In situ tests for interactions between acid mine water and ferrihydrite sludge in the pyrite mine ”Elbingerode” (Harz Mts.; Germany)

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Abstract: A sludge containing mainly ferrihydrite, but also aluminium-hydroxide, gypsum and carbonate phases, originated by the treatment of acid mine drainage, has been disposed of inside the pyrite mine “Elbingerode” (Harz Mts.; Germany) and is to be stored there for the intended flooding period. Mobilization of elements in the system acid mine water (AMW) – ferrihydrite sludge – pyritic ore is therefore decisive. For experimental investigations a 38 m long heading in the mine was sealed, flooded with acid mine water (pH 1.7; Fe: 3600 ppm; SO_4: 19000 ppm) and gradually filled with ferrihydrite sludge. Percolation and transfluence of the sludge by AMW was simulated in subsequent tests. In situ sampling was carried out via an integrated tube system. The sluicing of small amounts of ferrihydrite sludge caused a partial remobilization of the buffering elements including iron. Further addition of ferrihydrite sludge caused a decrease in aluminium and iron concentrations and a gradual increase in pH in well defined buffering levels. Subsequent tests simulating percolation and transfluence by AMW showed no demonstrable mobilization of iron.

1 INTRODUCTION

In the former pyrite mine "Einheit", today Bergwerk Elbingerode of the GVV mbH (Germany, Saxony-Anhalt) more than 10 million tons of pyritic ores were produced in a complex underground mining to a max. depth of 480 m as raw material for the production of sulphuric acid in the former GDR. Production ceased in August 1990 and in 1995 the controlled flooding reached the current level.

A sludge containing mainly ferrihydrite, but also aluminium-hydroxide, gypsum and carbonate phases, originated by the treatment of acid mine drainage, has been disposed of inside the mine. The aim was to investigate whether the further influx would have an adverse effect on the future quality of the rising flood water. .

Hydrogeochemical modelling of interactions between acid mine water (AMW) and ferrihydrite sludge with PHREEQC (Parkhurst, 1995), based on monitoring data of the mine water during the first flooding period, demonstrates a local and temporary remobilization of iron from the sludge (Hansen, 1998). The reactive contact of acid mine water and ferrihydrite sludge causes a successive acidic dissolution of pH-buffering mineral phases like carbonates, Al-hydroxides and finally ferrihydrite, depending on the ratio of acidity and buffering substances.

Moreover remobilization of ferric iron can increase with the oxidation of pyrite (acidic + reductive dissolution). In situ tests combined with hydrogeochemical modelling shall enhance qualitative and quantitative understanding of the complex processes in the system AMW - ferrihydrite sludge - pyrite to facilitate predictions about the geochemical in situ behaviour of ferrihydrite sludge in the mine for the intended flooding period.

2 EXPERIMENTAL SETTING

For experimental investigations of metal mobility in the system AMD – ferrihydrite sludge – pyrite ore a large-scale, in situ experiment was carried out over a period of 12 months. For experimental purposes, a 38 m-long heading containing an open volume of about 260 m³ was sealed with a bitumen-impregnated wall. The test-heading is situated on the second level of the mine in an area with low-grade ore deposits.

According to planned experimental stages the discharge of acid mine water was via two intakes on roof and bottom of the heading (Figure 1). Suppressed water could overflow by a spillway. Ferrihydrite sludge was gradually injected via an intake 1 m below the roof. Inflow and outflow volumes of acid mine water, ferrihydrite sludge and suppressed water volumes were measured for volume and mass balancing.

