Immobilisation of trace metals in sulfidic mine tailings

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Abstract Metals released by oxidation of sulfide minerals may be associated to minerals in tailings. This study comprises field sampling, chemical and mineralogical characterisation, structural investigations and quantification of the tailings uptake capacity by batch uptake and column experiments. Uptake capacity of tailings of different composition sampled at the mines in Kristineberg, Aitik and Zinkgruvan has been studied for Cu and As. The metal removal capacity relates to the acid neutralising capacity and the sulfide content. Results indicate arsenic and copper to bind by similar processes to minerals. Binding mechanisms has been studied by X-ray Absorption Near Edge Structure (XANES).

Key Words tailings, heavy metals, attenuation, sorption experiments, XANES

Introduction

Oxidation of sulfide minerals in mine waste can result in extensive generation of metal laden leachates. Metals released by sulfide oxidation may escape the waste via groundwater discharge, but may also be attenuated by various processes in which the metal ions are re-associated with the solid matter. This includes precipitation of secondary minerals under both anaerobic and aerobic conditions and adsorption of metals to surfaces of both parent and secondary minerals. Evidences for this was given by results from an extensive sampling of groundwater in one of the tailings impoundment at Boliden’s Cu-Zn mine in Kristineberg (Holmström *et al.*, 1999 and 2001). The chemical composition of the discharge will be determined by chemical and/or microbial reactions between these minerals and water percolating into the waste. The mobility of metals is greatly influenced by the mineralogical composition of the waste and surrounding soils and also the chemical properties of the water (e.g. oxygen content, pH, dissolved solutes).

Precipitation of secondary solid phases and by sorption processes may occur under both oxic and anoxic conditions. In anoxic environments with an abundance of sulfate and readily degradable organic matter, sulfate-reducing bacteria (SRB) can use sulfate as terminal electron acceptor in the oxidation of either organic matter or molecular hydrogen (Perry, 1995). The hydrogen sulfide can react with soluble metal ions, e.g. from acid rock drainage, to form an insoluble metal sulfide and thus serve as a metal trap. Heavy metals like Cu^{2+}, Zn^{2+} and Pb^{2+} may be immobilised from anoxic porewater in tailings by forming secondary metal sulfides. This can be a result of two different processes: the precipitation of metals with dissolved hydrogen sulfide, and replacement reactions on existing sulfide phases. Metal substitution in metal sulfides are reported by e.g. Holmström *et al.* (1999) and Müller *et al.* (2002) who have observed enrichment in As, Cd, Cu, Ni and Pb below the oxidation front in tailings impoundments, and have attributed this process to either adsorption or solid – solution substitution. Also arsenic sulfides, like orpiment (As_2S_3), realgar (AsS) and arsenopyrite (FeAsS) have been proposed as secondary minerals in anoxic sediments and other environments with reducing conditions. In a study of sorption of arsenite on pyrite and troilite (FeS) using synchrotron based X-ray absorption spectroscopy (XAS), Bostick and Fendorf (2003) concluded that a FeAsS-like precipitate is formed in slightly sulfidic solutions under consumption of the iron sulfide phase.

Formation of metal carbonate phases may be another important mechanism regulating the release of metals from the deposits, e.g. siderite ($FeCO_3$), smithsonite ($ZnCO_3$), malachite ($Cu_2(OH)_2CO_3$) and cerrusite ($PbCO_3$). However, the solubility of the carbonate minerals is strongly pH-dependent, and siderite, smithsonite etc. can only potentially regulate the aqueous metal concentrations under neutral and alkaline conditions. At high pH metals may also precipite as hydroxides and/or mixed hydroxide and carbonate phases, such as hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) (Ostergren *et al.*, 1999).

Furthermore, silicate and aluminosilicate minerals, such as quartz and feldspars, are capable of adsorbing metal ions. Quartz, with a pH_{zpc} close to 2, exhibits negatively charged surfaces within a very wide pH-range (Stumm, 1992). This allows cationic metals to be adsorbed. Many clay minerals exhibit a permanent negative charge at the planes, which offers possibilities for attachment of metal cations to the mineral surfaces.

Association of metal ions to mineral surfaces and internal planes in sheet silicates occurs by two main mechanisms: ion exchange and surface complexation. Ion exchange is a reversible chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. Ion exchange reactions are often regarded as unselective with respect to different classes of ions with similar charge. Surface complexation is coordination reactions taking place at specific binding sites on mineral surfaces.

The main goals of the present study are to quantify the metal uptake capacity under anoxic conditions of tailings of different composition and to identify the processes significant for attenuation in short and long term perspective. The ultimate goal is to enable prediction of the quality of the discharge in a long term perspective from tailings of different properties or origin.

