Speciation and Colloid Transport of Arsenic from Mine Tailings

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Introduction

Inoperative mines contaminate surrounding ecosystems via transport of dissolved and particle-associated species of heavy metal(loid)s [1-4]. Efficient modes of contaminant transport in the environment are most commonly considered to occur within the dissolved phase. Recently, however, a number of field studies have implicated particle-associated transport of heavy metals in a variety of contaminated environments, most notably with respect to the colloid-associated transport of radionuclides in contaminated ground water systems [5-8]. Several laboratory-based column studies have similarly demonstrated that common natural colloidal minerals, such as iron (oxyhydr)oxides and clays, can be efficiently transported through both saturated and unsaturated porous media [9-13]. As such mineral colloids often strongly sorb metal(loid) contaminants [14, 15], they may therefore act to mobilize metal(loid)s as they are transported. Indeed, a number of laboratory-based leach experiments on packed beds of natural mineral-based media such as soils and sediments have demonstrated significant colloid-associated transport of a variety of metal(loid) contaminants, including As, Cu, Pb, Pu, and Zn [16-21]. In this study, columns of an arsenic-rich calcined mercury ore (i.e., calcines) have been leached with low molecular weight (LMW) organic acid solutions (containing oxalate and citrate in concentrations of 10–500 μM) in an attempt to simulate infiltration through the rooting zone of revegetated mine tailings, addressing (1) the physicochemical conditions under which colloids may be mobilized, (2) the speciation of arsenic in mobilized colloids, and (3) the extent of colloidal arsenic transport.

Methods and Materials

Unconsolidated calcines were collected from piles at the Sulphur Bank Mine site (Clearlake Oaks, CA). A geochemical description of this site is given elsewhere [22]. The calcines represent ore-containing rocks that were previously crushed and heated to approximately 700°C to remove Hg. The mine waste used in this study was obtained from the interior of a tailings pile (i.e., after discarding the outer layer of material in order to minimize the effects of weathering). It was then passed in dry form through a 2-mm sieve, with the <2 mm fraction being retained for use in column experiments.

Calcines were loaded and manually tamped into pre-weighed 25 mm by 500 mm plexiglass columns. An electrolyte solution containing 10mM NaCl and 1mM sodium azide (NaN_3, a bacterial sterilant) was pumped upwardly through the column at 1.0 mL/min, leaching approximately 13 pore volumes of fluid per day. The upward flow configuration served to minimize gravity-induced flow preference. The columns were capped upon completion of the first flush of water, reweighed, and the column pore volume (typically about 110 mL) estimated gravimetrically from the masses of the air-dry and water-saturated column. In all cases, the porosity of the calcine columns was found to be 0.44 ± 0.02.

Column leaches were performed in two stages. The column was first leached with at least 25 pore volumes of electrolyte solution (10 mM NaCl and 1 mM NaN_3) at pH = 5.7 ± 0.1. During this electrolyte throughput, most of the exchangeable Mg^{2+} and Ca^{2+} in the mine waste was rapidly replaced by Na^+ from the influent. This initial leaching step therefore helped ensure reproducibility of replicate column experiments to the extent that exchangeable cations impacted colloid transport. It also served to demonstrate the absence of any detectable particle mobilization in the absence of LMW organic additives. The second leaching stage consisted of a solution containing both oxalate and citrate (in concentrations of 10 - 500μM each) in addition to 10 mM NaCl and 1 mM NaN_3. Such influent solutions were again pre-adjusted to pH = 5.7 ± 0.1. In both leaching stages, a fractional sampler was utilized to continuously collect effluent discharged from the column. The effluent samples were regularly transferred to capped polypropylene tubes that were stored in the dark at 4°C. The effluent pH was periodically monitored using a Denver Instrument model 215 pH standardized with commercial pH buffers.

Arsenic speciation of the Sulphur Bank calcine and colloids eluted during a 500 μM organic acid leach experiment was performed using As K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy on bending-magnet beam station 13-BMD at the Advanced Photon Source (APS). To obtain a useable range of As EXAFS (i.e., beyond $k = 10.5$ Å^{-1}), interference of Hg L_α fluorescence with As K_α fluorescence measurements was minimized through enhanced energy resolution. Higher resolution was achieved by lengthening the shaping time of DXP digital electronics used to measure currents induced by fluorescent photons received by the 16-element Ge detector. High concentrations of Hg in the samples (~1,000 ppm) also caused sample self absorption and/or Ge detector deadtime, requiring correction of all As EXAFS spectra.