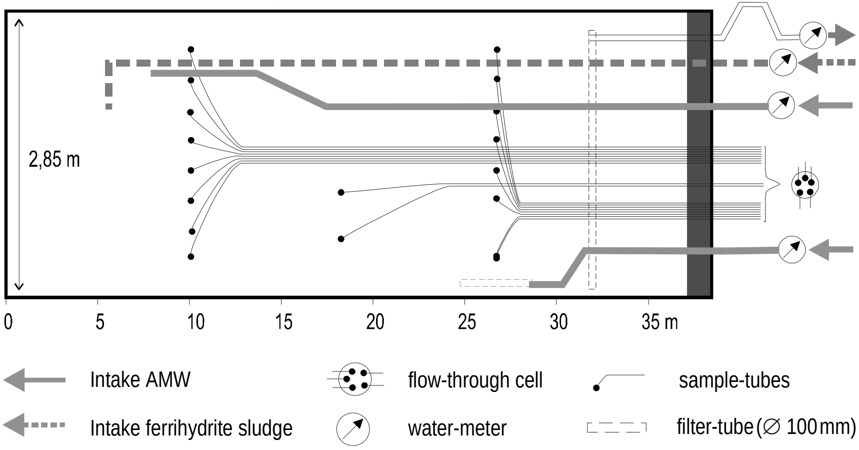

Figure 1 Principle arrangement of test heading

In situ sampling was done via an integrated system of 1”-tubes. Two centred sample units, each containing eight tubes - positioned at a vertical distance of 0.3 m and alternating horizontal distance of 0.5 m - allowed a 3-D sampling. Additionally two tubes were positioned beneath the walls, 0.5 m and 1.0 m above the bottom.

A flow-through cell was used for on-site measurement of pH, redox, temperature, conductivity and O_2. Samples were analysed for iron and sulphate concentrations. Selected samples were analysed in addition for manganese, calcium, magnesium, sodium and potassium. The solids content and chemical composition of ferrihydrite sludge were specified before addition and after completion of tests.

3 CONDUCT OF TEST

Various contact scenarios among acid mine water and ferrihydrite sludge were simulated. Every test period was followed by an equilibrium period of several weeks (Table 1). The individual test phases served to provide the most realistic possible simulation of processes such as can be expected in the further flooding.

Table 1 Test programme of the in situ experiment

Test Period	Description	Input [m³]	Duration [days]
1	Flooding with acid mine water	333	19
1a	Equilibrium period	81	41
2	Gradually sluicing of ferrihydrite sludge	222	64
2a	Equilibrium period	0	52
3	Percolation of ferrihydrite sludge by AMW	166	52
3a	Equilibrium period	0	67
4	Transfluence of ferrihydrite sludge by AMW	64,8	16
4a	Equilibrium period	0	48

The heading was flooded with 333 m³ via intake 1 with an acidic and highly mineralized water (pH 1.7; Fe: 3600 ppm; SO_4: 19000 ppm). Compared to the mean quality of waters in the flooded mine with pH-values around pH 3, this represents a worst case scenario. During the subsequent equilibrium stage (stage 1a), 81 m³ was replenished to compensate for seepage loss.

In the second stage 222 m³ of ferrihydrite sludge was gradually sluiced from the roof into the heading. The mean seepage loss decreased during the second stage from 3 m³/day to less than 1 m³/d.

For percolation and transfluence of deposited sludges AMW were gradually discharged from roof (stage 3) and bottom (stage 4).

The sampling was conducted daily in the phases of the discharge of sludge or mine water and weekly in the equilibrium phases. For this purpose the sample tubes were opened and the water in them was first drained.

4 RESULTS

4.1 Stage 1: Flooding

During the flooding period (1 + 1a) a slight decrease of pH from 1.7 to 1.5 corresponds with an increase of iron concentrations from 3600 ppm to 3950 ppm and sulphate concentrations from 19000 ppm to 20000 ppm resulting from the dissolution of iron salts (precipitates of pyrite oxidation during mining activities) from the heading walls.

4.2 Stage 2: Ferrihydrite sludge inflow

Figures 3 and 4 show the developments in the mean iron concentrations and the related pH values for the lower and upper heading section shown over the whole course of the test. In the course of the sludge inflow the mine water in the heading reacts homogeneously, despite a sedimentation of the sludge. Only in subsequent test phases does layering take place.

