

XAFS of Synthetic Iron(III)-Arsenate Co-Precipitates and Uranium Mill Neutralized Raffinate

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Abstract. XAFS studies were carried out for chemical speciation of arsenic species in uranium mill neutralized raffinate solids. To aid the structural characterization, synthetic iron(III)-arsenate co-precipitates were prepared to mimic the actual uranium mill tailings neutralization products. The principle components analysis method was used to validate the synthetic amorphous scorodite as a primary model compound for arsenate species in the raffinate samples under the specific precipitation conditions.

Keywords: XAFS, arsenic, environment, mine tailings, raffinate.

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INTRODUCTION

The arsenic speciation in mine tailings has drawn wide attention because of its environmental and health impact [1,2]. The high-grade uranium deposits in northern Saskatchewan, Canada, provides approximately one-third of the world's total uranium production [3]. Arsenic-bearing minerals (e.g. arsenopyrite, FeAsS) extensively exist in the uranium ore. During the mining process, most arsenic is leached out and left behind in an acidic sulfate waste solution (i.e., raffinate). The raffinate is generally lime neutralized, precipitated, and stored in a tailings disposal facility. The arsenic in raffinate solution is removed by precipitation with ferric iron, thereby producing low solubility iron(III)-arsenates [1]. A long term concern for the pore water in the final stored tailings is soluble arsenic originating from the neutralized raffinate solids, which depends on the arsenic speciation developed in neutralized raffinate solids.

Previous X-ray absorption near edge structure (XANES) work on the COGEMA McClean Lake neutralized tailing materials indicated that the dominant arsenic species involves arsenate [4]. In a recent X-ray absorption fine structure (XAFS) study [5] we determined that the arsenic local structure in neutralized raffinate solid materials, which have

preparation pH values up to 7, closely resemble that of amorphous scorodite. Amorphous scorodite, an As-Fe co-precipitation solids, identified previously based on its X-ray diffraction characteristics and an Fe/As molar ratio close to unity [6], has a local structure clearly different from typical arsenic-bearing ferrihydrite [5]. The arsenic and iron local structures of amorphous scorodite are similar, in terms of As-Fe interatomic distance and coordination number, to that of crystalline scorodite, where ferric iron octahedra and arsenate tetrahedra are alternately arranged. In this report we use the principle component analysis (PCA) method [7] to illustrate that synthetic amorphous scorodite provides an excellent model system for arsenic species in the uranium mining raffinates.

EXPERIMENTAL

A uranium mill raffinate solution without solid leach residual was neutralized under laboratory conditions to a range of terminal pH values from 2 to 6 [8]: sample raf #1, #2, #3, and #4 correspond to terminal pH of 2.18, 3.15, 4.04, and 6.09, respectively. A selected set of synthetic model compounds was used in this study, including crystalline scorodite (FeAsO₄·H₂O [9]), amorphous scorodite [6], Fe-As co-precipitates with Fe/As = 4 and pH of 4 (CPT-2) and with Fe/As = 4 and pH of 8 (CPT-4) as well as

arsenate adsorbed goethite with Fe/As = 4 (ads 4/1) and with Fe/As = 10 (ads 10/1). Detailed description of these samples is given elsewhere [5]. Most of the XAFS measurements were carried out using beamline 20-BM (Si 111 monochromator) at the Advanced Photon Source (APS). The XAFS data for the two iron(III)-arsenate coprecipitate samples CPT-2 and CPT-4 (Table 1) were collected at beamline X10C, National Synchrotron Light Source (NSLS). The data reduction and PCA analysis were performed using WINXAS version 3.0 [10]

RESULTS AND DISCUSSION

Principal component analysis (PCA) can be used to estimate the possible number of constituent species in an unknown sample set, and to identify as well the possible component species by target transformation [7].

A PCA test was first carried on two XANES data sets with some constituent overlapping, i.e., data set #1 composed of all model compounds and neutralized raffinate, and set #2, only including raffinate samples. The results are shown in Fig. 1.

