Speciation of Arsenic and Mercury in Mine Tailing Materials Mobilized by Natural Organic Acids

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Introduction

Mercury mine tailings (calcines) from inoperative mercury mines are generally thought to release significant quantities of mobile metal(loid) contaminants, such as mercury and arsenic, predominantly by solution-based (desorption and/or dissolution) phenomena. In contrast, we have recently shown that in the presence of strongly binding organic acids, such as citrate and oxalate (which are ubiquitous in vegetated environments), substantial quantities of As and Hg are mobilized through solid-phase (colloidal) transport processes [1-3].

Colloidal HgS (cinnabar and metacinnabar) and As sorbed to and/or coprecipitated with colloidal Fe (oxy)hydroxides make up one if not most of the mobile species within the saturated flow regime studied. In this experiment, citrate and oxalate partially dissolved Fe-rich binding matrices, enabling the release of colloids. The physical stability of the colloids, imparted by the homogenization of the surface charge by organic acids and maintained by low ionic strength conditions [4], facilitated the transport of Hg and As in quantities greatly exceeding those of dissolved species.

Methods and Materials

Columns were filled with Sulphur Bank deposit calcines (<2.0 mm) and conditioned by upwardly infiltrating 25 pore volumes of 10 mM NaCl + 1 mM Na-azide (as a biocide) solution. An organic acid solution (also containing the same concentrations of NaCl and Na-azide) consisting of 0.5 mM each of oxalate and citrate was then pumped through the column. Saturated flow was maintained at 1 mL/min, and effluent samples were taken at regular intervals.

Elements in solution (either in an unfiltered effluent containing no visible particles or, when the effluent contained visible particles, in 0.02-µm filtrates) were measured by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Citrate and oxalate were analyzed by ion chromatography. Total solids were measured gravimetrically after drying 25- to 40-mL suspensions at 110°C over several days.

The starting calcine was characterized by using scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS), electron microprobe microanalysis (EPMA), Hg L3-edge extended x-ray absorption fine structure (EXAFS) spectroscopy, and As K-edge x-ray absorption near-edge (XANES) spectroscopy. Colloids eluted from the column were characterized by using SEM-EDS, Hg L3-edge EXAFS spectroscopy, and As K-edge EXAFS spectroscopy.

Results and Discussion

The correlation between Hg and S in solution during the electrolyte leach suggests an initial dissolution of Hg-sulfate salts, such as schuetteite. Mercury was released into solution and transported primarily as cinnabar and metacinnabar colloids present in the source sediment (Fig. 1). Dissolved (filterable) As in effluent was below detection (<10 parts per billion or ppb) in effluent during the electrolyte and organic acid leach.

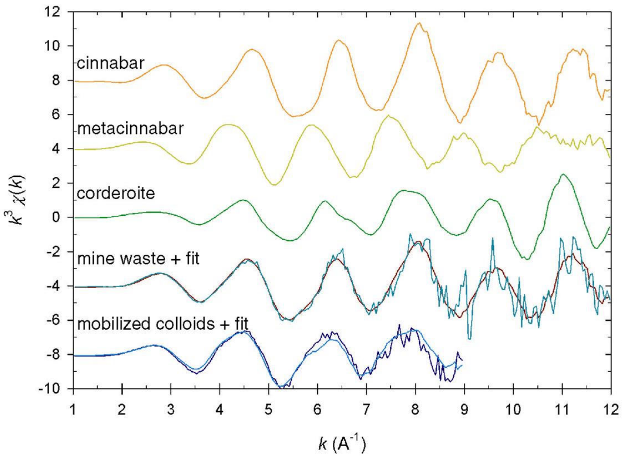

FIG. 1. Hg EXAFS of model compounds, calcine (60% cinnabar + 20% metacinnabar + 20% corderoite), and mobilized colloids (40% cinnabar + 60% metacinnabar).

Speciation of arsenic by EXAFS spectroscopy (Fig. 2) revealed that both the calcines and mobilized colloids likely contain crystalline phases, such as scorodite and/or arsenate-substituted jarosite, in addition to As(V) sorbed to Fe(oxy)hydroxides. The high sulfur content of mine tailings from the Sulphur Bank hot-spring-type deposit would be conducive to the formation of sulfate minerals into which arsenate could coprecipitate.

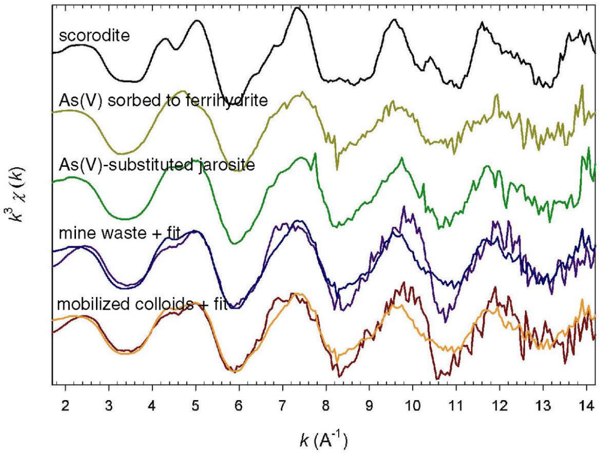

FIG. 2. Ar EXAFS of model compounds, calcine [40% As(V) sorbed to ferrihydrite + 40% scorodite + 20% As(V)-substituted jarosite], and mobilized colloids [40%As(V) sorbed to ferrihydrite + 35% scorodite + 25% As(V)-substituted jarosite].

The revegetation of inoperative mine sites, including the site at Sulphur Bank, is a management strategy that is frequently considered. Transport of colloids is largely governed by their physical stability, which is imparted by surface charge homogenization by adsorbates, such as organic acids derived from the rhizosphere and organic detritus. Citrate and oxalate in moderate concentrations bind to sediment surfaces and partially dissolve a cementing matrix, mobilizing colloids and elevating dissolved Fe and Al concentrations. This study demonstrates that Hg and As exist either as colloidal minerals or as sorption complexes on colloids in mine tailings. Their fate, therefore, may include deposition at significant distances from mine sites, expediting and broadening their ecological impact.

Acknowledgments

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