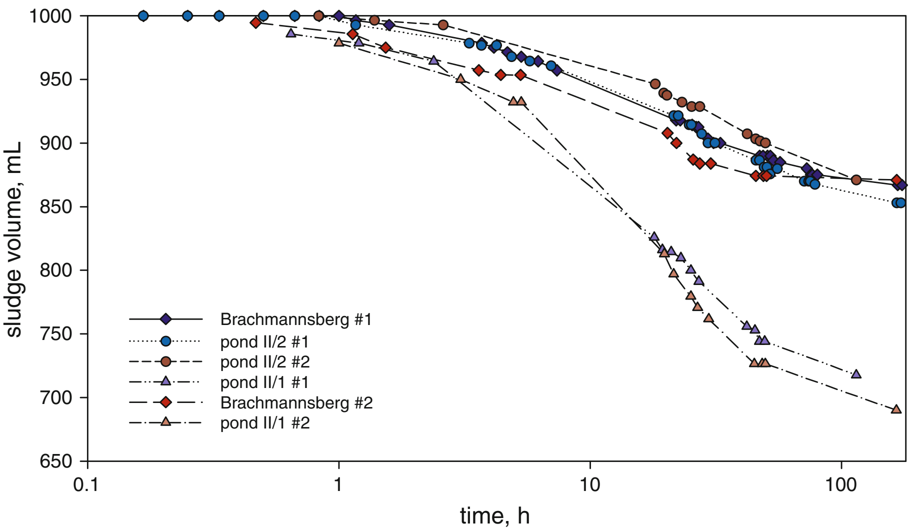
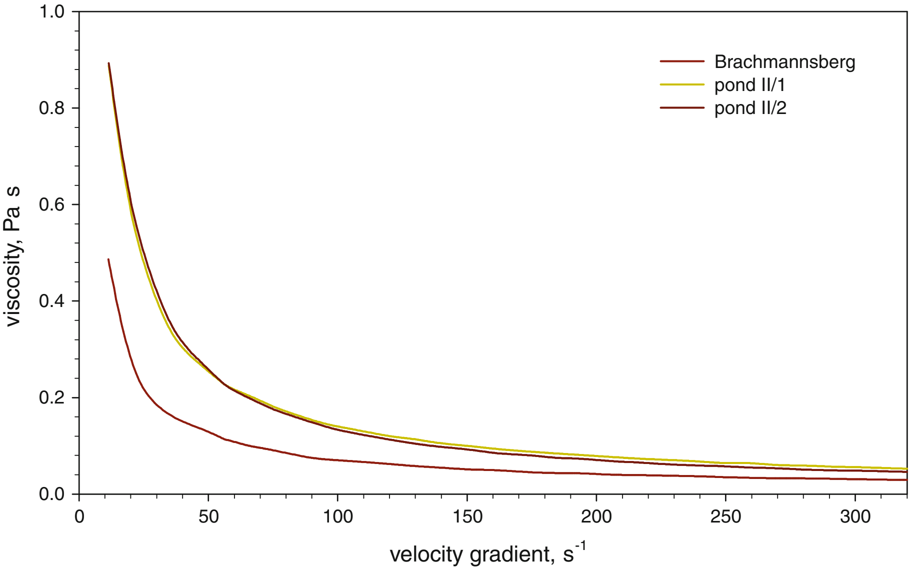


Fig. 3 Viscosity curves of the three LDS samples originating from pond II and from the Brachmannsberg northern pond measured with a Haake VT 500 (CR) Rheometer



as observed on the schematic flow curves for model time-independent materials by Seyssiecq et al. (2003). For all three sludge samples, 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 was diluted with water and consequently should have a viscosity, not exactly known, between the measured values and that of water (10^{-3} Pa s at 10 °C). However, water is expulsed during and after settlement, and the viscosity of the LDS once settled in the mine is therefore supposed to be the one measured in the laboratory. Furthermore, from the literature and previous investigations of the particle size distribution of Straßberg sludges, it is known that the d_{50} particle size ranges between 4.0 and 43 µm ($n = 22$; Klemm and Degner 2001; Zinck et al. 1997). Yet, the question remains whether the LDS sludge will stay settled or be eroded and transported by the mine water.