XAFS data were processed according to standard procedures [23] using IFEFFIT [24] via the Sixpack interface (http://www-ssrl.slac.stanford.edu/~swebb/). Quantitative Hg speciation in these samples was accomplished by least squares linear combination fitting of the EXAFS spectra of the calcine material and colloid samples with one or more reference EXAFS spectra of homogeneous As-bearing minerals and a ferrihydrite adsorption complex. After fitting an unknown spectrum with one reference spectrum, a second reference spectrum was added in the fitting procedure. The second species was operationally defined to be significant if its inclusion resulted in a ≥10% improvement in reduced χ^2, which is defined as

$$\text{reduced } \chi^2 = \tfrac{1}{N-P}\sum_{i=1}^{N}(\chi_i^{\text{obs}} - \chi_i^{\text{fit}})^2 \qquad (1)$$

where χ_i^{obs} is the ordinate of the EXAFS measured from the sample at the i^{th} energy point, χ_i^{fit} is the ordinate of the fitted EXAFS spectrum, N = number of data points in the fitted EXAFS energy range (scaled by the wavenumber k), and P is the number of fitted components.

Once the number of significant components had been identified, the fitting procedure was repeated with the added constraint that the components sum to 100 percent. The accuracy of speciation provided by this method is contingent upon the uniqueness of component EXAFS spectra, the completeness of the spectral library, evaluated by how close to 100 percent the sum of fitted components are (without restricting their sum to equal 100 per cent), and the recoverability of a single species within heterogeneous samples, estimated to be 10% [25, 26].

Results and Discussion

For all organic solution concentrations investigated, colloid-associated arsenic was mobilized, with the onset of particulate arsenic transport occurring later for lower LMW organic acid concentrations (Fig. 1).

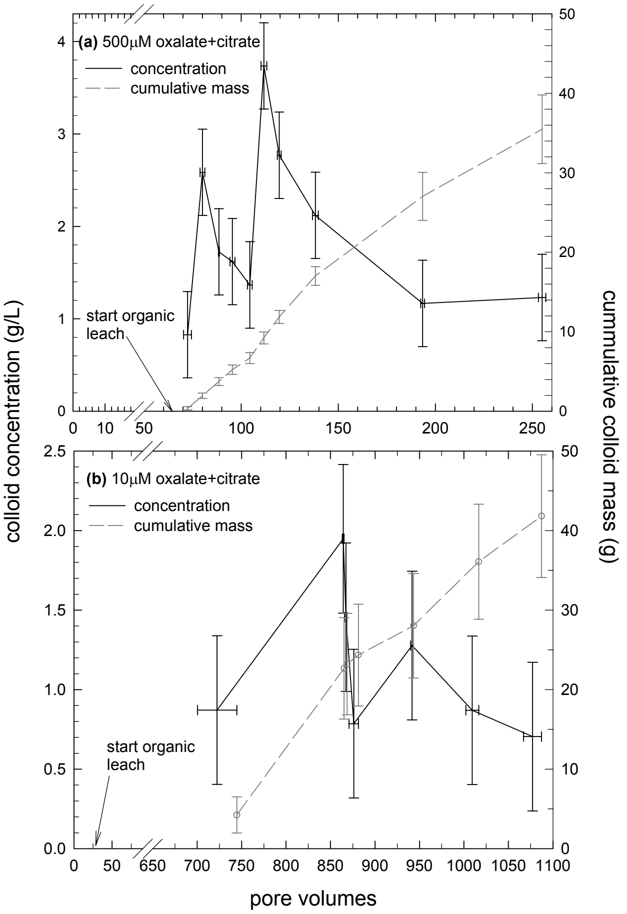

Fig. 1. Particle concentration and cummulative mass release over time, **(a)** 500 μM organic acid leach and **(b)** 10 μM organic acid leach. Vertical error bars represent 95% confidence intervals while horizontal bars indicate the extent to which column leachate was composited for each sample.