Methods

Tailings were collected at three different mines in northern Sweden (Kristineberg, Aitik and Zinkgruvan) with varying mineralogical composition. In addition fresh tailings were sampled in the concentrator in Boliden. The tailings deposited in Kristineberg contain high concentrations of sulfide minerals in contrast to the sulfide poor tailings at Aitik. The tailings deposited at Zinkgruvan are characterized by substantial concentrations of carbonate minerals. The tailings were sampled using core drilling in which the tailings are captured within a PVC liner to avoid oxidation. Fresh tailings were sampled in the concentrator in Boliden. All samples are stored in freezer. The elemental composition of tailings and pore-water has been analysed using ICP-AES/MS. The mineralogical composition of the tailings was characterised by X-ray Powder Diffraction using Rietveld analysis (Röntgenlabor Dr. Ermrich, Reinheim, Tyskland).

In this paper the uptake of Cu(II) and As(III) to tailings is studied in batch uptake experiments and column experiments at 25ºC. Oxidation during the experiments is minimised by using an inert atmosphere of nitrogen which was purified with respect to oxygen by purging through an alkaline pyrogallol solution. Subsamples of tailings were prepared immediately before each experiment under inert N_2-atmosphere. Solutions were prepared from deionized Milli-Q plus 185 water.

In the column experiments the inner diameter of the column was 10 mm, and the column was in each experiment filled to a height of 30 mm. Flow rate was 1.33 ml h^{-1}. Subsamples of approximately 5 ml were continuously collected using a sample collector in 10 ml plastic test tubes evacuated and filled with nitrogen. pH in the water samples was measured in daily in a set of samples using a Orion combination electrode calibrated in NIST standard buffers at pH 4 and 7. To avoid oxidation during measurement the solution was purged with N_2. No precipitates could be observed in any of the samples. The duration of each experiment was in average 3 weeks.

To distinguish between adsorption of copper to mineral and precipitation of copper hydroxide in the column experiment, pH was regulated to <5 to avoid precipitation of $Cu(OH)_2(s)$. In experiments with As(III) pH was adjusted to ca. 8.

Speciation and the local structure of metal ions associated with tailings are investigated by synchrotron based X-ray Absorption Spectroscopy. Unmanipulated tailings and secondary iron mineral samples and manipulated samples of tailings were analyzed. The manipulated samples were prepared by adding metals (Cu and As) to the tailings, to reach concentrations of ca. 15 – 80 µmol Me g^{-1} on a dry mass basis. Solid phase reference compounds for Cu and As (e.g. CuS, As_2O_3) were diluted with an appropriate amount of powdered boron nitride before analysis. As and Cu K-edge XAFS data were collected at the superconducting beam line i811 at MAX-lab, Lund, Sweden. Data were collected on moist samples in fluorescence mode (If/I0 against energy), using a Lytle detector, in the energy range from 150 eV before the edge to ca. 800 eV after the edge. Due to problems with the beam line we only got usable data for the XANES region, which mainly gives information about the oxidation state of the metals and some information/indications about the speciation.

Results

Elemental compositions of the tailings studied are presented in Table 1. The mineralogical composition of the tailings are presented in table 2.

The metal uptake capacity has been studied for Cu, As, Zn and Cd in batch and column experiments. For copper the main problem has been to distinguish between adsorbed copper and precipitation of copper hydroxide. The copper removal from the solution is strongly correlated to pH (Figure 1). At pH > 5 copper was strongly removed from the solution. This coincides with the onset of precipitation of copper hydroxide at these total concentrations.

To avoid precipitation of $Cu(OH)_2(s)$ in the experiments, pH was regulated by slowly adding HCl to pH»4.5. The amount of acid added for the different tailing also reflects the buffer capacity of the tailings. Tailings from Zinkgruvan showed the highest acid neutralization capacity. Tailings from Aitik and Kristineberg were less efficient in neutralising acidity. The tailings from Kristineberg and Zinkgruvan showed almost the same capacity to adsorb copper (Figure 2). This was ca. 5 times higher than the uptake capacity of tailings from Aitik. The reason for the low adsorption capacity of the tailings from Aitik is likely to be the low content of sulfide minerals. In the batch uptake experiments the resulting pH was dependent on the amount of Cu(II) added. While pH was 4.9 at the

Table 1 *Physicochemical data for tailings - selected elements.*

	Aitik	**Boliden**	**Kristineberg**	**Zinkgruvan**
Porosity (%)	30	35-40	35-40	28
BET area (m^2/g)	2.5	3.5	5	1
pH (pore water)	9.3	10.4	5.5	8.4
Main elements (%)				
SiO_2	58,2	22.2	37,4	61,4
Al_2O_3	16,5	5.5	13,1	12,0
Fe_2O_3	8,2	42.7	12,8	6,6
CaO	3,6	0.4	2,0	4,7
MgO	2,6	3.7	11,6	3,5
Minor elements (mg/kg)				
As	6	467	330	43,3
Cu	171	647	1 010	72,7
Pb	3	153	680	3 960
Zn	52	871	8 025	6 490
S	8 515	332 000	116 000	8 890

