Removal of uranium from a neutral mine water using uncoated and iron oxyhydroxide coated iron tailings.

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Abstract Mine water (pH 8) from the Lovisagruvan mine contains 25 µg/L of uranium. Magnetite tailings, uncoated or coated with iron oxyhydroxide, was tested in column experiments as filter material for removal of uranium. The uncoated filter systems did not retain uranium or change the pH. Coated filters, however, led to a significant pH increase, particularly in the down-flow columns and 97–99 % uranium was removed, as long as pH was ≥10.5. A formation of a Ca-UO_2-CO_3-species as well as co-precipitation with and adsorption to an assumed Ca-OH-CO_3-phase (and adsorption to the iron oxyhydroxid at pH >8.5-9) may explain the observations.

Keywords Uranium, mine water treatment, neutral mine water, iron oxyhydroxide filter

Introduction

Lovisagruvan is a small mine in the Bergslagen province, mid Sweden, with a yearly production of some 40 000 metric tons of rock containing 50 % of sulfide ore (lead-zinc-silver). Water is continuously pumped from the mine at a rate of ca 5 m^3/h into a sedimentation pond above ground, after passing through three sedimentation ponds underground (at depths of 145, 105 and 55 m, respectively). The mine water is eventually released into a recipient, after a residence time of around three days in the final sedimentation pond above ground. The concentration of zinc and lead in the water, after sedimentation, is of the order 700 and 400 µg/L, respectively, but there is also a residual concentration of uranium at the level 25 µg/L, mainly as dissolved species (>80 %). The water is near neutral (pH around 8) with an alkalinity around 2 meq/L (Fahlqvist *et al.* 2012).

Various geological barriers or filters, serving as metal scavengers and adsorbents, can be designed and used for treatment of mine water. Geologic materials coated with iron oxyhydroxides have been shown to be efficient as metal adsorbents and filters for treatment of mine water (Benjamin *et al.* 1996, Chang *et al.* 1997). Both cationic metal species as well as anionic metal complexes can be adsorbed and retained by such filters. Barriers and filters can, in general, be designed for down-flow or up-flow, *i.e.* the direction of the water flow is down-words from top to bottom or up-words, from bottom to top. Both types have their advantages. The down-flow filter has an easier construction, but the water distributes more evenly in an up-flow filter, and the risk for clogging (or channeling) is less because fine material is less prone to accumulate in the bottom of the filter (Forsvarsbygg 2009).

The efficiency of a magnetite based filter, with or without iron oxyhydroxide coating and down-flow or up-flow design, to reduce the uranium concentration in the Lovisa mine water is studied in the present project. The efficiency to reduce the concentrations of zinc and lead has previously been reported (Fahlqvist *et al.* 2012).

Material and methods

Filter material

Iron tailings with magnetite residues from Stråssa, a closed iron mine located near Lovisagruvan, were used as filter material. Both uncoated tailings (UT) and iron oxyhydroxide coated tailings (ICT) were tested. The iron oxyhydroxide coating was prepared from a slurry of iron sulfate ($FeSO_4$, Nitor; 82 g), water (1.5 L) and lime kiln dust (SMA, Spectra A; 1 L) that was mixed with the magnetite tailings in two steps: (1) Proportion 0.2 L slurry to 1 L tailings, exposure for 24 hrs; (2) Sieving and drying and new exposure, proportions 0.15 L slurry to 1 L tailings from step (1).

Column tests

Columns were made of plastic drainage pipes (diameter 160 mm and length 650 mm) with plastic tubings attached to both ends. The columns were packed with 75 mm coarse gravel which distributes the incoming water over the entire filter surface. A geotextile was placed on top of the gravel to prevent the filter material from mixing with the gravel, followed by 500 mm of tailings, another geotextile and 75 mm of gravel on top. Four columns were prepared; two with untreated tailings (UT) and two with iron oxyhydroxide coated tailings (ICT). One down-flow and one up-flow column was designed for each type, UT and ICT (Fig. 1).