Chemical analysis of eluted colloids and 0.02-μm filtrates of column effluent indicated that over the timeframes of the column experiments (1 week to several months), all measurable arsenic mobilized from the column was in particulate forms (Fig. 2).

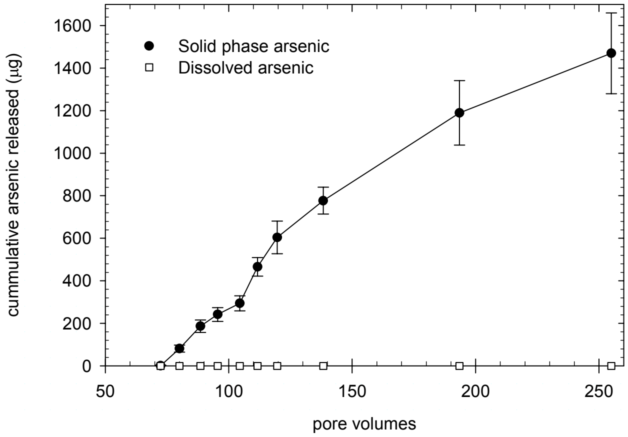

Fig. 2. Release of arsenic during leaching of a packed column of mercury mine tailings.

The EXAFS spectra of reference compounds and mine-related materials are illustrated in Fig. 3, revealing the presence of As(V)-Fe(oxy)hydroxide surface complexes or coprecipitates and As(V)-substituted jarosite ($KFe_3(SO_4,AsO_4)_2(OH)_6$) species in both the mine calcine and colloids mobilized during leaching experiments.

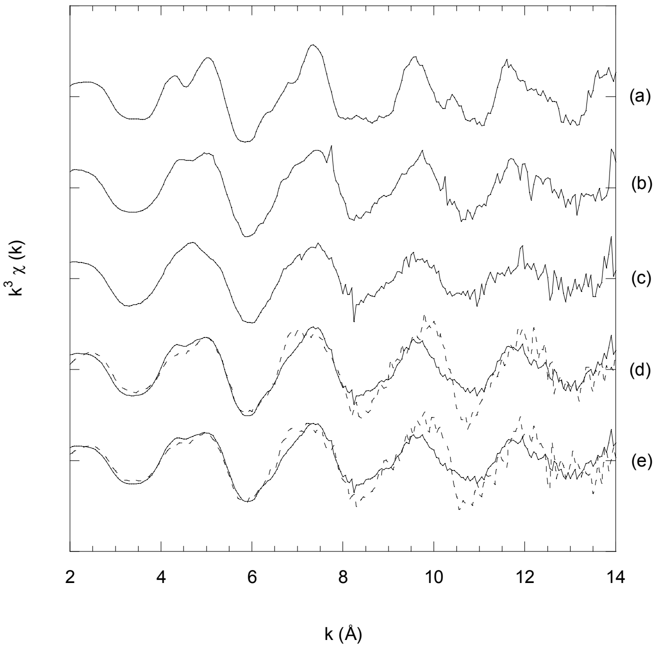

Fig. 3. XAFS spectra of the arsenic minerals (a) scorodite, (b) As(V)-substituted jarosite, and (c) As(V) adsorbed to ferrihydrite, which partially comprised the reference spectral database used for least squares linear combination fitting; (d) <45 μm size fraction of mine tailings, and (e) colloids eluted during a column leaching experiment (experimental data appear as dotted lines while solid lines are the linear combination fits).

The results presented in this study are of particular potential relevance to revegetated mine tailings environments. Revegetation is a common strategy in such settings in order to hinder erosion [27]. However, when exposed to toxins such as dissolved Al, which is prevalent under the acidic conditions typical of mine tailings environments [28], plants commonly exude organic acids such as citrate into the rhizosphere as a defense against Al phytotoxicity [29]. Chemical conditions that render colloidal mine tailings materials susceptible to mobilization when exposed to appropriate physical conditions (e.g., periods of intense rainfall) are therefore conceivable in revegetated mine tailings environments. Consequently, the transport of colloid-associated arsenic from revegetated mercury mine tailings sites may be environmentally harmful in certain locations where small, populated water bodies are hydrologically proximate to those sites.

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