At the beginning of the test phase 2, when small quantities of sludge are mixed with a large quantity of acid water, there are signs of a slight increase in the iron concentrations from 3950 ppm to around 4200 ppm, and this is attributable to the acidic re-dissolution of ferrihydroxide.

The further sludge inflow and the related follow-up with buffer phases, together with dilution by the neutral and slightly mineralized sludge water, leads to a reduction in the concentrations with a simultaneous increase in the pH value in buffer stages at pH 2.3, pH 3.8 and pH 6.

The reaction conversion of the carbonate buffer phases and the resulting release of calcium leads to a massive precipitation of gypsum. This gypsum can be found both in sedimented sludge and as crust on the surface of the heading walls.

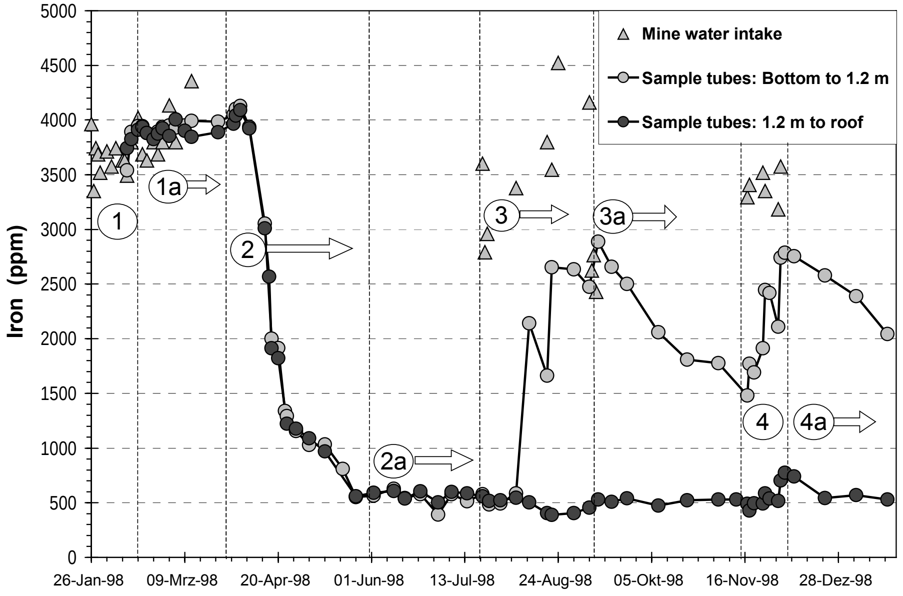

Figure 2 Development of iron concentrations in the test heading in the individual test phases

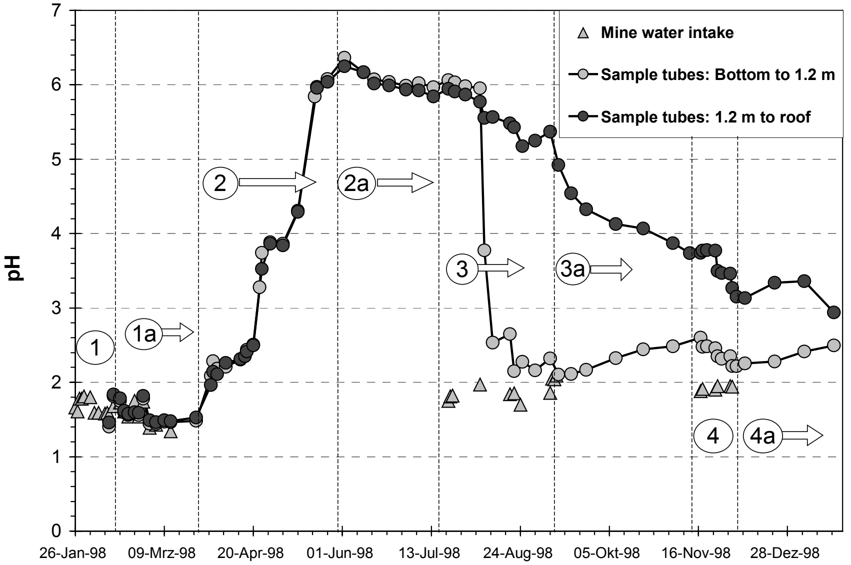

Figure 3 Development of pH values in the test heading in the individual test phases