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 10 L/d. Total volumes through the filters were 1 600–3 100 L. Sampling was performed daily (except for the first days when samples were taken more frequently) five days a week during thirteen months. Samples of non-filtered water were taken every time more water was added to the container.

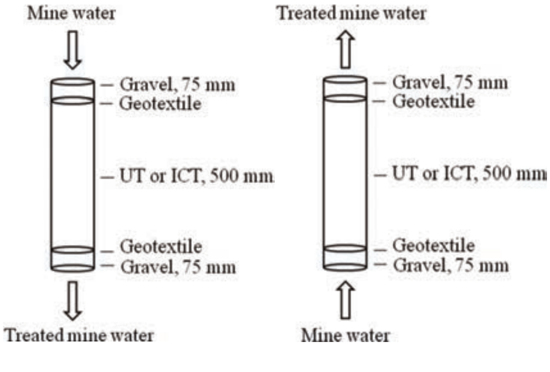

Fig. 1 *left (a) Model of down-flow filter.; right (b) Model of up-flow filter.*

Precipitation tests

Removal of uranium from solution by precipitation/co-precipitation was studied in batchwise tests. (1) Saturated $Ca(OH)_2$ -solution (between 0–25 mL) was added to 25 mL of filtered (0.45 µm nylon filters) mine water; totally 33 batches.

(2) Saturated $Ca(OH)_2$ -solution (between 0–25 mL) was added to 25 mL of filtered (0.45 µm nylon filters) mine water, followed by $FeSO_4$ that was added to give a total concentration of 0.8 g Fe/L; totally 26 batches.

Water analysis

Water samples from the tests were filtered through polycarbonate filters with different pore sizes (0.1 µm, 0.4 µm, 0.2 µm and 0.05 µm for column test samples; 0.45 µm for the precipitation test samples) and analyzed with respect to 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 metal analysis (filtered as described above, but also non-filtered from column tests) were acidified to 1 % HNO_3 (distilled acid), and rhodium solution (Merck) was added as an internal standard.

Results and discussion

Characterization of the mine water

Results from analyses of the mine water are given in table 1. The high pH and the significant alkalinity indicate the presence of carbonates in the bed-rock. The water is saturated with respect to $CaCO_3$ but below saturation with respect to $CaSO_4$ (Ca-concentration

	El. cond. (µS/cm)	Redox potential (pe)	pH	Alkalinity (meq/L)	Sulfate (mg/L)	Uranium (µg/L)
Mean value	390	2.5	8.06	2.3	52	25
Std. dev.	32	0.49	0.30	0.44	4.0	3.9
N	22	22	22	22	8	9

Table 1 *Electrical conductivity, redox potential, pH, alkalinity, sulfate and uranium concentrations in the water from Lovisagruvan (mean and standard deviation).*

around 40 mg/L). The redox potential (pe) corresponds to an apparent standard potential E° of 0.60-0.65 V, which is slightly below 0.70-0.75 V that is the expected range for environmental waters in contact with air (Allard 1982).

Column tests

Initially the UT filtration led to a pH-increase to 8.5, but as more water passed through the columns the values decreased to the initial level, *i.e.* around 8 or slightly below (Fig. 2a). The ICT filtration led to an initial pH-increase to 12.6, due to the presence of lime kiln dust from the coating process. After some 1500 L had passed the column a pH-level of around 8 was obtained in the up-flow system and around 10, or slightly below, in the down-flow system (Fig. 2b). Thus, there is no significant pH-effect from the UT-system at steady-state. In the ICT-system, with the added lime kiln dust, there is no remaining pH-effect after some 1500 L in the up-flow systems, but still an enhanced pH in the down-flow systems. Possibly also this effect will level out with time (after a larger volume has passed through the column).