Tracer tests in the Straßberg Mine indicated mean effective velocities for the mine water of 0.01 to 0.14 m min^{-1} (95 % confidence interval; Wolkersdorfer and Hasche 2001). Using the results of Fig. 3 and considering the length of the mine galleries ($\approx$2,000 m), gives a velocity gradient around 10. Because viscosity is not directly proportional to the velocity gradient (as in the case of a Newtonian fluid), we cannot directly asses the corresponding viscosity value from Fig. 3. This means that the curve cannot be linearly extrapolated to obtain a precise viscosity value corresponding to the velocity gradient within the mine. We tried to evaluate this value and calculated a regression curve for the sludge sample pond II/2 (Eq. 1):

$$\eta = 9.0492 \times \delta^{-0.9157} \tag{1}$$

with η the viscosity in Pa s, and δ the velocity gradient in s^{-1} ($R^2 = 1.00$).

On a 2,000 m gallery, at a velocity of 0.14 m min^{-1} and a laminar flow, this would be equal to a viscosity of around 2,450 Pa s. Thus, the measured mine water velocities within the Straßberg Mine are too low to physically erode the LDS once settled. This is also true for other mines, as no natural flow within galleries will be large enough to reach a velocity gradient of 100 s^{-1} or more. These calculated results can be backed up by a Hjulström diagram (Hjulström 1935), which proves that the likelihood of eroding the sludges, once they have settled, is very low (Fig. 4).

Mine Water Chemistry and Sludge Composition

All three accessible shafts of the Straßberg Mine comprise different mine water compositions (Table 1). At the Main Pit, where the water was pumped into an underground sump before being discharged into the Biwender adit, the total iron concentration is 10.7 mg L^{-1}, with a pH of about 6.5 but a relatively high net acidity (total acidity, k_B, is higher than the total alkalinity, k_A). These waters have high concentrations of sulphate, calcium, iron, and other metals and semi-metals. This corresponds to the regular monitoring data in the mine (pers. comm. Ronny König 2008). In addition, the water at the Main Pit and Glasebach contains higher HCO_3^--concentrations than Brachmannsberg and Alexisbad, due, presumably, to the injected LDS. Tracer tests have shown that the water in the Straßberg Mine flows from north to south (Wolkersdorfer and Hasche 2001). The suspended LDS, or the water that reacts with the sludge, is transported from the Westfield to the Glasebach Pit, but also to the Main Pit, since the mine water pumps create an artificial flow in this direction. No LDS water flows to the Brachmannsberg site and so the HCO_3^--content there is lower.

Water-sludge Batch Tests: Evolution of Water Chemistry

The aim of the water-sludge batch tests was to quantify the influence of the LDS sludge on the chemistry of the mine water. Because of the large water volume needed for the experiments (50 L of Alexisbad water), it was impossible to keep the water at or below a temperature of 4 °C. Consequently, the chemistry of the Alexisbad water sample used for the batch tests has changed between sampling and the laboratory experiments. Alkalinity (acid capacity k_A) decreased from 0.340 mmol L^{-1} at sampling to 0.0475 mmol L^{-1} at the start of the experiments and acidity (base capacity k_B) from 13.76 to 0.635 mmol L^{-1}, respectively (Table 2). Moreover, the pH of the Alexisbad water decreased from 5.54 at sampling to 4.15 at the start of the laboratory experiments as a result of iron hydrolysis. At the same time, the iron values in the Alexisbad mine water decreased.