During the inflow of the ferrihydrite sludge the substance concentrations measured must be considered in relation to a theoretical concentration development, which is calculated via the displacement and dilution of the roadway water by the sludge water (pH: 7.7; Fe: <1 ppm; Al: <1 ppm). The dilution curve calculated represents a reference base on which the mobility behaviour of the metals can be assessed (Figure 4 and 5). As long as the measured concentrations are above the calculated concentration development for a pure dilution, there is a re-dissolution of metals from the solids fraction of the sludge.

Re-dissolution of iron only takes place in the initial inflow stages. The mobilization phase ends when the calculated dilution curve is no longer reached. The concentrations measured subsequently can only be explained by the precipitation of iron.

The mobility phase for aluminium lasts considerably longer. Precipitation reactions of the aluminium only set in above a pH of 2.5.

4.3 Stage 3 and 4: Transfluence and Percolation

The fresh inflow of acid and highly mineralized water leads to a sub-layering of the buffered heading water, which is considerably less mineralized as a result of the dilution and precipitation reactions. The acid water in this phase thus lies directly on the sludge (Figure 2 and 3). Compared to the inflowing water, the acid water layer displayed lower iron concentrations and higher pH values – on a level around pH 2.3. There was no demonstrable re-dissolution of iron wither with a flow over the sludges or a flow through them.

After the end of the test the deposited sludge had been almost completely decarbonized. The calcium and manganese contents were strongly depleted, which sulphate and iron were enriched. In accordance with the mobility behaviour (Figure 5, only later precipitation) aluminium is only enriched in the upper area of the approx. 60 cm-high sludge layer.

5 CONCLUSION

The hydrogeochemical substance conversions observed can be retraced with the help of thermodynamic model calculations.

Figure 6 shows the modelled development of the mineral phase composition in the solubility equilibrium with the staged buffering of an acid mine water using ferrihydrite sludge. The details relate in each case to a volume of 1 litre. The mixing ratios between the ferrihydrite sludge and the acid mine water correspond to the conditions set in the test.

The modelled pH values of the aqueous phase in solubility equilibrium with the solid phases follow the "characteristic levels" of the buffer curves measured. On the basis of the modelling, it is possible to allocate the three different buffer levels to a succession of equilibrium settings. On a pH level between pH 2.2 and 2.5, jarosite as an iron-fixing phase is stable (Germain et al., 1994).

