Prevention of ARD through stabilization of waste rock with alkaline by-products—results from a meso-scale experiment

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Abstract Stabilization of acid mine waste by mixing alkaline by-products (fly ash (FA), lime mud (LM) and green liquor dreg (GLD)) was used in order to reduce ARD and the concentrations of trace metals. Results after three years point to high acid neutralization in the leachates for all alkaline additives. Trace metal concentrations in the leachates are on average reduced by 96% compared to the reference system mainly due to sorption. The flow rate through FA-amended systems is much lower compared to the LM- and GLD-amended systems, probably due to formation of hard pans.

Key Words waste rock, fly ash, green liquor dregs, lime mud, trace metals

Introduction

To avoid anoxic conditions reclamation, which may include covering or encapsulation of historical mine waste (reductive dissolution and iron(III) mediated oxidation of pyrite) the waste can be mixed with an alkaline material to obtain neutralization and increased immobilization of trace elements (Sartz and Bäckström 2007). It is also possible to make an impermeable layer if the additive reacts with the waste and form hardpans (Li et al. 2001). Mixing can either be made using heavy machinery or by injection. By injecting the material as a slurry the historical and cultural values can be preserved to a greater extent since the visual appearance is not changed.

Injection/stabilization have been used in a historic mining districts in the western US, where approximately 2—3.5 million tons of tailings have been in situ limed with calcite and $Ca(OH)_2$ or CaO. Alkaline materials were tilled into the waste and it was found that after 10 years pH had increased with two pH units (Davis et al. 1999). The stabilization experiments aim at simulating an injection or stabilization, where weathered mine waste is mixed with an alkaline material (by-products such as fly ash, lime mud, green liquor dreg and lime kiln dust) in order to neutralize present acid and increase the immobilization of trace metals. Under optimal conditions the alkaline materials will also react with the mine waste isolating surfaces from further oxidation. Formation of hard pans serving as impermeable layers is also possible.

Methods

The stabilization experiments are designed to simulate the changes (both chemical and hydraulic) when a weathered and acidic historical mine waste is mixed with a strongly alkaline material. Layering chosen in the experiments should be compared with the situation at a real remediation, where alkaline material is being injected and forms discrete zones with only alkaline materials, as opposed to thorough mixing of the materials.

Barrels (PE-platistic) with a height of 1.5 m and diameter of 0.8 m (total volume 0.7 m³) were used for the experiments. At the outlet a coarse drainage layer (washed gravel, 8—16 mm) was used to avoid clogging.

Mine waste and the alkaline materials were layered in the barrels. The number of layer as well as the proportion of alkaline material varied between the different systems (fig. 1). To minimise the risk of clogging and increase hydraulic conductivity 25% expanded clay aggregates (Leca) was added to the systems.

Historical mine waste fom Ljusnarsbergsfältet, Kopparberg, Sweden, were used in the experimet. It is a heavily weathered complex sulphidic waste rock and 200—300 years old. Prior to the experiments mine waste aggregates (secondary minerals) were crushed and sieved (0—13 mm).

Lime mud (LM), green liquor dreg (GLD) and fly ash (FA F) from pulp and paper industry, aged fly ash (FA E) from bio fuel were selected. Detailed description of total and leachable concentrations for the different alkaline materials can be found in Sartz et al. 2009. In short, however, the mine waste contains high concentrations of trace elements.
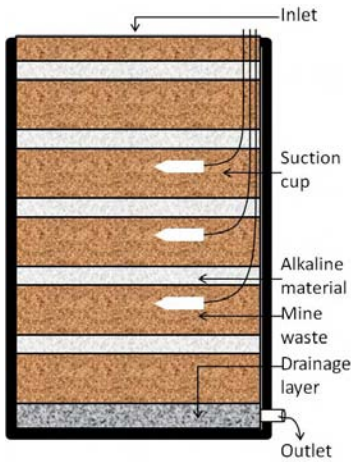
System	Alkaline material (%)	Alkaline material	No of alkaline layers
T1	50	Ash F	3
T2	10	LM	11
T3	0	None	0
T4	10	Ash F	7
T5	25	GLD	3
T6	10	GLD	11
T7	10	Ash E	11
T8	25	Ash E	10

Figure 1 *Principal outline of the experimental systems. Red layers illustrate the mine waste and the white layers the alkaline materials. Number of layers is the main difference between the different systems*