The batch experiments showed (Fig. 5) that mixing the mine water and the LDS increased total alkalinity and decreased total acidity (Fig. 6). This can even be seen in the first batch test, where only 0.5 % of LDS was used. The pH increased to 7.07–8.05. This pH increase, compared to the mine water, was due to the residual carbonate in the LDS (Table 1); these pH values are high enough to cause iron and aluminium oxides to precipitate. Table 3 also indicates that the carbonate in the fresh LDS sludge was consumed, as the fresh sludge had 10 % carbon and the

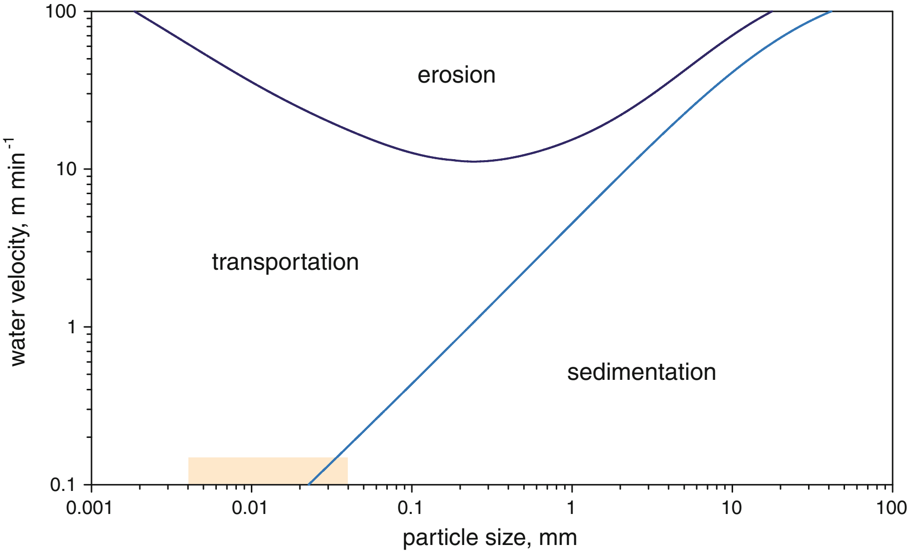


Fig. 4 A Hjulström diagram, relating the areas of sediment erosion, transportation, and sedimentation to the water's flow velocity (Hjulström 1935); the *coloured field* indicates the expected velocities and particle sizes in the Straßberg mine. The transportation/erosion *line* in the original diagram has broader transition zones than shown here

Fig. 5 Total alkalinity curve of the batch experiments with Alexisbad mine water and the two different types of LDS. Abscissa is in logarithmic scale starting at 0.5 % and shows the increasing sludge content added to the mine water. The error range of the measurements is within the size of the *symbols*

