Removal of zinc and lead from a neutral mine water using iron tailings and iron oxyhydroxide coated iron tailings

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Abstract

Lovisagruvan is a lead and zinc mine with elevated metal concentrations (370 µg/L Pb, 690 µg/L Zn) in slightly alkaline (about pH 8) mine water. In this study iron tailings, untreated and coated with iron oxyhydroxide, respectively, were used as filter materials to lower the concentrations of Pb and Zn. One upflow and one downflow column of each filter material were used. Columns with uncoated tailings removed 97.5 % zinc and 99.7 % lead while columns with coated tailings removed 95.9 % zinc and 97.7-98.9 % lead.

Key words: mine water treatment, neutral mine water, zinc, lead, iron oxyhydroxide

Introduction

Lovisagruvan is a mine located in mid Sweden where sulfide ore (lead-zinc-silver) has been mined since 2004. Every year around 40 000 metric tons of rock (containing 50 % ore) is mined. Water is pumped up from the mine at a rate of 5 m³/h and is first collected in three sedimentation ponds underground before it is pumped to a sedimentation pond above ground (residence time about three days). Surface water is then released. Water from Lovisagruvan, with a near neutral to slightly alkaline pH (7-8), is mainly contaminated with lead (370 µg/L) and zinc (690 µg/L). Previous investigations have shown that the present treatment method and the present concentrations do not meet the regional recipient criteria (generally Pb and Zn below 50 µg/L) and the water thus needs further treatment (Sartz et al. 2011).

Filtration methods to lower metal concentrations

Adsorption of metals to a filter material lowers the waters metal concentrations when particles or metal ions get attached to surfaces of the filter material. Adsorption depends on pH, cations generally adsorb at a higher pH and anions at a lower. For metals like lead and zinc (mainly present as cations at neutral pH) adsorption increases with pH. According to Drever (1997) almost all ions are attached to solid iron oxyhydroxide at pH 5 (Pb) and pH 7 (Zn). An increase in pH is not desirable for this water since higher pH can cause the metals to be part of anionic complexes such as carbonates or hydroxides which increases the dissolved metal concentrations.

There are many different types of filters, two common ones are downflow and upflow filters. In a downflow filter the water is added from the top and is flowing

down through the filter. It is an easy construction but the filter can get clogged if fine material accumulates at the bottom. In an upflow filter the water is added from in the bottom and is pumped up through the filter material. According to Forsvarsbygg (2009) the water is distributed evenly in an upflow filter, the contact between water and filter material is high and the risk of clogging is smaller because fine material is less likely to accumulate. To increase the adsorption of metals the filter material can be coated with iron oxyhydroxides that will work as surfaces for adsorption. Benjamin et al. (1996) describes iron oxide (or iron oxyhydroxide) as a good adsorbent of both free metal cations and metals in anionic complexes. Many previous studies have shown that iron oxyhydroxide increases the filters effect (Chang et al. 1997, Benjamin et al. 1996).

To treat the water from Lovisagruvan Sartz et al. (2011) filtered it through different materials in upflow filters in 1 m³ scale. The filter that contained iron tailings from Stråssa (a former magnetite mine located close to Lovisagruvan) showed the best results; lead and zinc concentrations decreased 68 % and 52 %, respectively.

This study

Four columns with two types of materials were used, untreated iron tailings from Stråssa (UT) and the same tailings coated with iron oxyhydroxides (ICT). One upflow filter and one downflow filter were set up for each filter material. The purpose of this study was to determine if UT or ICT is the most effective material for removing zinc and lead and if upflow or downflow filters is the most suitable filter type. Tailings from Stråssa were characterized to determine if metals could leach from the material. The result is going to determine what kind of treatment method that is to be used after the sedimentation pond at Lovisagruvan. A full scale filter would, according to Sartz et al. (2011), have to be of volume 60-70 m³.