Eight different systems were designed to represent the alkaline materials, thickness of layers and number of layers (fig. 1). Mine waste is always present as the layer just above the drainge layer. At the beginning (December 2006) 60 L of water was added at each occasion until leachates were obtained. After that 30 L has been added every other week prior to sampling. Until may 2010 it amounts to 820 L of water corresponding to an L/S ratio of around 1. In order to determine if any hard pans had formed flow rate was measured by adding 30 L of water and then measure the accumulated volume leaving the systems for 7 hours at 15 minutes interval. At every sampling occasion pH, electrical conductivity, redox potential, alkalinity (endpoint pH 5.4) and dissolved oxygen was measured directly in the field. Sulphate was determined with capillary zone electrophoresis, elements with ICP-MS and iron(II) with a spectrophotometric method. Saturation estimates have been performed using PHREEQC and the results are expressed as saturation index (SI), where -0.5 to 0.5 are considered to be in equilibrium with a solid phase.

Results and discussion

In the reference system (T3) pH is fairly stable around 4.5.-5 while all the treated systems have pH at least one unit higher. The treated system with the lowest pH is the one containing 10% lime mud (T2) and the system with the highest pH (around pH 7) is the one containing 50% fly ash F (T1). Alkalinity, on the other hand, is highest in the systems treated with only 10% lime mud (T2) and 10% green liquor dreg (T6). These materials contain high concentrations of carbonate and the acidic mine waste probably dissolves the carbonates at a higher rate. Saturation indices indicate slight sub saturation (SI -1.2 to -0.2) for calcite ($CaCO_3$) in all systems except for in the reference. Calcium concentrations is also governed by equilibrium with gypsum ($CaSO_4$) in all systems.

Aluminum concentrations have decreased significantly since the start of the experiment (around 75%). The highest aluminum concentrations are found in the reference (T3) where the concentrations still after 3½ years are around 300 mg/L. In all other systems the concentrations are between 0.25 and 25 mg/L. Saturation estimates indicate that gibbsite ($Al(OH)_3$) is over saturated in all systems (SI 2.8—4.3) while jurbanite ($AlOHSO_4$) is closer to equilibrium (SI -1.4 to 2.4).

Since the start of the experiment the iron concentrations have increased and then started to decline again. Highest iron concentrations (1 000 mg/L) are found in the reference (T3). Second highest concentrations (around 200 mg/L) are found in T5 (25% GLD) followed by T2 (10% LM), T7 and T8 (fly ash E). The iron concentrations in T1 (50% fly ash F), T4 (10% fly ash F) and T6 (10% GLD) are lower (between 1 and 10 mg/L). It has been found that almost all dissolved iron consists of iron(II) indicating that the high concentrations are caused by reductive dissolution of secondary iron (hydr)oxides originating from the weathered mine waste.

High concentrations of reduced iron in solution will lead to a pH decrease when the iron is oxidized and hydrolysed. This latent acidity must be considered during a full scale remediation since pH can drop several units further down stream in the recieving waters.

Lead concentrations (fig. 2) are highest in the reference (T3) with concentrations around 600 µg/L. Second highest lead concentrations (50—90 µg/L) are found in the systems treated with 10% lime mud (T2) and 10% GLD (T6). Lead concentrations in the other systems are between 5 and 25 µg/L. Cerrusite ($PbCO_3$) and anglesite ($PbSO_4$) are found to be slightly sub saturated in all treated systems ($PbCO_3$, SI -3.7 to -0.9; $PbSO_4$, SI -4.9 to -1.9). However, anglesite is found to be close to equilibrium (SI -0.6) in the reference system indicating that it might be an important solid phase at lower pH.

Cadmium concentrations (fig. 2) are very high in the reference system (almost 2 000 µg/L). Lowest concentrations (below 15 µg/L) are found in T1, T2 and T8. Cadmium concentrations in the other systems are around 100—300 µg/L. Otavite ($CdCO_3$) is found to be slightly sub saturated in all treated systems (SI -2.3 to 1.2).

Copper concentrations in the reference system (fig. 2) are 3½ years after the start of the experiment around 30 mg/L compared to 400 mg/L initially. Highest concentrations for the treated systems are found in T4 (10% fly ash F) and T5 (25% GLD); between around 0.45 mg/L. The lowest copper concentration (a few µg/L) was found in the system treated with 50% fly ash E (T1). The correlation (r^2, n 103) between dissolved copper (log) and pH was found to be 0.70, indicating that pH is a very important factor for reducing the copper concentrations. Malachite ($Cu_2(OH)_2CO_3$) is found to be slightly sub saturated in all treated systems (SI -2.9 to -0.6).

Zinc concentration (fig. 2) in the reference at the latest sampling is around 1 100 mg/L while the lowest concentrations (below 1 mg/L) are found in T1, T2 and T8. Zinc concentrations in the other treated systems are between 25 and 300 mg/L.