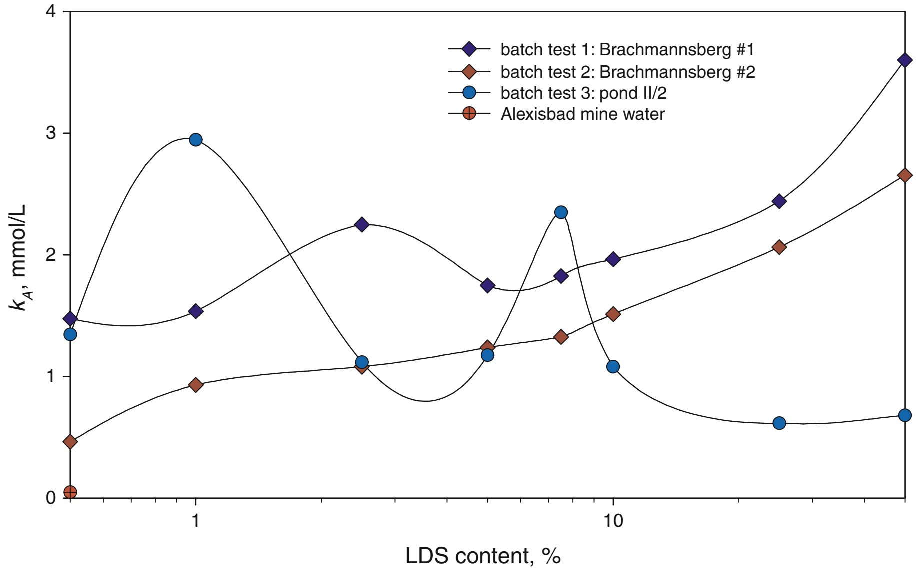
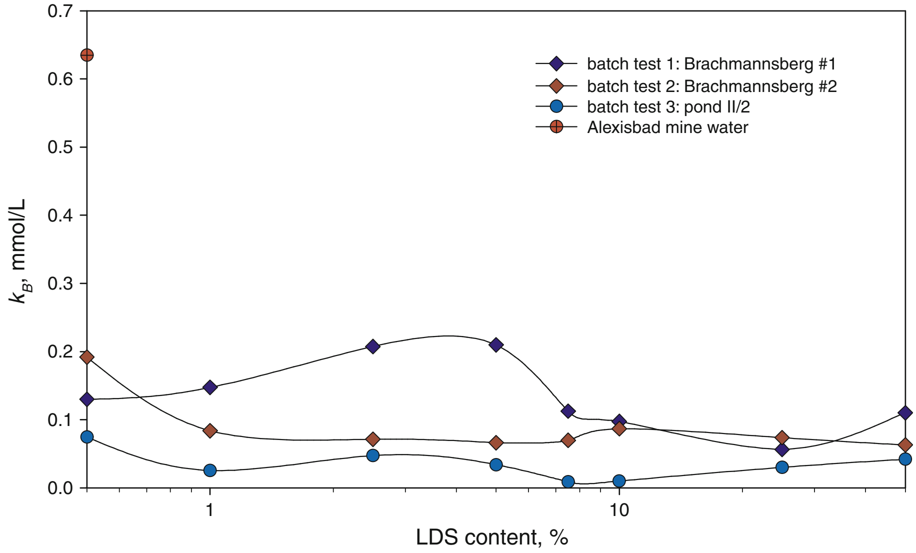


Fig. 6 Total acidity curve of the mixing experiments using Alexisbad water with the two different types of LDS. Abscissa is in logarithmic scale starting at 0.5 % and shows the increasing sludge content added to the mine water. The error range of the measurements is within the size of the *symbols*



floating sludge in the Main shaft only had 1.5 %. The higher sulphur concentrations in the floating sludge in the No. 539 shaft shows is attributed to the activity of sulphate-reducing bacteria, which is supported by the lower redox values of the water and the H_2S smell regularly encountered at that site.

The ferric iron concentrations in the water were measured after the batch experiment with Fluor Shaft (batch experiment No. 3) and Brachmannsberg (batch experiment No. 2) LDS and were mostly below the 0.01 mg L^{-1} detection limit. The only exceptions were 0.02 mg L^{-1} ferric iron for batch experiment No. 3 with 5 % LDS, and 0.01 mg L^{-1} ferric iron for batch experiment No. 3 with 25 % LDS. Considering the precision error and low concentrations, we conclude that the ferric iron concentration in the mine water generally decreased as a result of the LDS addition.

Concerning total iron concentrations (Fig. 7), the results show differences in the two batch experiments. In experiment No. 2, with only 0.5 % LDS, the total iron dropped to 0.04 mg L^{-1}. With a higher LDS percentage, the total iron concentration remained at this value or decreased. Yet, the results were different in experiment No. 3. At 0.5, 1, 2.5, 10 and 50 % LDS, the total iron concentration was below 0.02 mg L^{-1}, but between 2.5 and 10 % LDS, the total iron concentration increased (0.24 mg L^{-1}) above the concentration in Alexisbad water at the time of the laboratory experiments (0.15 mg L^{-1}), indicating redisolution of iron from the sludge. However the LDS percentage in the mine water was under 1 % in the Straßberg mine and very likely in all other mines as well (water sludge ratio as of the year 2000). The latter result agrees with the slightly increased k_B-values of this experiment.

