

As Speciation and Effects of pH and Phosphate on the Mobilization of As in Soils from a Lead Smelting Site

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Introduction

Arsenic in soils from the Asarco lead smelter in East Helena, Montana was characterized by X-ray absorption spectroscopy (XAS). Arsenic oxidation state and mineralogy were analyzed as a function of depth and surface distribution using bulk and microprobe XAS. These results were compared with data from macroscopic scale desorption/dissolution experiments. The experiments focused on the effects of phosphate and pH on the desorption/dissolution of As.

Methods and Materials

Fifteen samples were analyzed by XAS to assess the solid-state speciation of the mine-waste contaminated soils. The XAS analyses also included several reference standards including NaAsO_2 and $\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$ in varying ratios in order to semi-quantitatively estimate percentages of As [1]. Reference minerals were also obtained from the Excalibur mineral company including: elemental As, scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), arsenopyrite (FeAsS), orpiment (As_2S_3), realgar (AsS), and löllingite (FeAs_2). Sample spectra were also compared with reference materials consisting of As(V) sorbed onto ferric hydroxide ($\text{Fe}(\text{OH})_3$) or goethite ($\alpha\text{-FeOOH}$). All bulk XAS analyses were performed at the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) facility (beamline 20-BM) at the Advanced Photon Source at Argonne National Laboratory in Argonne, IL. At minimum, three scans per sample were collected for the samples and reference materials. Samples for analysis were selected in order to examine change of speciation with depth and surface distribution. Two sampling sites were selected for XAS analyses at each depth. The remaining sample analyses were performed from eight separate surface sites. The electron storage ring operated at 7 GeV. Arsenic K-edge spectra were collected at ambient temperature in transmission mode. A 0.5 mm premonochromator and a Si(III) double crystal monochromator detuned by 20% to reject higher-order harmonics was employed. The beam energy was calibrated by assigning the first inflection of the absorption edge of arsenic foil to 11,867 eV. X-ray absorption near edge (XANES) and x-ray absorption fine structure (XAFS) spectra were collected in both transmission and fluorescence modes with a solid-state 13-element detector. Results from the fluorescence detectors were used in data analysis by WINXAS 2.0 [2]. The collected scans for a particular sample were averaged, the spectra were then normalized, and the background was removed by spline fitting. The 1st derivatives of the averaged spectra were employed in order to assess As oxidation states in the bulk samples. Arsenic absorption edge energies increase with increasing oxidation state. The LC-XANES function in WINXAS 2.0 was employed in order to compare near-edge features of the sample spectra to those of the reference materials. This tool can be used to obtain general proportions of the mineral species of As present.

Graphical comparison can be made by multiplying each data point (absorption at a particular energy) in a standard spectrum by the weighted partial concentration score for that standard. The weighted data points for each standard identified as being present in the sample are then added together and plotted. The resulting XANES spectrum represents the approximate contribution of each standard to that spectrum.

In addition to the bulk XAS analyses, X-ray fluorescence microprobe (XFM) analyses were performed on sample As-8 at GeoSoilEnviro Consortium for Advanced Radiation Sciences (GSECARS) Beamline 13-ID-C. For this analyses a 2 mm by 2 mm area of an epoxy mounted thin section was scanned past the K-edge energy for As(V) ($\approx 11,867$ eV) to encompass As(0), As(III), and As(V) fluorescence and re-scanned at the K-edge for As(III) ($\approx 11,860$ eV, As(0) will also be detected at this energy). In this manner, maps of As fluorescence can be made for total As and As(0)/As(III) showing qualitative differences at specific locations between As(0)/As(III) and As(V).

Results

Arsenic is mainly found as As(V) though there exists ample evidence of the presence of As(III) and As(0). Fig. 1 shows comparisons between the 1st derivative of the background corrected XANES for sample As-7 (representative of most of the samples examined), sample As-8, As(V), As(III), and elemental As. Sample As-8 was unique as it contained a mélange of As oxidation states. This sample was chosen for more in depth study on d/d of As and metal immobilization based on its As heterogeneity and high concentrations of trace metals. Sample As-8 was also epoxied and thin sectioned for analysis via a XAS microprobe. Fig. 2 shows the image of the thin section and provides qualitative evidence that As(III) and/or As(0) exists in the sample.