Governing parameter for immobilization of metals is pH; directly or indirectly. The main goal with the addition of alkaline materials is to increase pH in the leachate and therefore pH is
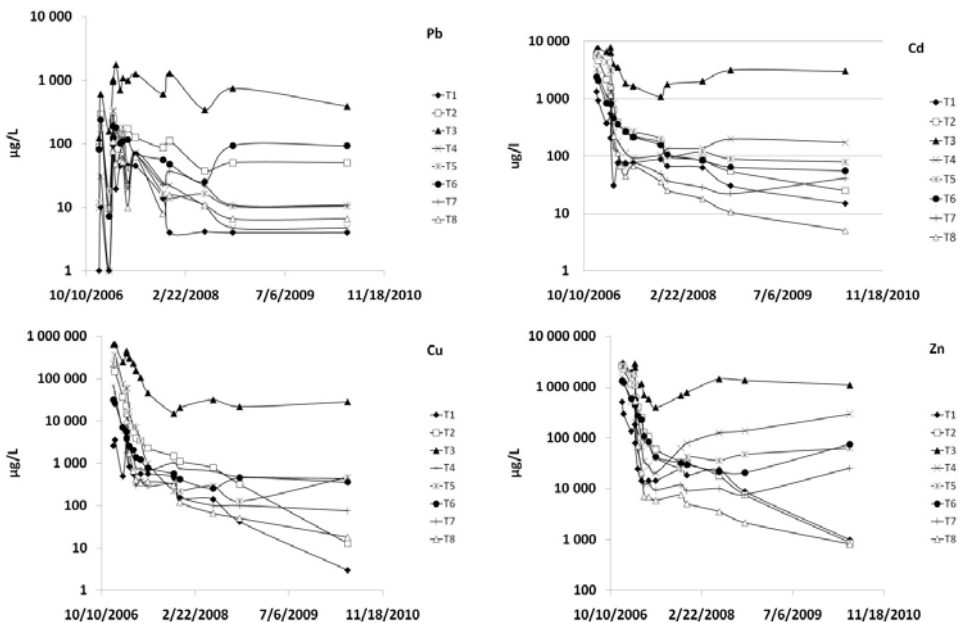

Figure 2 Lead, cadmium, copper and zinc (µg/L) in all systems during the first 3½ years. T1: 50% fly ash F, T2: 10% lime mud residue, T3: reference, T4: 10% fly ash F, T5: 25% green liquor dreg, T6: 10% green liquor dreg, T7: 10% fly ash E, T8: 25% fly ash E. See fig. 1 for detailed descriptions of the different systems

an important parameter to evaluate. It is evident that pH has increased in all treated systems in comparison with the reference system. The increase in pH is, after 3½ years, between 1.3 (T2) and 2.7 (T1) units. The increase in pH is, however, not as great as expected. The system with lowest pH (excluding the reference) is the system treated with 10% lime mud (T2).

When it comes to reduction of trace elements it is expressed as the proportion of the concentration in the reference system at the last sampling occasion. The average concentration reduction of all trace elements (lead, cadmium, copper and zinc) in all systems is approximately 96% after 3½ years. It is, however, very hard to say which system is working best but it seems that the systems treated with fly ash (T1, T7 and T8) and 10% lime mud (T2) have a slightly higher reduction of trace element concentrations than the other systems. However, the worst performing system (T4) is also amended with fly ash (10%).

Flow rate measurements showed that in T1 no water had appeared after 7 hours. In T8 9.5 L was measured followed by T7 (12 L), T4 (12.5 L), T6 (14 L), T2 and T5 (15.5 L). As a comparison, after 7 hours 18 L had left the reference system. When inspecting the systems it becomes clear that a low flow rate is accompanied by high pH and thus high metal immobilization. It is obvious that a longer residence time improves the chemistry of the systems.

Conclusions

Results show that pH in the systems treated with alkaline materials increased between 1.3 and 2.7 pH units compared to the untreated reference. Increased pH resulted in a significant decrease in trace element concentrations, averaging a concentration reduction around 96%. The main trace element reduction is probably due to sorption since discrete solid phases are not formed for the trace elements.

When it comes to comparison of the different systems it seems that systems T7 and T8 (containing fly ash E) are working best, followed by T1 (containing 50% alkaline material) and T2 (10% LM). The systems that seem to be the least effective are T4 (10% fly ash F), T5 (25% GLD) and T6 (10% GLD). It is, however, clear that alkaline materials can be used in order to reduce the leachate of trace elements from historical mine waste deposits. Longer residence time clearly improves the quality of the leachates.

Acknowledgements

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