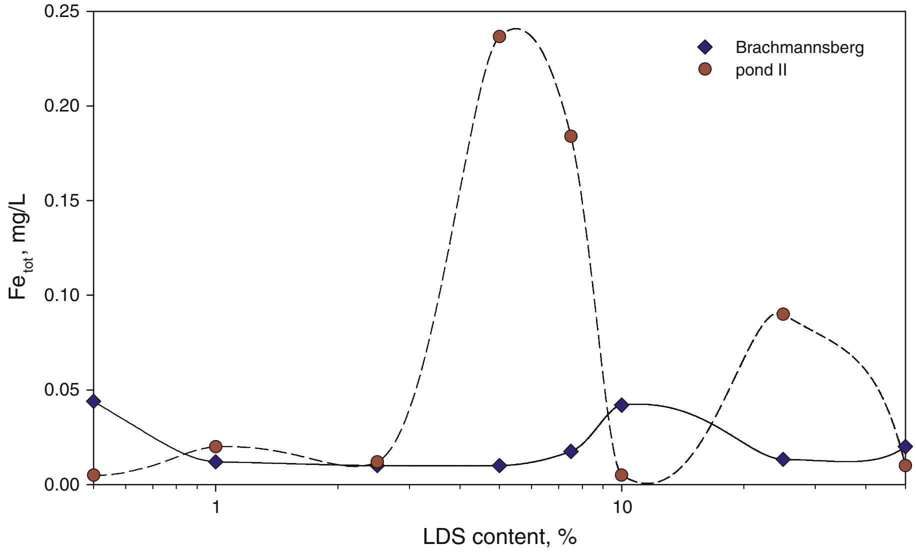


Fig. 7 Fe_{tot} concentrations in the batch experiments of Alexisbad water with the LDS of pond II and Brachmannsberg. Abscissa is in logarithmic scale starting at 0.5 % and shows the increasing sludge content added to the mine water. The error range of the measurements is within the size of the *symbols*

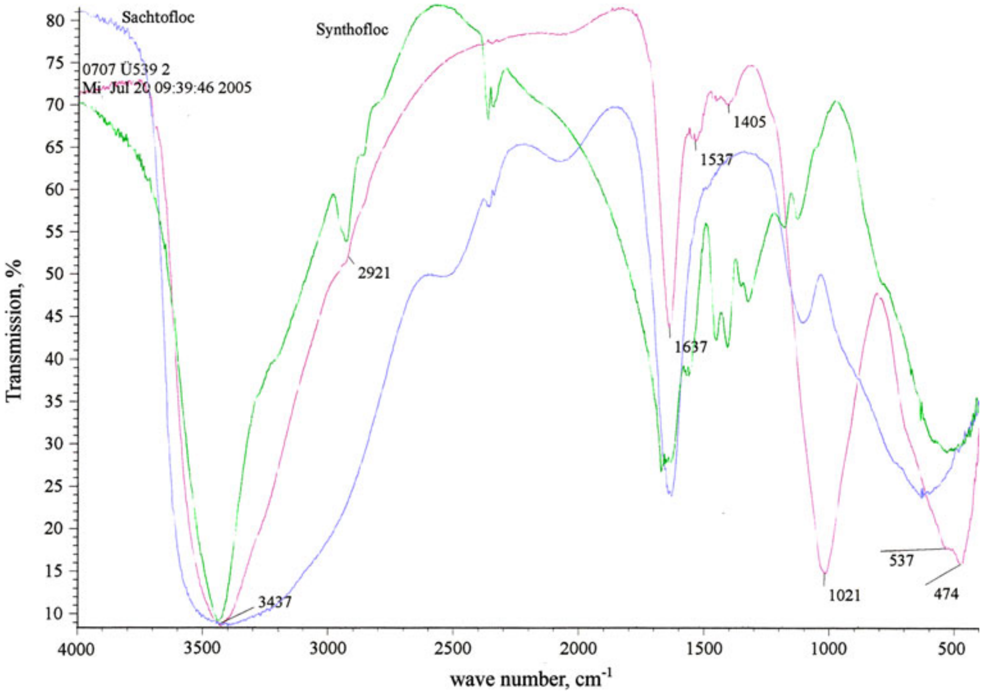


Fig. 8 Composite of IR spectra of Sachtofloc (*blue line*) and Synthofloc (*green line*) as well as the No. 539 shaft floating sludge (*pink line*). Axis titles modified from the original German and legends added to the lines

Thus, mixing the mine water and LDS decreases total acidity and iron concentrations and increases pH and total alkalinity; mine water quality was improved by the addition of the LDS.