Materials and methods

Characterization of the water from Lovisagruvan

Mine water was filtered through polycarbonate filters with different pore sizes (0.1 µm, 0.4 µm, 0.2 µm and 0.05 µm). Mine water was analysed for pH (electrode Lab 850, Schott Instruments), electrical conductivity (electrode Conductivity meter FE30/FG3, Mettler Toledo), alkalinity (titrator Titroline easy, Metrohm), sulfate (IC, Metrohm) and metals (ICP-MS, Agilent 7500 cx). Samples for sulfate analysis were filtered (0.2 µm polypropylene filter) prior to analysis. Samples for metal analysis were acidified to 1 % HNO_3 (distilled in clean room) and rhodium solution (Merck) was added as an internal standard.

Characterization of the iron tailings

Leaching tests L/S 2 and L/S 8 were made with deionized water (18.2 MΩ). Availability test was performed according to NT ENVIR 003 (Nordtest 1995) and oxidised availability test according to NT ENVIR 006 (Nordtest 1999). Availability tests were performed at L/S 100 without and with hydrogen peroxide, respectively, at pH 7 and pH 4.

Column tests

To make the iron oxyhydroxide coating a slurry containing iron sulfate ($FeSO_4$, Nitor) in the proportion 82 g to 1.5 L water and 1 L lime kiln dust (SMA, Spectra A) was prepared. Lime kiln dust was used as an adhesive and to make the iron oxyhydroxides precipitate. The slurry was mixed with the tailings in two steps, initially in the proportion 0.2 L slurry to 1 L tailings. Next day, when the material had dried, slurry in the proportion 0.15 L to 1 L tailings was added.

Columns were made of plastic drainage pipes**,** diameter 160 mm and length 650 mm, with plastic tubings attached to both ends of the columns. The columns were first packed with 75 mm coarse gravel which distributes the incoming water over the entire filter surface. On top of the gravel a geotextile was placed to prevent the filter material to mix with the gravel. Then 500 mm of tailings was packed followed by geotextile and 75 mm gravel on top of the column. Four columns were made like this, two with untreated tailings (UT) and two with iron oxyhydroxide coated tailings (ICT). One filter of each type was designed as a downflow filter and one of each type as an upflow filter (Figure 1).
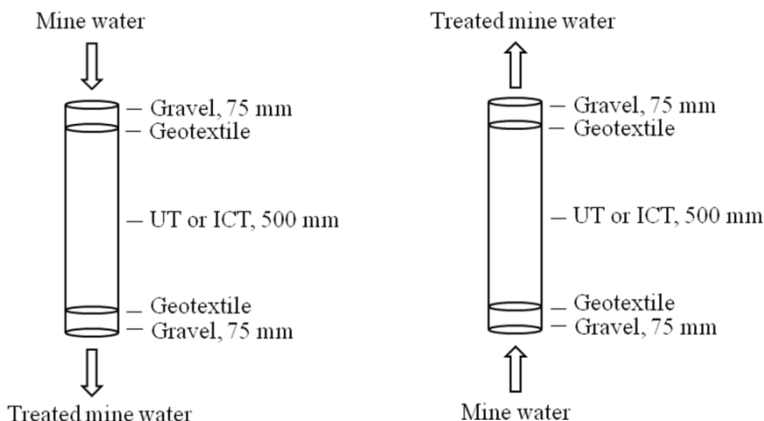

Figure 1a *Model of downflow filter.*   **Figure 1b** *Model of upflow filter.*

Water from the mine was pumped from the sedimentation pond above ground into a 1 m^3 container and transported to the laboratory. A pump (Fontänpump, FP 1000, Gardena) was placed in the container to keep any particles from settling. Water was pumped from the container to the columns at a rate of approximately 20 L/day (Figure 2). Total volumes through the filters were 1 300-1 600 L. Sampling was performed daily (except for the first days when more samples were taken) five days a week during five months. Samples of non-filtered water were taken every time more water was added to the container. Samples were analyzed in the same way as described above.

Figure 2 Picture of the column tests.