The redox potential in the UT filters started at higher levels than for the incoming water (pe 3.1 compared to 2.5) but the redox potential decreased during the test period, ending at pe 1.1. In the ICT filters the redox potential started at pe around -0.1, increasing to 1.1 in the up-flow filter and 0.1 in the down-flow filter. The corresponding apparent standard potentials E° would, however, be around 0.68-0.70 V initially in both the UT and ICT systems, *i.e.* slightly higher than for the incoming mine water. The measured potentials after more than 1500 L through the columns correspond to apparent E°-values around 0.54-0.58 in both systems, *i.e.* a slight reduction of the potential but still representing aerated solutions. Uranium would be entirely in the hexavalent state at these potentials.

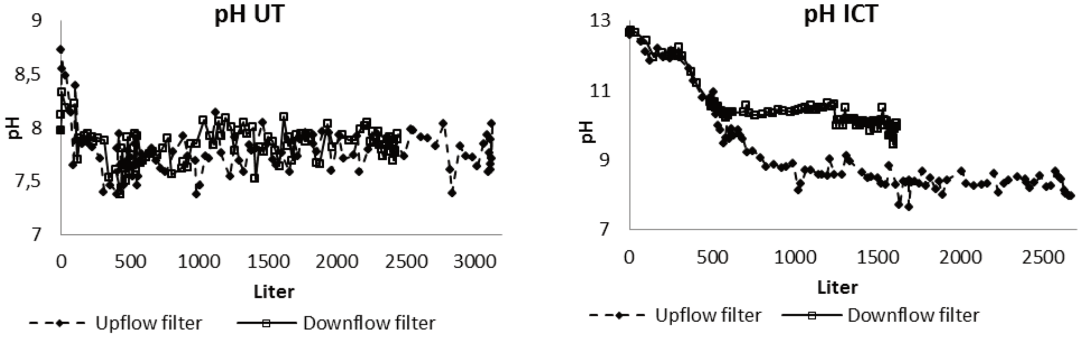

Fig. 2 *left (a) pH in water filtered through UT (pH in incoming water: 8.06); right (b) pH in water filtered through ICT (pH in incoming water: 8.06).*

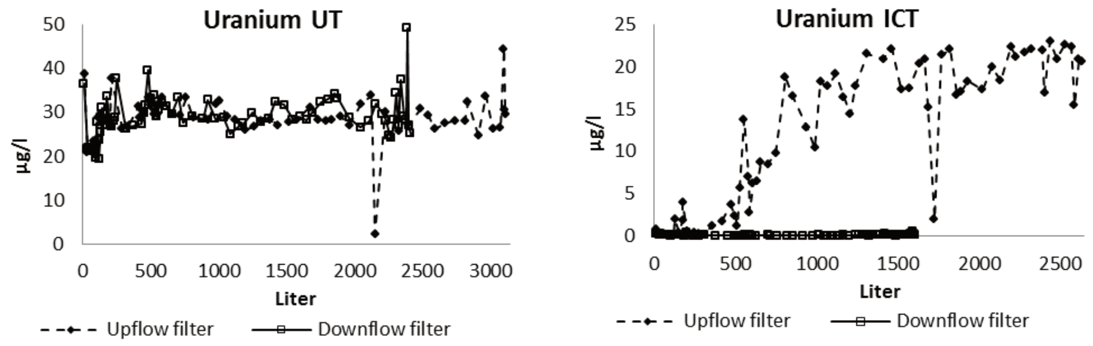

***Fig. 3** left (a) U in water filtered through UT (U concentration in incoming water: 25 µg/L); right (b) U in water filtered through ICT (U concentration in incoming water: 25 µg/L).*

Alkalinity increased from 2.3 meq/L to 2.5 meq/L through the UT filters. ICT filters initially raised the alkalinity to about 40 meq/L, but after 400 L the alkalinity was 1.8 meq/L in the up-flow filter and 2.0 meq/L in the down-flow filter. An increase in alkalinity (in UT) may reflect uptake of carbon dioxide from the atmosphere and at the same time a pH-buffering effect that kept pH constant at the level 8–8.5. The initially high alkalinity from the ICT filters would be caused by residual alkalinity from the added lime kiln dust that was flushed from the filters. The alkalinity decrease in the ICT after long time indicates the loss of carbonate by flushing out from the filter, or the precipitation of Ca-carbonate.