Table 2 *Mineralogical composition of tailings (wt-%).*

	Aitik	**Boliden**	**Kristineberg – sample #1**	**Kristineberg – sample #2**	**Zinkgruvan**
Pyrite (FeS_2)	<2	48.7 ±3.4	34.4 ± 2.7	7.9 ± 1.2	<2
Muscovite ($KAl_3Si_3O_{10}(OH)_2$)	14,5 ±5.9	11.2 ±2.7	24.2 ± 2.6	9.6 ± 1.9	26.1 ± 1.9
Quarts (SiO_2)	12.3 ±2.2	24.5 ±2.2	11.5 ± 3.0	14.1 ± 3.0	24.7 ± 2.4
K-feldspar ($(K,Na)AlSi_3O_8$)	23.8 ±2.5	<2	<2	<2	9.4 ± 2.0
Chlinochlore (chlorite group)	5.7 ±1.0	11.0 ±2.9	21.4 ± 5.0	26.8 ± 3.2	5.3 ± 1.0
Anortite ($CaAl_2Si_2O_8$)	18.4 ±3.0	<2	<2	<2	<2
Hornblende (amphibole group)	3.6 ±2.3	<2	<2	15.2 ± 5.0	7.7 ± 2.0
Albite ($NaAlSi_3O_8$)	21.7 ±2.7	<2	<2	<2	7.7 ± .6
Microcline ($(K,Na)AlSi_3O_8$)	<2	<2	<2	<2	19.1 ± 3.4
Talc (Mg3[Si4O10](OH)2)	<2	<2	8.5 ± 2.0	8.0 ± 1.6	<2
Sanidine ((K,Na)AlSi3O8)	<2	<2	<2	8.7 ± 3.0	<2
Pyrrhotite (Fe_7S_8)	<2	<2	<2	9.7 ± 0.9	<2

lowest concentration of Cu(II) added, pH was 4.4 at equilibrium at the highest concentration of Cu(II).

Batch and column experiments for arsenic performed demonstrated that tailings from Kristineberg has the highest adsorption capacity and Aitik the lowest capacity to remove arsenic (Figure 3). The magnitude of arsenic removal from water by tailings from is the same as for copper, indicating that the arsenic and copper bind to the same type of binding sites on the mineral surfaces. However, for tailings from Zinkgruvan the adsorption of copper is twice as high compared to adsorption of arsenic, indicating that other mineral then sulfides may be involved. The important of sulfide rich tailings for arsenic attenuation is clearly illustrated in a column experiment where a sulfide rich tailing (Boliden) is compared to a sulfide poor tailing (Zinkgruvan). In the column experiments with As(III) the resulting pH was in the range range 7.8 to 8.7. Since the pH dependency in adsorption of As (III) is not as pronounced as that of metal cations, such as Cu(II), we consider this variation of be of minor importance for the interpretation of the experiments.

Our Cu XANES data show that the unmanipulated sample from Boliden is dominated by CuS (Figure 4). In the other unmanipulated samples, both the tailing samples and the secondary iron minerals, the concentrations of both Cu and As were below the detection limit. The tailing samples with added Cu (15–80 μmol Cu g^{-1}; pH 5.5–8.9) probably contain a mixture of CuS and $Cu(OH)_2$. For arsenic the XANES data indicates that the unmanipulated sample from Boliden is dominated by arsenopyrite, FeAsS (As^0), or arsenic sul-

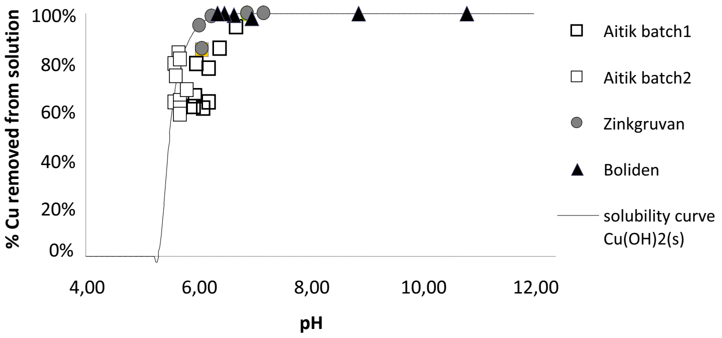

Figure 1 *Results of batch experiments. Uptake of Cu(II) at different pH to tailings of different composition.*