Results and discussion

Characterization of the water from Lovisagruvan

Results from analyses of the mine water are shown in Table 1. Filtration studies indicate that more than 50 % zinc and almost 75 % lead was associated to particles bigger than 1 μm. Just a small fraction (10-15 %) was associated to particles in the size interval 0.05 μm - 1 μm and 36 % Zn and 14 % Pb was assumed to be dissolved.

Table 1 *Electrical conductivity, pH, alkalinity, sulfate and metal concentrations in the water from Lovisagruvan. (Mean and standard deviation).*

	El. cond. (μS/cm)	pH	Alkalinity (meq/L)	Sulfate (mg/L)	Zinc (μg/L)	Lead (μg/L)	Uranium (μg/L)
Mean value	390	8.04	2.3	51	690	370	25
Std. dev.	35	0.34	0.50	4.0	390	250	3.9
n	17	17	17	6	9	9	9

Characterization of the iron tailings

Leaching tests (L/S 2 and L/S 10) and the availability tests showed that metal leaching from the iron tailings were low. However, significant concentrations of uranium was released; 0.023 mg U/kg dw (SD: 0.0053, n=6). In the oxidized availability test 0.065 mg U/kg dw (SD: 0.0091, n=2) was leached. This indicates that uranium is leached at a higher rate during oxidizing conditions.

Column tests

Initially the UT filtration increased the pH (about 0.5 pH units) but as more water passed the values decreased to about the same as for the untreated mine water (pH 8.04) (Figure 3a). pH in water filtered through ICT were initially high (about 12.6) due to the lime kiln dust used in the coating procedure. After 500 L pH had decreased to approximately 10.7 (Figure 3b). pH in the upflow filter continued to drop to 8.5 (which is only 0.5 pH unit higher compared to pH in incoming water) but for the downflow filter the decrease ceased.

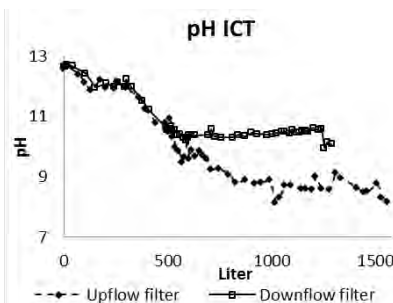**Figure 3a** *pH in water filtered through UT (pH in untreated water: 8.04).*   **Figure 3b** *pH in water filtered through ICT (pH in untreated water: 8.04).*

Alkalinity increased from 2.3 meq/L to 2.5 meq/L through UT filters. ICT filters initially raised the alkalinity to about 40 meq/L but after 400 L the alkalinity were 1.6 meq/L in the upflow filter and 1.8 meq/L in the downflow filter. Electrical conductivity increased in the ICT filters from 390 µS/cm to 8 500 µS/cm. After 500 L the electrical conductivity had decreased to the same level as for ingoing water. UT filters did not change the electrical conductivity. The initially high alkalinity and electrical conductivity from ICT filters was caused by residual alkalinity from the added lime kiln dust flushing out of the filters. Sulfate concentrations did not change passing UT but were much higher in water filtered through ICT (about 500 mg/L compared to ingoing waters 51 mg/L) but after 200 L flow the contents were just a few mg/L higher than the ingoing waters.

Zinc concentrations decreased 97.5 % through UT and 95.9 % through ICT (Figure 4). Any difference in capacity of the two different filter types (upflow and downflow) was not noticeable.
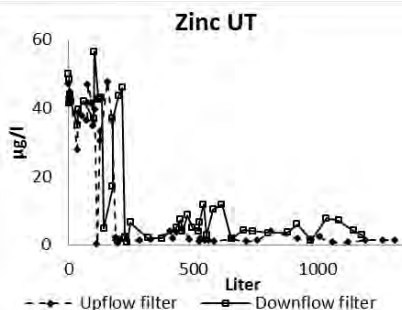
Figure 4a *Zn in water filtered through UT (Zn concentration in ingoing water: 690 μg/L).*
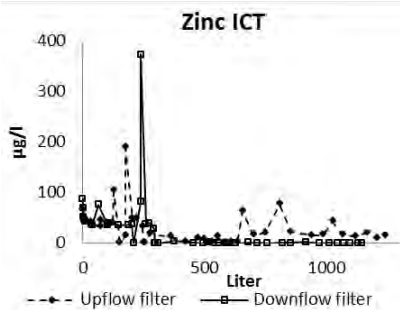
Figure 4b *Zn in water filtered through ICT (Zn concentration in ingoing water: 690 μg/L).*