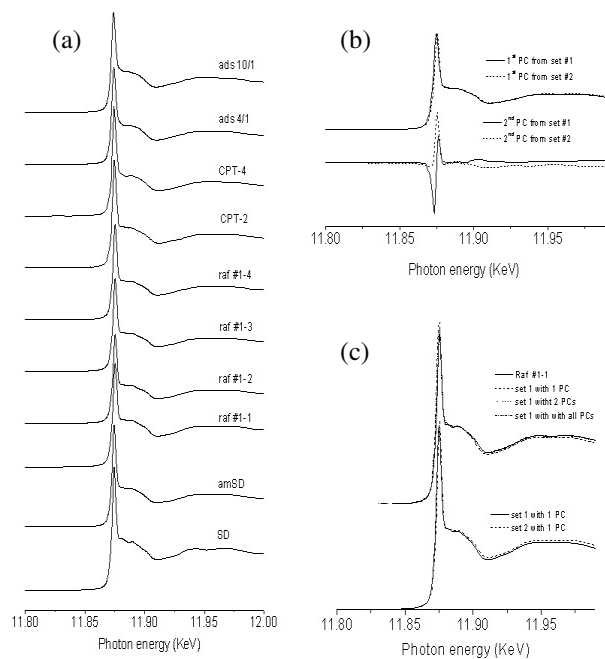


FIGURE 1. PCA of XANES data. (a) As K-edge XANES used in this study (see text for description); (b) The first two PC components obtained from data set #1 (including all synthetic model compounds and neutralized raffinates) and from set #2 (including only raffinate samples); (c) XANES reconstruction with PC components. Reconstruction of raf #1 with one, two and all PCs generated from data set #1 (upper); comparison for spectra reconstructed with first PC generated from data set #1 and #2, respectively.

A close resemblance is seen between the first PCs obtained from data set#1 and set#2 (Fig. 1b). The decomposition of PCs to XANES spectra was further tested by spectrum reconstruction with different number of PCs (Fig. 1c). It is apparent that adding more PCs beyond the first one does not improve the quality of reproduction significantly, indicating that the first PC is the dominate component among all PCs of the raffinate system and the contribution from others are negligible. Comparison is also made between reconstructed spectra of the first PC generated from the two data sets, individually, indicating again a good match between them (Fig. 1c). This match shows that the similar first PC is shared among all the XANES spectra involved in the two data sets. Since arsenate is the arsenic oxidation species known to exist in the all the synthetic model components, arsenate is also the dominate arsenic oxidation species in the raffinate compounds. This conclusion verifies the visual examination of XANES data (Fig. 1a) and is consistent with previous studies [2,4,5].

PCA was carried further to two XAFS data sets, i.e., data set #1 composed of all model compounds and neutralized raffinate, and set #2, composed of CPT-2 and CPT-4 and raffinate samples. Table 1 lists the normalized weights for the first four PCs estimated in the two cases. In the case of the data set #1, the resulting weight values reveal the existence of a dominate PC (Fig. 2), which accounts for more than 70% of the total contribution. On the other hand, there might be two additional minor PCs whose significance is comparable to each other and both not negligible. This observation is reasonable because data set #1 contains a more diverse range of As local structures. In the case for data set #2, PCA reveals again the existing of a dominate PC but the weights for the two minor PCs are less significant than those in set #1. Figure 3 shows a comparison between the $k^3\chi(k)$ XAFS spectra of raf #1 and the reconstructed spectra with one PC, two PCs, and three PCs, respectively. The inset is the enlargement of $k^3\chi(k)$ around k of $\sim 5 \text{ \AA}^{-1}$. These reconstruction results indicate that the first PC is the dominate component, and the reconstructed spectra carry all major spectrum features of raf #1. Adding more PCs in the reconstruction process leads to only minor improvements.