Investigation of Polymer Flocculent in the Mine Water

None of the two IR spectra of the floating sludges in the two shafts showed a clear indication of polymer flocculent (Fig. 8). The sludge sample from No. 539 shaft had a slight indication in the range of the CH_2/CH_3 wave number 2,921 cm^{-1}, but none of the other peaks or indications typical of the flocculants could be observed. No indication of the polymer could be found in the sample from the Main Shaft. Because the method is very sensitive and even very small amounts of the polymer would have been able to be qualitatively identified, we concluded that none of the polymer or the sludge injected into the mine in the area of the Westfield was leaving the mine though the flooded shafts.

Modelling with PHREEQC

Adding LDS in a certain percentage range clearly improves mine water quality. However, the LDS percentages used for the batch experiments were much higher than the actual

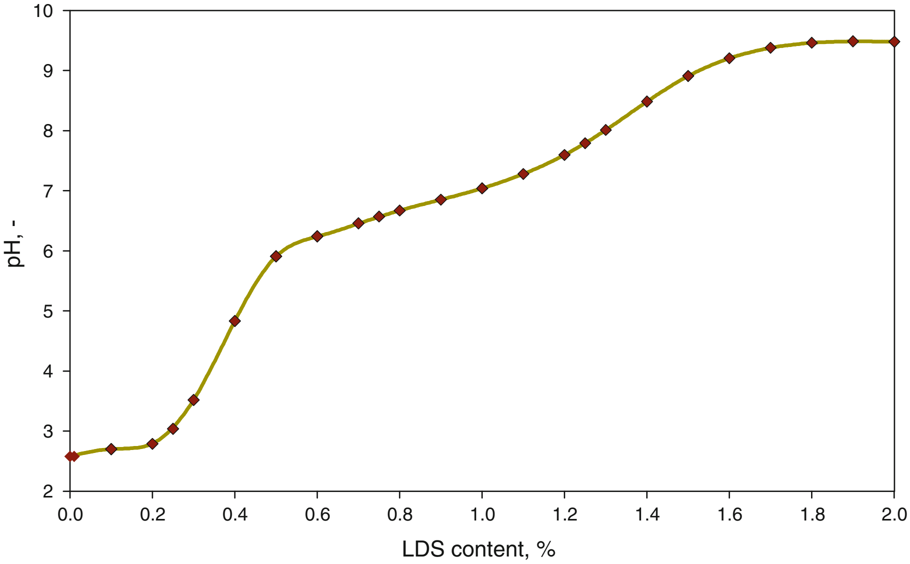


Fig. 9 Water pH curve obtained by modelling with PHREEQC. The abscissa shows the increasing sludge content in the Westfield mine water used for the modelling

situation in the mine. We therefore used the chemical thermodynamic code PHREEQC (Parkhurst and Appelo 1999) to model the water-sludge interactions at lower sludge concentrations. The modelling results and a hierarchical cluster analysis were then used to evaluate which ratio between LDS and mine water best fits the water chemistry in the Main Pit.

The PHREEQC modelling resulted in a pH of 10.1 for pure water reacting with the minerals equivalent to the bulk composition of the LDS (water No. 2). This agrees well with the pH of 9.9 measured in the ponds (Kindermann and Klemm 1996). A higher percentage of LDS causes the pH to increase (Fig. 9). It appears that a minimum LDS percentage of 0.2 % is required for the sludge to start buffering the mine water. Between 0.5 and 1 % sludge, the pH of the modelled mine water ranges between 6 and 7. At LDS percentages above 2 %, the pH increases to that measured in the settling ponds. The pH measured in the Main Pit on March 12th was 6.53. Considering only the pH, the volume of LDS in the mine water was therefore between 0.5 and 1 %, corresponding to the PHREEQC results.