There were a few extreme values, probably caused by particles (samples were not filtered prior to metal analysis). Concentrations seemed to be lower with increasing volumes of water passing the systems.

Lead concentrations decreased 99.7 % through both UT filters. In the ICT upflow and downflow filter lead concentrations decreased 97.7 % and 98.9 %, respectively (Figure 5).
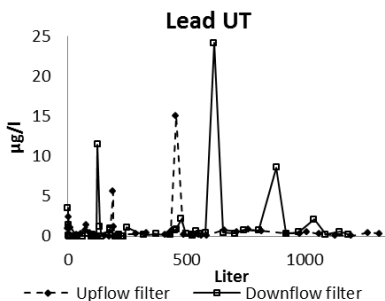

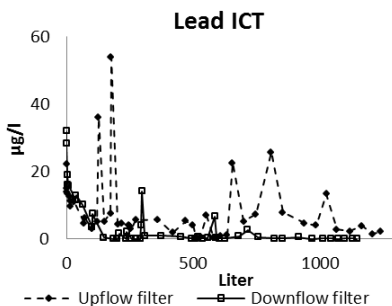**Figure 5a** *Pb in water filtered through UT (Pb concentration in ingoing water: 370 μg/L).*

Figure 5b *Pb in water filtered through ICT (Pb concentration in ingoing water: 370 μg/L).*

Both zinc and lead concentrations decreased more when passing UT compared to ICT which indicates that physical filtration is the dominating process in the filters because the concentrations are not lowered further when the iron oxyhydroxide is added. Trace metal removal was higher in all columns compared to the filtration through polycarbonate filters with an exact pore size. This indicates that also some adsorption occurs in the columns. The results can be compared with the results from the similar filter in 1 m³ scale that has been tested by Sartz et al. (2011) in direct connection to the sedimentation pond where zinc decreased with 52 % and lead with 68 %. This difference in filter efficiency can be partly explained by the fact that the flow through the 1 m³ filter was higher, especially in the beginning

which can have created preferential flow paths in the filters. Metal concentrations in the sedimentation pond were also higher during those tests which could have an effect on the filter capacity.

In the UT filters the uranium concentration increased from 25 µg/L to 28 µg/L. In ICT filters the uranium concentration was lowered with 99.0 % in the downflow filter and 77.9 % (97. 4 % before 300 L) in the upflow filter. Uranium is expected to be adsorbed the most at lower pH and forms anionic complexes at high pH found in the ICT filters. In this study the columns with high pH reduced the most uranium and a problem with increasing uranium concentrations appeared in the ICT upflow filter when pH decreased after 500 L. It is clear that the adsorption of uranium depends on pH.

Conclusions

Iron tailings from Stråssa, untreated or coated with iron oxyhydroxides, lowered the concentrations of zinc and lead in the mine water from Lovisagruvan. Zinc concentrations decreased 97.5 % in UT filters and 95.9 % in ICT filters. Lead concentrations decreased 99.7 % in the filters with UT and with 97.7 % (upflow) or 98.9 % (downflow) in ICT filters. However, iron tailings seemed to leach uranium. Uranium concentrations increased from 25 µg/L to 28 µg/L in the columns with UT but was reduced in the ICT columns, especially in the downflow filter (99.0 %). There were differences depending on pH between the two ICT filters. For UT filters no differences were seen comparing the upflow and downflow filters. Considering all aspects we recommend a downflow filter (because of the easier construction) with untreated tailings at a full scale test at Lovisagruvan.

Acknowledgements

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