

Strategy for instant neutralisation and metal immobilisation in ARD

Lotta SARTZ^{1,2}, Mattias BÄCKSTRÖM², Stefan KARLSSON^{1,2}, Bert ALLARD¹

¹*Man-Technology-Environment Research Centre, Örebro University, SE-701 82 Örebro, Sweden, lotta.sartz@oru.se*

²*Bergskraft Bergslagen, Harald Ols gata 1, SE-714 31 Kopparberg, Sweden*

Abstract For ARD filters, reactive barriers are often the methods of choice. Some problems are recognised though; iron precipitation cause hydraulic changes and inhibition of neutralising phases. Instead of filter/barrier installation alkalinity is suggested to be added in an aqueous phase (leach beds). Addition of a highly alkaline solution to different ARD results in a rapid, almost instant neutralisation, precipitation of metals (Fe, Al) as well as almost quantitative coprecipitation and sorption of trace metals at near neutral pH. Generation of alkalinity on-site, added to ARD as an aqueous phase, would be a fast and simple ARD treatment method.

Key Words precipitation, co-precipitation, sorption, HFO, HAO, leach beds

Introduction

Historical mine waste dumps typically contain highly weathered material with coarse grain sizes and very high concentrations of metals (e.g. Cu, Zn, Cd, Pb, As). As a result, many historical waste rock dumps have provided the vicinity acidity and metals for an extended period of time. Accumulation of metals at river banks, stream sediments, lake shores etc are hence common in surrounding areas (España et al. 2006). Still there is a risk with large quantities of metals precipitated (as hydroxides/oxy hydroxides) or bound (via adsorption and/or coprecipitation) to secondary phases of iron, aluminum and manganese as solubility and sorption conditions for Fe, Al and Mn phases can change and thereby mobilise attached metals.

Another possibility is, however, to add alkalinity to the acid rock drainage and thereby inducing precipitation of amorphous iron and aluminum phases. At circum neutral pH these precipitations will act as effective sorption phases for the dissolved trace elements in the water. Addition of alkalinity to the acid water can be performed through, for instance, a slag leach bed (Simmons et al. 2002). However, other types of alkaline by products can be used in a similar manner.

Rapid neutralisation and metal immobilisation by addition of an aqueous strong base is still a rather uncommon ARD treatment method outside the active mine sites. This method should however have great potential for well-defined ARD discharges as it does not involve clogging and passivation of neutralising surfaces, which are common problems with filters and barriers receiving iron-rich ARD.

The main objective of this study is to study the fate of the trace elements when three distinctively different mine waters are mixed with an ash leachate in 25 steps. As a consequence, three experimental titration curves are achieved, one for each mine water. This paper focuses on the behavior of the trace elements found in both the acid rock drainage (Cd, Cu, Pb, Zn, Ni and Co) and in the fly ash leachate (Cr and Mo).

Methods

Mine waters were sampled at different locations, while fly ash leachates were prepared in the laboratory (L/S 10 batch leaching). Three different mine waters were selected for the study: (1) mine water from Bersbo (BO) historical copper mines, Åtvidaberg, Sweden, (2) mine water from the Bondstollen shaft (LB) and (3) mine water from the Gustaf shaft (LG), both from the Ljusnarsberg historical mine site, Bergslagen area, Sweden. Fly ash was sampled from a CFB-furnace utilizing wood and peat fuel, from a nearby energy producer (E.ON).

Selected mine waters represent an iron-rich water with low pH and high concentration of zinc (BO), an aluminium-rich water with moderately high pH and high concentrations of zinc, copper and lead (LB), as well as an iron- and aluminium-rich water with moderately low pH and rather low trace element concentrations (LG).

Prior to mixing in 25 different proportions (0–50% ash water for BO and 0–25% ash water for LB and LG) both the acid mine waters and the ash leachate were filtered through 0.40 µm poly-

carbonate membrane filters. The mixing tubes were shaken on an end over end shaker for 7 days and allowed to settle for 24 hours; prior to sampling of the overlying water phase.