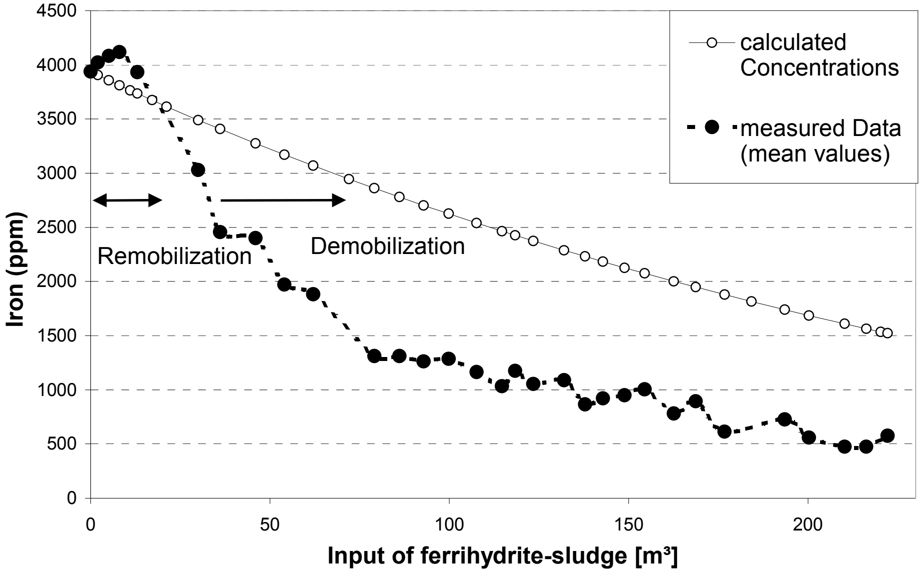

Figure 4 Iron mobility during phase 2

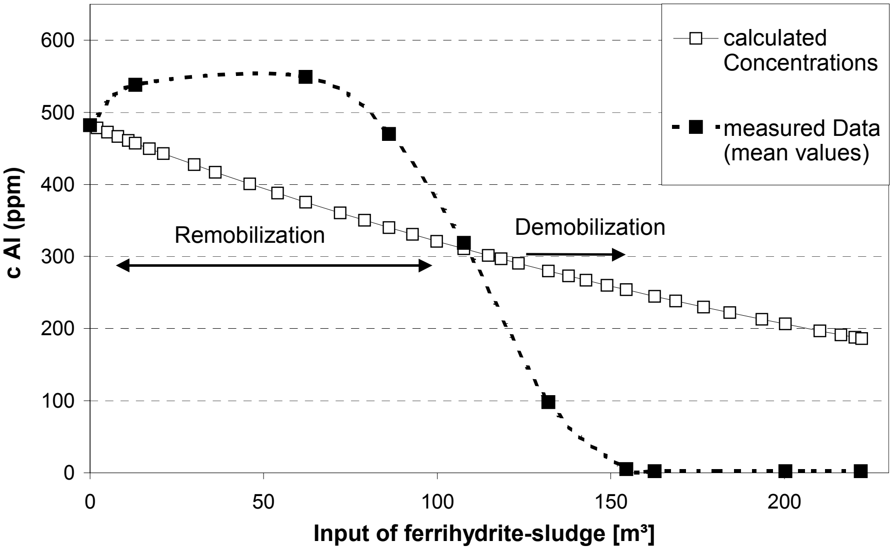

Figure 5 Aluminium mobility during phase 2

The subsequent provision of carbonate buffer capacity leads to a rise in the pH value. Jarosite becomes unstable and ferrihydrite represents the preferred iron-fixing mineral phase at pH values of around pH 3.8. At the same time there is a precipitation of jurbanite ($AlOHSO_4$). At a pH level of around pH 6 siderite forms finally.

