Chemical Speciation of Arsenic in Uranium Mine Tailings by XAFS

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Introduction

In the ever-evolving world of environmental issues, the ability to understand and predict the stability and bioavailability of heavy metal contaminants (e.g., arsenic) in mine waste is becoming increasingly more important. Environmental regulations have become more stringent, and a mine's ability to operate a mill tailing facility is directly related to its capacity to predict long-term stability of the waste. Traditionally, the stability of mine waste was predicted using various thermodynamic models in conjunction with powder x-ray diffraction (pXRD) data to determine material composition and assorted wet chemistry techniques to determine total species concentrations. Recent works by Waychunas et al.[1] and Brown et al.[2-4] have shown that synchrotron-based techniques, such as x-ray absorption spectroscopy (XAS), are powerful tools to enhance our understanding of the geochemistry of mine waste.

This work will demonstrate that synchrotron-based techniques are a useful tool to understand the mineralogy associated with the JEB Tailing Management Facility (TMF) in Northern Saskatchewan. The TMF contains, or will contain, uranium mill tailings from McClean Lake, Midwest and Cigar Lake ore bodies that are high in arsenic (up to 10%) and nickel (up to 5%).[5] The long-term goal of the TMF is to control the release of these contaminants to the surrounding groundwater. Currently, the release of contaminants is controlled by (i) understanding long-term solubility of the tailings through the control of mineralization, (ii) understanding solids chemistry of the tailings, and (iii) understanding diffusion as a principal transport mechanism of contaminants.

Methods and Materials

Cogema Resources Inc. supplied nine samples for x-ray absorption studies (XAS). Three samples were synthetic ferric arsenate (FeAsO4, Scorodite) prepared by Dr. G. Demopoulos at McGill University. Two samples were crystalline ferric arsenate as determined by pXRD, and a third standard was characterized by pXRD as amorphous. Along with the model compounds, six samples from various points in the mill cycle were supplied. Two neutralized raffinate samples (precipitate from liquid tailings), which were precipitated in the laboratory, with two different iron-to-arsenic ratios (3.5 and 1.3) were supplied. Two leach residue samples, that fed the tailings neutralization circuit, were supplied. Two dried tailing samples from the tailings thickener underflow (feed to TMF) were provided with an arsenic concentration of ~1000 ppm, one sample was supplied "as is," and the second sample had undergone a gypsum dissolution procedure.

The XAS spectra were collected at the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT)[6] bending magnet beamline located on the 7.0 GeV storage ring, Advanced Photon Source (APS), at Argonne National Laboratory. The As K- (11867 eV) edge spectra were recorded using a fixed-exit double-crystal monochromator with Si (111) crystals. This configuration provides an effective energy range from 3-27 keV with a resolving power of ~7000. The photon energy scale for the double-crystal monochromator was referenced to the inflection point of the Au K-edge of a thin gold foil at 11918 eV. The relative energy scale was reproducible within ±0.1 eV. All the spectra presented here represent the average of at least three scans.

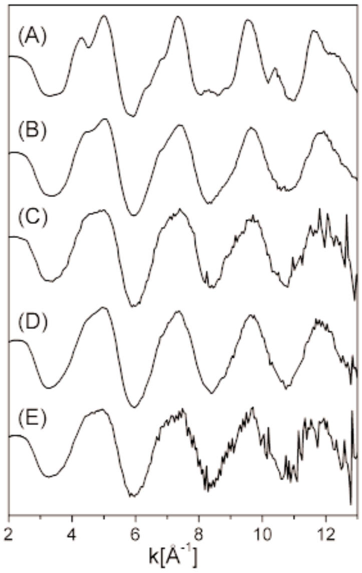

FIG. 1. A comparison of the k vs $k^3\chi(k)$ of a crystalline (A) and amorphous (B) ferric arsenate and arsenate adsorbed on FeOOH (C) against a neutralized raffinate (Fe/As 3.5) (D) and tailings (E).