The UT filters did not change the electrical conductivity, but in the ICT filters the conductivity increased from 390 µS/cm to 8 500 µS/cm. After 500 L the electrical conductivity had decreased to the same level as in the incoming water. The initially high electrical conductivity from the ICT filters would be caused by residual alkalinity from the added lime kiln dust.

Sulfate concentrations were unaffected after the UT columns but were initially much higher in water filtered through the ICT (about 500 mg/L compared to 52 mg/L in incoming water). However, after 200 L the concentrations were only a few mg/L above the level in the incoming water. Possibly there was some sulfate remaining from the coating process (using $FeSO_4$).

Uranium concentrations increased slightly in the UT filters, from 25 µg/L in incoming water to around 28 µg/L in the up-flow filter and 29 µg/L in the down-flow filter and remained stable throughout the test period (Fig. 3a). Leaching tests of the material used in the filter showed, that the magnetite tailings contained leachable uranium in the range 0.023-0.065 mg U/kg dw. Thus, the tailings had a uranium content at the 0.1 ppm-level or higher, which is not unexpected since the granitic host-rock would have a uranium content at least at the ppm-level. Evidently, the reduction of the uranium concentration by adsorption in the UT filters was minor, or negligible.

In ICT filters the initial removal of uranium was 97 % in the up-flow filter and 99 % in the down-flow filter. The down-flow filter continued to be effective throughout the test period, when pH was above 9.8-10, while the uranium concentrations started to increase in the up-flow filter after about 400 L (Fig. 3b), and reaching around 20 µg/L after around 1000 L, corresponding to a pH of 10–10.5. At the end of the test period the values were almost as high as in the incoming water (22 µg/L compared to 25 µg/L).

Thus, when comparing uranium concentrations with pH values for the water passing

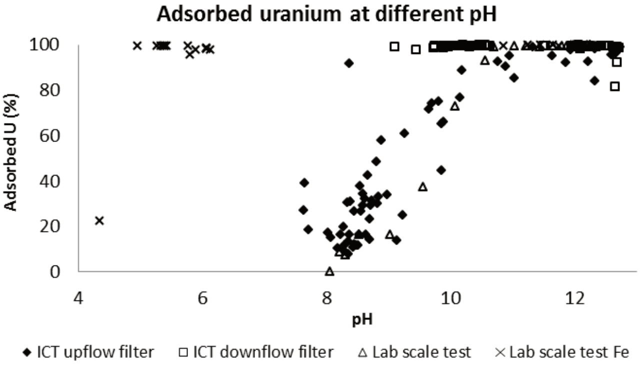

Fig. 4 *Reduction of the uranium concentration in solution as a function of pH in the ICT up-flow and down-flow filter columns; also precipitation tests (lab scale test) with addition of $Ca(OH)_2$, as well as with Fe(II) plus $Ca(OH)_2$.*

through the ICT filters (Fig. 2b and 3b) there is an obvious correlation. Uranium concentrations are increasing with decreasing pH in the up-flow filter systems, starting at pH around 11. In the down-flow filter systems the concentration did not increase even though pH dropped below 10.

Precipitation tests

Initial pH (before $Ca(OH)_2$-addition) was 8.06. Addition of 1 to 3 mL of saturated $Ca(OH)_2$-solution led to an increase in pH to around 11.2. The concentration of uranium in solution decreased from 26 µg/L to about 0.1 µg/L (>99 % reduction, Fig. 4). Subsequent additions of saturated $Ca(OH)_2$-solution led to further pH-increase to a maximum of 12.3 after 25 mL, close to the equilibrium pH of the $Ca(OH)_2$-solution around 12.5-12.6. The uranium concentrations in solution remained constant at the 0.1 µg/L-level. The addition of $Ca(OH)_2$ also led to the formation of a white precipitate, notably $CaCO_3$, since the original mine water is in equilibrium with calcite. Kaplan *et al.* (1998) also noted a significant decrease in uranium(VI) concentrations above pH 10.3 in the presence of carbonate solids. In the experiment with iron addition the decrease in uranium concentrations starts already at pH 5 and above. The lowest uranium concentrations were obtained at pH >10.