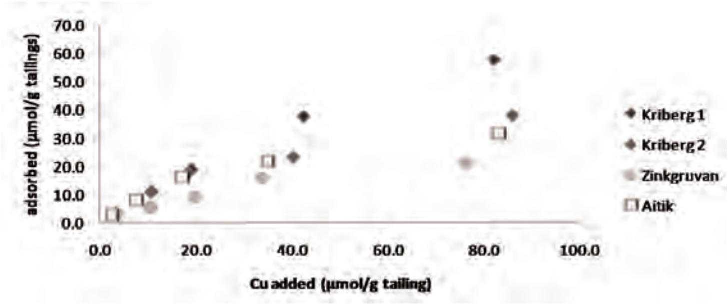

Figure 2 *Copper adsorption from aqueous solutions at pH 5 by tailings from Aitik, Zinkgruvan and Kristineberg. Results from batch uptake experiments.*

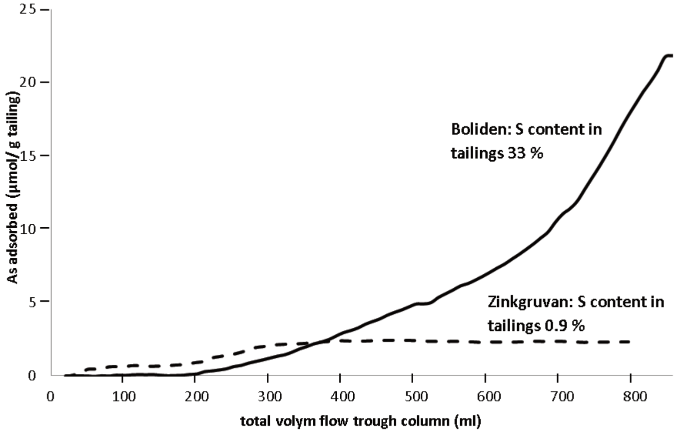

Figure 3 *Arsenic adsorption from aqueous solution at pH=8 by tailings from Boliden and Zinkgruvan. Results from column experiments (flow rate 1.8 mL/h).*

fide, As_2S_3 (As[III]) (Foster *et al.*, 1998; Slowey et al, 2007). In the manipulated samples there is either a mixture between FeAsS (or As_2S_3) and AsO_4^{3-} (As[V]) adsorbed to goethite/gibbsite or as a precipitate e.g. scorodite ($FeAsO_4 \times 2H_2O$) as in the sample from Boliden (50 µmol As g^{-1}) or only As(V) (adsorbed or as a precipitate) as in the sample from Kristineberg (not shown). Thus, for the mine tailing sample from Boliden our XANES results clearly shows that the added metal (Cu and As) occurs in a different form than the metal originally present in the tailing. Furthermore, our results indicate that all the tailing samples contain CuS to some degree. The speciation for arsenic in the unmanipulated tailings seems to differ more. The sample from Boliden, a fresh tailing directly from the concentrator, is dominated by FeAsS while the aged tailing from Kristineberg probably is dominated by As(V) (adsorbed or as a precipitate).

Conclusions

- Several of the tailings sampled in the field exhibit a high pH and all samples show large acid neutralising capacities.
- Cu(II) is strongly removed from the aqueous solution at pH >5.5.
- XANES spectroscopy indicate that Cu(II) is bound in a form resembling $Cu(OH)_2(s)$.
- The uptake capacity with respect to As relates to the tailings content of sulfide minerals.

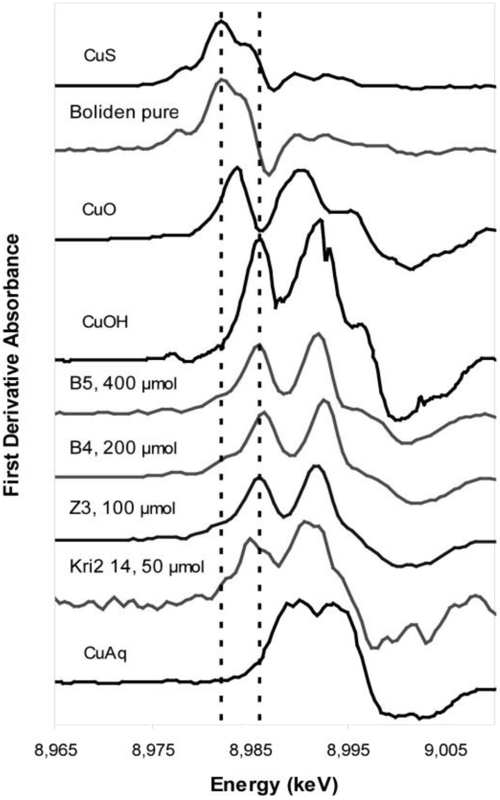

Figure 4 *X-ray absorption near edge structure (XANES) spectra for copper in reference compounds and in mine tailings from Boliden (B), Zinkgruvan (Z) and Kristineberg (Kri). Spectra for unmanipulated mine tailings (Boliden pure) and for mine tailing samples where Cu has been added (B4, B5, Z3 and Kri 2) are shown.*

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