



Effects of pH and phosphate on metal distribution with emphasis on As speciation and mobilization in soils from a lead smelting site

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Abstract

Arsenic in soils from the Asarco lead smelter in East Helena, Montana was characterized by X-ray absorption spectroscopy (XAS). Arsenic oxidation state and geochemical speciation were analyzed as a function of depth (two sampling sites) and surface distribution. These results were compared with intensive desorption/dissolution experiments performed in a pH stat reactor for samples from the site with the highest degree of As heterogeneity. The objectives of the study were to investigate the solid-phase geochemical As speciation, assess the speciation of As in solutions equilibrated with the solids under controlled pH (pH=4 or 6) and Eh (using hydrogen or air) environments, observe the effects of phosphate on the release of As into solution, and examine the effects of phosphate on metal mobility in the systems. Arsenic was predominantly found in the As(V) valence state, though there was evidence that As(III) and As(0) were present also. The dominant geochemical phase was scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). The pH was controlled in the pH stat experiments by the addition of equinormal solutions of monoprotic (HNO_3), diprotic (H_2SO_4), or triprotic (H_3PO_4) acids. For many of the divalent metal cations, solution concentrations greatly decreased in the presence of phosphate. Solutions were also analyzed for anions. Evidence exists for sulfate release into solution. More As was released into solution at lower pH. A slight increase in solution arsenate occurs with the addition of phosphate, but the risk posed from the increased desorption/dissolution of As must be weighed against the decrease in solution concentrations of many metals especially Pb. If tailings from this site underwent acidification (e.g., acid mine drainage), in situ sequestration of metals by phosphate could be combined with placement of subsurface permeable reactive barriers for capture of As to reduce the risk associated with arsenic and trace metal mobilization. Results from this study could be used in risk management plans for sites similar to the Pb smelter site examined here.

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Keywords: Arsenic; Trace metals; Mine tailings; Remediation; X-ray absorption spectroscopy; Lead; Phosphate

1. Introduction

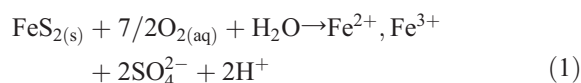
Local and regional contamination of soils and groundwaters by metals from mine and smelter sites is

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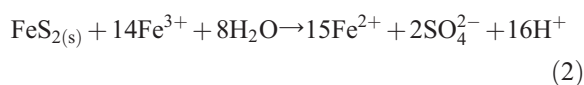
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a global problem. Mine tailings piles undergoing oxidation are a major source of acid mine drainage (AMD) containing metal contaminants. Surface waters, soils, and groundwaters are all potential sinks for AMD. The oxidation of metal sulfides leading to proton production commonly found in mine tailings can be generalized by the following equations (Singer and Stumm, 1970):

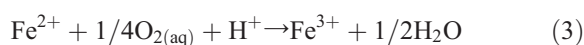
Oxidation of pyrite by oxygen in the presence of water:



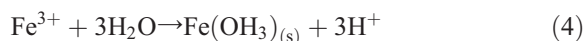
Oxidation of pyrite by ferric iron (abiotic):



Oxidation of ferrous iron by oxygen:



Precipitation of ferric iron (Fe^{3+} hydrolysis):



The oxidation of metal sulfides is accelerated by the presence of bacteria (Colmer and Hinkle, 1947) such as *Thiobacillus ferrooxidans*. Eq. (3) determines the rate of the overall acidification process; and bacteria accelerate the overall process sixfold by catalyzing reactions (1) and (3) above (Singer and Stumm, 1970). Thus, the oxidation of mine tailings by biologically catalyzed processes is quite rapid and leads to an overall decrease in pH. With decreasing pH, the mobility of trace elements tends to increase due to mineral dissolution, proton competition for surface binding sites, and increased surface potential (Yin et al., 2001). These mobilized trace metals can rapidly contaminate ground and/or surface waters depending on the physical and hydrogeological features at a particular site. Possible methods to counteract oxidation and the effects of microbes in mine tailings include oxygen exclusion (e.g., burial of tailings in abandoned mine shafts) (Holmström and Öhlander, 1999), raising the pH with lime (Catalan et al., 2002), bactericides (Singer and Stumm, 1970), and in situ transformation of trace element species (Zhang and Ryan, 1999).

In situ transformation of metals by phosphates shows great promise in minimizing the risk from trace metals at mine waste sites. Once formed, metal-phosphate precipitates, such as chloropyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$], are extremely stable. The pH where this metal phosphate is stable ranges from below 2 to above 10 (Scheckel and Ryan, 2002). Many forms of phosphates for in situ metal stabilization have been examined in previous studies including apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$] (Ma et al., 1993), bonemeal (poorly crystalline apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$; Hodson et al., 2000; 2001), CaHPO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (Wang et al., 2001). Other studies have examined the reduction of bioavailable lead by phosphate amendments as measured by a physiologically based extraction procedure (Basta et al., 2001; Hettiarachchi et al., 2001), worm uptake (Pearson et al., 2000), and plant uptake (Basta et al., 2001; Zwonitzer et al., 2003).

Phosphate may effectively compete with arsenic (especially arsenate) for surface binding sites on solids. Thus, there may be concerns with regard to arsenic desorption caused by the addition of phosphates for in situ immobilization of metals. Phosphate has been shown to affect arsenite and arsenate sorption on iron oxides (Jackson and Miller, 2000; Hongshao and Stanforth, 2001) and soils (Wauchope, 1975; Livesey and Huang, 1981; Wasay et al., 2000; Smith et al., 2002; Qafoku et al., 1999). The specificity of a solid for arsenate versus phosphate may simply be related to the order of sorption. Results from experiments by Liu et al. (2001) show that arsenate displaces previously sorbed phosphate to a slightly greater degree than when arsenate is the initially sorbed species and phosphate is added. They concluded that arsenate and phosphate compete for similar surface sites on the goethite surface. Hongshao and Stanforth (2001) found that arsenate and/or phosphate sorption by goethite occurred in two phases, a rapid initial sorption phase and a slower phase dominated by the formation of surface precipitates. Boisson et al. (1999) examined mine waste contaminated soils amended with steel shot, beringite, and hydroxyapatite. Hydroxyapatite amendments decreased Pb in CaNO_3 extractions, but increased water extractable As. In studies on acid washing of As-contaminated soils, phosphoric acid (9.4% solution) was most effective in removing As (99.9% removal) from the solids (Tokunaga and

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