A comparison was further made among the $k^3\chi(k)$ target transformation results for amorphous scorodite (SD), arsenate adsorbed goethite with Fe/As = 4 (ads 4/1), and crystalline scorodite (SD) to determine the possible dominate arsenate species in the raffinate system with the PCs estimated from raffinate and CPT system, i.e., data set #2 (Fig. 3).

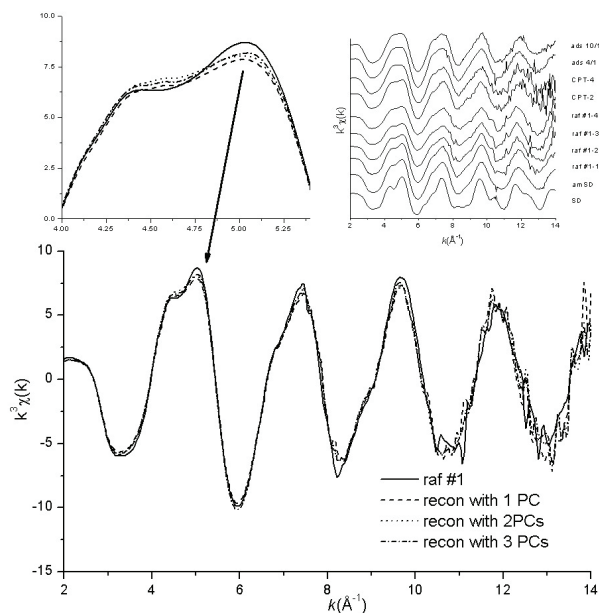


FIGURE 2. Lower panel: Comparison between the $k^3\chi(k)$ of a raffinate sample (raf #1) and the reconstructed spectra with one PC (dash), two PCs (dot), and three PCs (dash-dot), respectively. The upper-left inset is a close-up view of the $k^3\chi(k)$ oscillation at k of $\sim 5 \text{ \AA}^{-1}$. The upper-right inset shows all the raw data.

The target transformation residual is 9.5%, 18.8%, and 28.4% for amorphous scorodite, adsorption phase, and crystalline scorodite, respectively. It is apparent that amorphous scorodite is most likely the major arsenate species in the raffinate system under investigation. There might be some minor arsenate adsorption species developed there, but the arsenate adsorption phase does not seem to be the major species in the raffinate system under investigation, as indicated by both the target transformation (Fig. 3) and the PC weight value (Table 1).

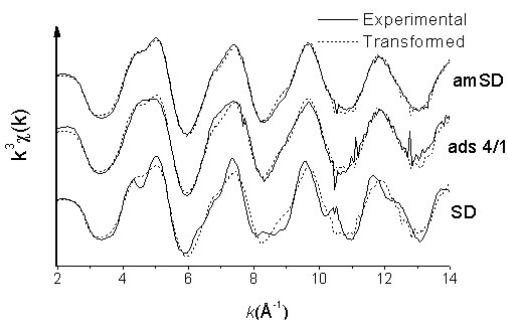


FIGURE 3. Comparison between experimental data and their reconstruction with PC components obtained from data set #2 for amorphous scorodite, arsenate adsorption goethite (ads 4/1), and crystalline scorodite, respectively.

TABLE 1. Weights for the first four PCs estimated from XAFS data: data set #1 is composed of model components and raffinate samples; set #2 is composed of CPT-2, CPT-4 and raffinate samples.

PC number	Weights set #1	Weights set #2
#1	1.000	1.000
#2	0.190	0.224
#3	0.111	0.084
#4	0.111	0.084

CONCLUSION

PCA analysis for As K-edge XANES and XAFS data for neutralized raffinate solids as well as relevant synthetic model compounds reveals that arsenate is the dominant arsenic oxidation state, and synthetic amorphous scorodite represents the dominant arsenate species in the uranium mining raffinate system for the terminal pH range studied here.

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