The co-precipitation with iron (as Fe(III)-hydroxide) in the whole pH-range 5–12 and with $CaCO_3$-$Ca(OH)_2$ at pH>10 is the logical explanation to the almost quantitative removal of uranium from solution. The results from the up-flow ICT filter is similar to the precipitation experiment with addition of saturated $Ca(OH)_2$-solution, and the results from the down-flow ICT filter reflect the precipitation with both iron and $Ca(OH)_2$. Possibly there is also a formation of UO_2-CO_3 surface complexes that contributes to the transfer of uranium from solution to the solid phase. Also the iron oxyhydroxide coating contributes to the adsorption on the solid filter phase at pH 8.5-9 and above.

There was no significant difference in the uranium retention between the up-flow and down-flow systems (ICT) during the first 500 L, but from 500 to 1500 L, the retention was gradually reduced in the up-flow system but constant in the down-flow system. This was a reflection of the change in pH, decreasing from around 10.5 to 8 in the up-flow system but only down to around 10 in the down-flow system. The differences between up-flow and down-flow may be the result of different flow-rates and hold-up times (lower flow-rate in the down-flow systems). Eventually, the two flow directions will establish the same steady-state conditions. It seems evident, that the assumed Ca-OH-CO_3-phase is largely responsible for the uranium retention and that this phase is gradually washed-out from the filter matrix. The iron oxyhydroxide is an active adsorbent at pH of 8.5-9 and above.

Uranium speciation

Uranium is hexavalent (as uranyl, UO_2^{2+}) in all the systems, and none of the systems are saturated with respect to any well-defined solid uranium mineral phase. Hydroxide complexes would dominate in a carbonate free system (Allard 1982; Missana *et al.* 2002). However, the mine water has an alkalinity at the level 2–3 meq/L. The dominating uranium species in incoming mine water, as well as in the water passing through the UT filter, can be assessed as $UO_2(CO_3)_2^{2-}$, with contributions of other anionic species, $UO_2(CO_3)_3^{4-}$, and possibly also $(UO_2)_3(CO_3)_6^{6-}$ (Allard *et al.* 1984). Other species present would be $UO_2(OH)_2$ and UO_2CO_3, both neutrally charged and present at much lower concentrations (%-level or less). According to Zheng *et al.* (2003) the uncharged complex $Ca_2UO_2(CO_3)_3$ may form in near neutral $CaCO_3$-solutions. The formation of a Ca-UO_2-CO_3 complex was also suggested by Gustafsson *et al.* (2009). Calcium concentrations are around 40 mg/L in the mine water, and additional calcium may be released from the coating.

Conclusions

Uranium is not retained by the uncoated filter matrix (UT) at pH 8. Adsorption is minor, since the mineral surfaces would be negatively charged (pH_{zpc} <8), as well as the dominating uranium species (carbonate complexes) in solution.

Uranium is almost quantitatively retained by the iron oxyhydroxide coated filter matrix (ICT) at pH around 10 or above. The retention process may be co-precipitation with an assumed (ill-defined) Ca-OH-CO_3-phase, as well as adsorption on the solid iron oxyhydroxide coating as long as pH is around 8.5-9 or higher. Retention is minor in the coated (ICT) system at pH around 8, *i.e.* pH of the original mine water. Thus, the assumed Ca-OH-CO_3-phase seems to be largely responsible for the uranium retention and this phase is gradually washed-out from the filter. The iron oxyhydroxide is an important adsorbent, but only at pH of 8.5-9 and above.

Further studies are in progress of the nature and detailed composition of the coating (elements and phases), its uranium-holding capacity and its stability, as well as of the uranium speciation.

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