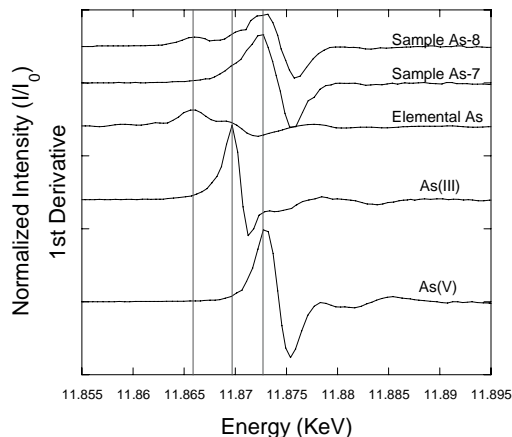


Fig. 1

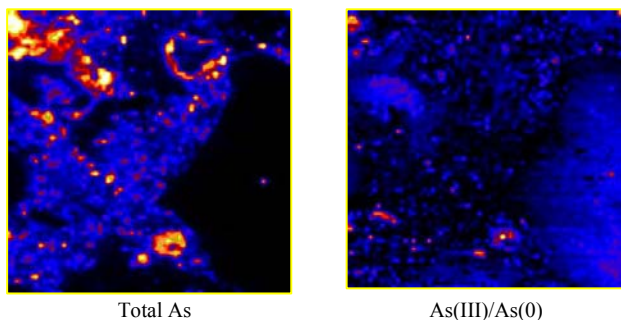


Fig. 2

The LC XANES fitting function in WINXAS 2.0 was employed to compare sample and standard XANES spectra. The LC XANES function provides a weight attributed to each standard in the fitting procedure to the actual sample. An example of an LC XANES fit is given in Figure 3 for sample As-8.

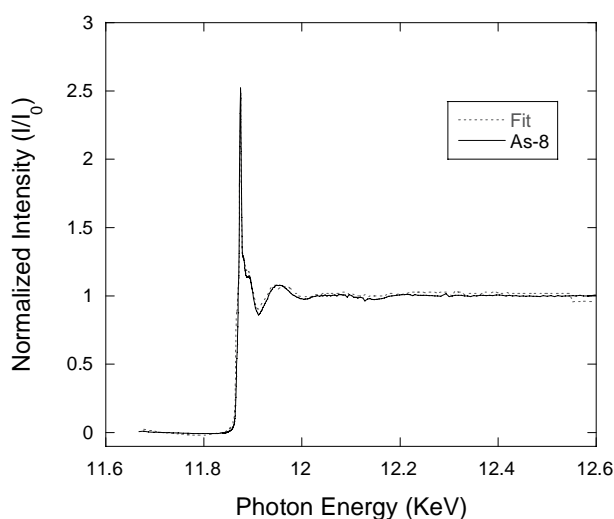


Fig. 3

For the two sampling sites where XAS analyses were performed on samples from different depths, the results show that with the exception of the uppermost As-8 sample, the As speciation is similar with depth. The total arsenic concentrations decrease with depth, but the solid phase speciation remains relatively constant. The arsenic is predominantly in the As(V) oxidation state and mainly found as scorodite. The surface distribution of As is also dominated by oxidized As in the form of scorodite.

Discussion

Results from XAS studies on the samples reveal the presence of three oxidation states of As in samples from the smelter site As(0), As(III), and As(V). Furthermore, the surface distribution and depth distribution of As are dominated by scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Thermodynamic equilibrium models suggest that the solubility of scorodite is minimal at around pH 4 [3, 4]. Scorodite stability depends on other often interdependent factors including crystallinity, kinetics, and surface transformations (i.e. ferric hydroxide precipitate coatings) [5, 6]. Thus, conclusions based on XAS results suggest that As in solution should be minimal at pH 4. The macroscopic-scale data from the pH stat experiments contradict this conclusion. At pH 4, the solution As is probably dominated by contributions

from non-scorodite sources including elemental As (perhaps from arsenopyrite), As_2O_3 , and weakly sorbed As(V). Thermodynamic models suggest that arsenopyrite, elemental As, and As_2O_3 are unstable under the conditions in this study (and in the field) [7]. Therefore, kinetic factors control the dissolution/desorption of As in these samples.

Phosphate slightly increases the total amount of As in solution from these samples especially at lower pH. Arsenic (V) increases relative to As(III) in solution presumably from displacement by phosphate. The concentrations of metals, such as Cd and Pb, released into solution are reduced 5-10 fold in the presence of phosphate. The increased risk of As d/d from the presence of phosphate should be assessed in light of the reduced risk from the solubilization of other metals. Furthermore, if an in-situ phosphate amendment treatment were employed, the As(V) released would be more susceptible to retention (relative to As(III)) by concurrent risk management strategies such as strategic placement of permeable reactive barriers containing zero-valent iron.

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References

- [1] C.A. Impellitteri, K.G. Scheckel, J.A. Ryan, *Environ. Sci. Technol.* 37, 2936-2940 (2003).
- [2] T. Ressler, *J. Synch. Rad.* 5, 118-122 (1998).
- [3] E. Krause, V.A. Ettel, *Am. Mineral.* 73, 850-854 (1988).
- [4] N.J. Welham, K.A. Malatt, S. Vukcevic, *Mineral Eng.* 13, 911-931 (2000).
- [5] D.K. Nordstrom, G.A. Parks, *Am. Mineral.* 72, 849-851 (1987).
- [6] R.G. Robins, *Am. Mineral.* 72, 842-844 (1987).
- [7] B.W. Vink, *Chem. Geol.* 130, 21-30 (1996).