Except for the conservative parameters Na and SO_4, the ion concentrations decreased as the LDS percentages increased (Table 4). The differences between the modelled composition and the Main Pit water can be explained by the substitution of the equilibrium phases for the real mineralogical composition of the LDS and that “rain water” was used in the model to react with the sludge. Cu was not considered in the CIPW-norm; therefore, we added Cu-pyrite as an equilibrium phase in the PHREEQC input file.

In order to determine which modelled LDS percentage (Table 4) would closely mimic the mine water composition measured at the Main Pit (Fluor Shaft), we used a

Table 4 Mine water composition obtained from modelling a mixture of the theoretical Westfield mine water with PHREEQC for an increasing LDS sludge percentage; main ions: mg L^{-1}

Model 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

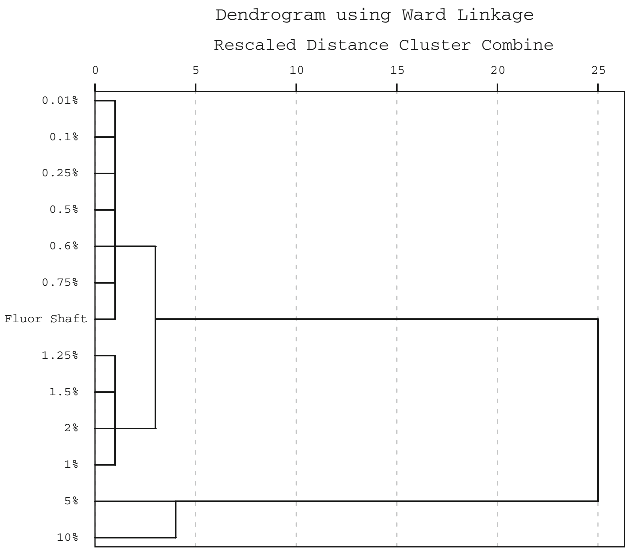


Fig. 10 Results of the hierarchical cluster analyses shown as a dendrogram. Input datasets are the sludge-mine water mixtures according to Table 4 and the composition of the mine water in the Fluor shaft. It shows that the Fluor shaft's mine water composition is close to the Westfield mine water with a 0.75–1.25 % sludge content. The values on the ordinate indicate the sludge percentage in the Westfield mine water

hierarchical cluster analysis and displayed the results in a dendrogram (Fig. 10). By doing so, similarities between the results could be graphically displayed. Based on those results, an LDS percentage of 0.75 (model No. 6) in the mine water causes a water composition that equals that of the Main Pit mine water.

Conclusion

This laboratory-based work has shown that injection of low density sludge from a mine water treatment plant into a flooded underground mine would improve mine water quality. Batch experiments and a chemical thermodynamic model demonstrated that only 0.2 % of the Straßberg LDS was needed to start buffering the mine water and increase the pH and that 0.5–1 % of the carbonate-rich LDS sludge added to the mine water increased the pH to near-neutral levels and decreased potentially problematic metals in the mine water. The batch experiments clearly showed that at those percentages, the metals were not remobilized after the sludge was injected into the mine. Furthermore, rheological investigations of the actual sludge showed that the mine water's velocity is too slow to mobilize the sludge once it has settled, yet 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. IR-spectroscopy of floating sludges in two of the three shafts gave no indication that sludge or the flocculants were being discharged from the mine. In addition, the pH-Eh-conditions in the mine are within the thermodynamic stability field of iron oxi-hydrate, so remobilisation under the thermodynamic conditions in the Straßberg mine is unlikely.

Although the Straßberg LDS composition was used for this study, the same components (excess calcite, iron oxides and hydroxides, sulphate) are found in other low density sludges. Moreover, we used water from two different mines, but the conclusions with respect to total alkalinity, total acidity, and dissolved iron concentrations were the same. The methodology and the general tendency developed for the study of the Straßberg mine LDS and its interaction with mine water can therefore be applied to other mines as well.

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