Colour rich precipitates were observed during mixing at the bottom of the tubes. After 7 days the samples were filtered through 0.4 µm polycarbonate filters and analysed for pH, electrical conductivity, alkalinity (endpoint pH 5.4), sulphate (Agilent ^{3D}CE system) and elements (ICP-MS, Agilent 4500) after preservation with nitric acid (1%). In order to estimate the loss of elements from the solutions measured concentrations were compared to the conservative concentrations (assuming conservative mixing only). Conservative concentrations for the relevant elements were calculated according to the following formula:

Conservative concentration = $X_{ash\ water} \times C_{ash\ water} + (1-X_{ash\ water}) \times C_{mine\ water}$ where X is the fraction of ash water and c indicates the concentrations in ash and mine waters.

Results and discussion

As the acid mine waters are mixed with increasing amounts of alkaline ash water, major elements like iron, aluminium, zinc, manganese and magnesium are removed from solution through adsorption and coprecipitation mechanisms, as well as precipitation of various amorphous solid phases. Regardless of sorption or precipitation; if the element is a major constituent, this will affect the pH and alkalinity of the solution and, naturally, also trace element solubility. Titration curve and precipitated amounts of major elements for the BO system is given in fig. 1.

As pH increases in the three systems (increasing fraction of ash water) almost quantitative precipitation occur for primarily iron, aluminum and manganese. The amount of precipitates was calculated as the difference between the conservative concentrations and the measured concentrations. Formed precipitates are probably largely amorphous and this has also been confirmed in earlier studies (Tonkin et al. 2002). They showed, using XRD, that all formed precipitates were amorphous with minor amounts of schwertmannite and goethite below pH 3.8. For the remainder of the paper we will use the terms HFO (hydrous ferric oxides) and HAO (hydrous aluminium oxides) for the formed precipitates.

Due to different original concentrations different amounts are precipitated in the different systems. The differences in amount of precipitates will of course have an effect on the sorption and coprecipitation of trace elements since the total capacity will differ. There is also a large difference between the pH₅₀ (pH where 50% of the element is adsorbed) between the different systems; the BO system has considerably lower pH₅₀. The BO system is dominated by iron and a pH₅₀ of 3.9 can be found. Similar pH₅₀ is also found in the LG system, where iron is present as well. For aluminum that is known to precipitate at higher pH than iron pH₅₀ around 6 are found for the LB and LG systems. However, in the BO system a pH₅₀ of 4.1 is found. This is most likely a result of coprecipitation with the massive precipitation of iron.

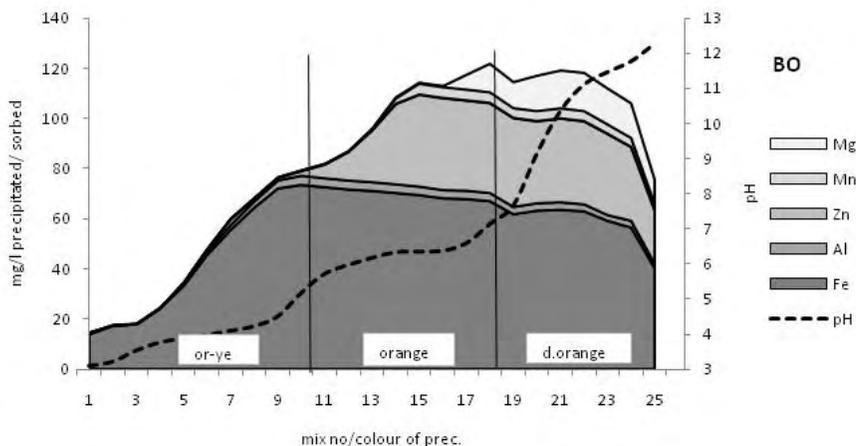


Figure 1 Precipitated/sorbed amounts of major elements (in mg/L), pH and colour of precipitate for the BO-system

Trace elements from the mine waters

Trace elements with highest contribution from the mine waters are copper, zinc, cadmium and lead. Sorption curves were created by comparing the amount in solution with the total amount according to the conservative calculations. It is very clear that in the BO system the trace elements are removed at much lower pH than in the other systems (fig. 2). The precipitated amount of iron is much greater in the BO system, thus indicating sorption or coprecipitation as the major mechanism behind the removal of trace elements.