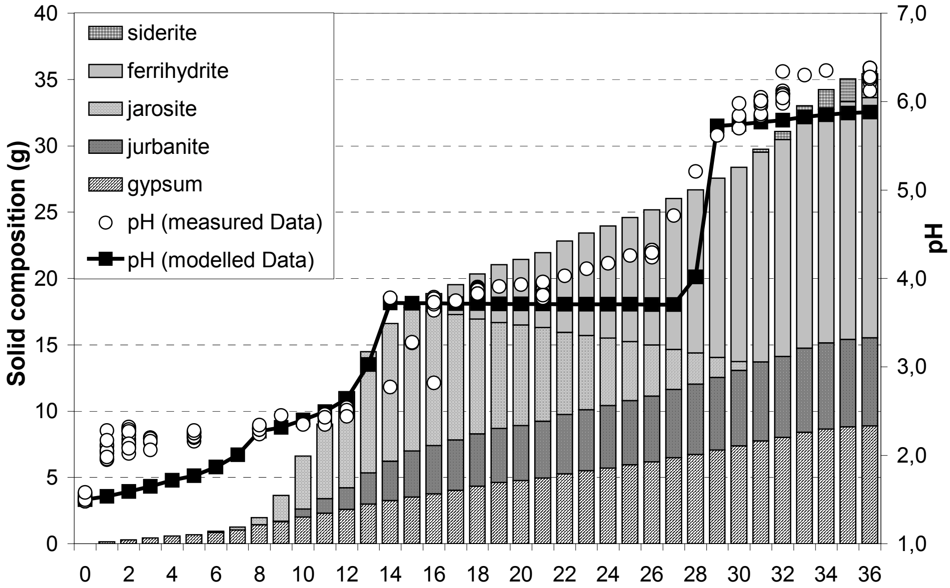

Figure 6 Modelled mineral phase assemblage of ferrihydrite sludge during stage 2 and equilibrium pH of aqueous phase compared with measured pH-values in stage 2

Beyond these acid-buffer interactions, the iron fixed in travalent form in the sludge is thermodynamically not stable in its solubility equilibrium with pyrite. With the precipitation of mineral products (gypsum, hydroxosulphate phases of aluminium and siderite) the reactive pyrite surface of the mineralization on the heading walls is inactivated, however. There is no quantitatively measurable acid-reductive or only reductive re-dissolution of the iron.

Intensive sampling and thermodynamically modelling of processes of an in situ experiment proved to be a useful method of evaluating predictions for complex problems such as the backfilling of ferrihydrite sludge in acid waters of a pyrite mine as investigated here.

REFERENCES

Germain M., Tassé N. & Bergeron M., 1994. Limit to Self-Neutralisation in acid mine tailings - the casa of East Sullivan, Quebec, Canada. In: Alpers C.N. & Blowes D.W. (ed): *Environmental geochemistry of sulfide oxidation. Am. Chem. Soc. Symp. Series* 550, 365 - 369.

Hansen C., 1998. *Modellierung der hydrogeochemischen Entwicklung saurer Grubenwässer – Flutung der Schwefelkieslagerstätte Einheit bei Elbingerode (Harz).* Diploma Thesis, Technical University of Clausthal, Clausthal-Zellerfeld (in German).

Parkhurst D.L., 1995. *User's guide to PHREEQC – A computer program for speciation, reaction-path, advektive-transport, and inverse geochemical calculations*. U.S. Geological Survey, Water Resources Investigations Report 95-4227.

Testy in situ na interakcje między kwaśnymi wodami kopalnianymi i szlamem żelazistym w kopalni pirytu „Elbingerode” (Góry Harzu, Niemcy)

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Streszczenie: Szlam zawierający głównie związki żelaza, ale również wodorotlenek glinu, gips i fazy węglanowe, powstały w trakcie obróbki kwaśnych wód kopalnianych, został składowany w kopalni pirytu „Elbingerode” (Góry Harzu, Niemcy) i ma tam pozostać w okresie zamierzonego zalewania kopalni. Mobilizacja pierwiastków w systemie: kwaśna wody kopalniana (AMW) - szlam żelazisty - ruda pirytowa, ma więc znaczenie decydujące w rozważaniach środowiskowych. Dla badań eksperymentalnych uszczelniono w kopalni chodnik o długości 38 m zalany kwaśną wodą kopalnianą (pH 1,7; Fe: 3600 ppm; SO_4: 19000 ppm) i stopniowo wypełniano szlamem żelazistym. Przesączanie i przenikanie szlamu przez kwaśne wody kopalniane (AMW) było symulowane w kolejnych testach. Pobieranie próbek in situ przeprowadzono poprzez połączony system rur. Śluzowanie małych ilości szlamu żelazistego powodowało częściową re-mobilizację pierwiastków buforujących łącznie z żelazem. Dalsze dodanie szlamu żelazistego spowodowało spadek koncentracji glinu i żelaza i stopniowy wzrost pH do dobrego poziomu buforującego. Kolejne testy symulujące przesiąkanie i przenikanie AMW nie wykazały zauważalnej mobilizacji żelaza.