Results

Figure 1 shows a plot of k vs. $k_3\chi(k)$ for two synthetic ferric arsenates (crystalline and amorphous), an arsenate adsorbed on a 2-line ferrihydrite, laboratory-neutralized raffinate (Fe/As 3.5) and a dried tailing sample. For all the spectra shown in Fig. 1, a principal sine wave is evident, which is the result of the backscattering associated with the first shell around the arsenic, As-O. The fine structure, evidenced by shoulders and splitting on the main wave pattern, is associated with scattering from the higher shells, in this case, As-Fe. The spectra for the crystalline ferric arsenate is in excellent agreement with the previous work of Foster et al.[3] Crystalline ferric arsenate is characterized by the fine structure on the first oscillation at ~4.5 $Å^{-1}$, whereas the amorphous ferric arsenate shows a significantly reduced peak to valley in the fine structure. This change in fine structure relates to a decrease in the long-range order within the material. When the precipitated raffinate solids and tailings samples are compared with crystalline and amorphous ferric arsenates, the mill samples appear not to form the more crystalline material. The first oscillation at ~4.5 Å^{-1} in the precipitated raffinate solids and tailings has a flat top, no splitting, and remains unidentified.

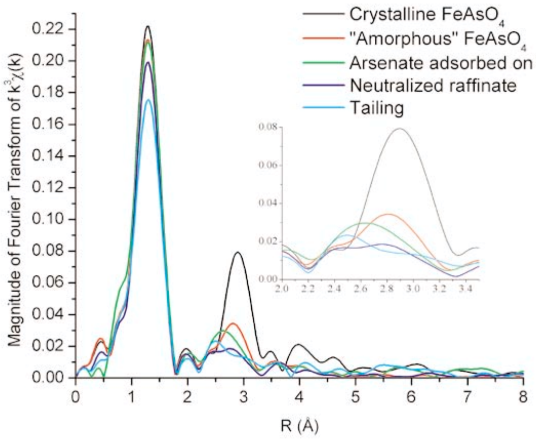

FIG. 2. A comparison of the Fourier transform magnitude As K-edge k^3-weighted EXAFS of the crystalline and amorphous ferric arsenates, arsenate adsorbed on FeOOH against the neutralized raffinate (Fe/As 3.5) and tailing samples.

Figure 2 shows a comparison of R versus Fourier transform magnitude of $k^3\chi(k)$ from the data shown in Fig. 1. The first feature at ~1.27 Å (uncorrected for phase shift) is associated with the As-O single scattering. The second feature at ~2.8 Å is reflective of the local structure linked with the higher shells. When the crystalline and amorphous ferric arsenates are compared, the scattering due to As-Fe decreases in intensity between the two samples. As mentioned above, the sample was characterized using laboratory techniques as amorphous but actually look as if it may have a microcrystalline structure with a length scale too short to be observed with traditional XRD. A truly amorphous material does not show the scattering of the higher shells, and therefore the existence of higher shells reflects the presence of some crystallinity in the material. The arsenate adsorbed on FeOOH has a broad band centered at ~2.6 Å. The exact structure of the adsorbed arsenate from this data is unclear.

The Fourier transform of the k vs $k^3\chi(k)$ of the raffinate and tailings are overlaid in Fig. 2. Both Fourier transforms appear to be composed of two bands that are linked with the local environments around the arsenates. The band at ~2.8 Å is in good agreement with that found for the amorphous ferric arsenate. The source of the second band, at shorter distance, remains unknown.

Discussion

XAFS techniques were applied to study the mineralogy of arsenic in the precipitated raffinate solids and tailing samples from a tailings preparation circuit of a uranium milling facility. When compared to both crystalline and amorphous ferric arsenates, the data show that both the tailings and raffinate were not composed of a single type of material. In the raffinate solids, there is evidence of a ferric arsenate-like phase, most probably "amorphous," with a second unknown component with a slightly shorter arsenic-iron distance. Interestingly, the intensity of both species in the raffinate solids (but not shown) were not related to the Fe/As ratio.

The XAFS of the tailings show the same two features at higher R distances that were observed in the raffinate solids except for a difference in the relative ratios of the two features. The peak, which could be related to the unidentified species, is higher in intensity when compared to the raffinate solids. Some more work needs to be accomplished before an unambiguous assignment for the different arsenic species in the raffinate solids and tailings may be made.

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