In general the highest pH_{50} values are found for the LB system indicating that HAO has lower capacity for trace elements compared to HFO. This is also confirmed by the fact that in general the pH_{50} values for the trace elements in the different systems follow the order with decreasing amounts of HFO in the systems. It is clear that the LG system is more like the LB system than the BO system despite the fact that the LG system contains more iron than the LB system. This might indicate that the HAO has coated the HFO surface to a certain degree and thereby reducing the capacity of the HFO (Schemel et al. 2007). It must, however, not be forgotten that the BO system has a capacity double the other systems.

Trace elements from the ash water

Trace elements from the ash water are primarily chromium and molybdenum. When comparing the measured concentrations with the concentrations assuming only conservative mixing it becomes apparent that molybdenum behaves as an anion with strong sorption at low pH and low sorption at higher pH (data not shown). This indicates that the assumed predominant species is MoO_4^{2-} for molybdenum in solution. For chromium this also seems to be true for the LB system, where the chromium concentrations are low at low pH and high at higher pH. It is therefore assumed that chromium is found as an anion (chromate) in solution. However, in the LG and BO systems, chromium behaves as a typical cation with low concentrations at higher pH. The main difference between the systems is the concentrations of dissolved iron, and the iron concentration is much lower in the LB system. It is thus likely that the high concentration of dissolved iron (predominantly ferrous iron) reacts with the hexavalent chromium to form trivalent chromium in a redox reaction (Fendorf and Li 1996).

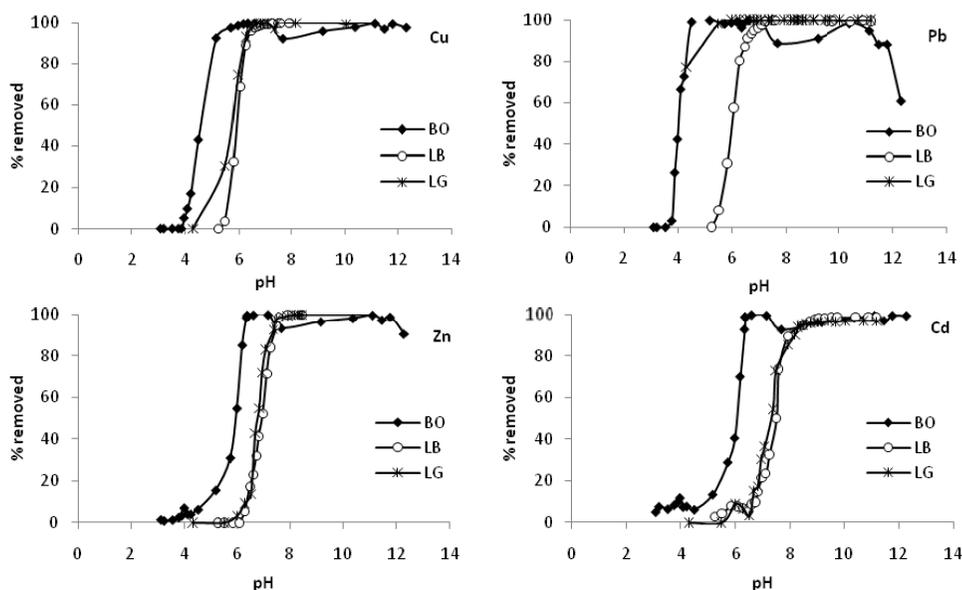


Figure 2 Per cent copper, zinc, cadmium and lead removed from solution as a function of pH. Per cent removed calculated as difference (in %) between measured concentration and conservative concentration (i.e. total available amount in the system)

Conclusions

Our study has shown that the addition of ash water will induce precipitation of HFO and HAO and thereby inducing trace element sorption. It is also clear that the composition of the formed HFO/HAO mix determines the efficiency of the sorption for different trace elements. It is also apparent that the amount of precipitating iron will determine the effectiveness of the removal of the trace elements. Sorption occurred much earlier (often one pH unit or more) in the system with high iron concentrations compared to the systems with lower iron concentrations.

Removal of cadmium and zinc is difficult below pH 8 if the amount of precipitate is low. Using ash for generation of alkaline water may be a problem with regards to chromium and molybdenum. It is, however, possible to avoid problems with molybdenum by keeping the final pH around 7. Chromium(VI) from the ash water will be reduced into chromium(III) and precipitated as the hydroxide in the presence of iron(II) from the mine waters.

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