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Immobilization of Arsenic(V) during the Transformation of Ferrihydrite: A Direct Speciation Study Using Synchrotron-based XAFS Spectroscopy

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In the present study, we investigated the behavior of arsenic (As) during the transformation of poorly crystalline iron(III) hydroxide, ferrihydrite. Adsorbed As on solids gradually decreased as ferrihydrite transformed to crystalline goethite and hematite. X-ray absorption fine structure (XAFS) analysis indicated that the As immobilization dominantly resulted from the incorporation of arsenate into poorly crystalline ferrihydrite under present experimental conditions.

Arsenic is present in all natural environments and, being extremely toxic for living organisms, is of health and ecological concerns.[1] The occurrence of As in soils, sediments, and aquifers is mainly from natural processes, as well as being from anthropogenic activities.[1,2] The mobility of As in soils and sediments is influenced by sorption/desorption reactions, solid-phase precipitates, and coprecipitation with metal ions.[2] The importance of iron oxides in controlling the mobility of As in natural environments has been well studied.[1–3] Arsenic commonly exists as arsenate (As(V)) in oxic soils and sediments, and is often associated with poorly crystalline iron hydroxide minerals, such as ferrihydrite.[2,4] As(V) can be sequestered from solution during the precipitation of soluble Fe resulting in the formation of the ferrihydrite in the presence of As. Ferrihydrite precipitation is also used in industrial treatments to remove As from contaminated water.[3] However, ferrihydrite is thermodynamically metastable and transforms to more stable crystalline phases such as goethite and hematite under oxic conditions.[2] Several changes in As(V) partitioning would occur during this transformation, because goethite and hematite have different surface area, sorption capacity, and crystallographic structure characteristics compared with ferrihydrite. However, the fate of As during this transformation process is not clear.

The objective of this study was to carry out a detailed examination of how ferrihydrite transformation influences the As partition between water and solid phases. For the objective, we conducted transformation experiments under controlled conditions and observed As species during the transformation directly using X-ray absorption fine structure (XAFS) spectroscopy. Our study provides valuable insights on the long-term mobility of As in contaminated environments and on water treatment methods for As removal in effluents.

Laboratory experiments were performed by aging of ferrihydrite coprecipitated with As(V). The coprecipitated ferrihydrite was synthesized by neutralization of acidified solutions containing Fe(III) and As(V) using a titration system.[5] The As/Fe molar ratios in the solids were fixed at 0.001 and 0.01. Precipitate slurries were then allowed to age for 84 days at pH 6.0 in a water bath at 50 °C. Solid and water samples were taken at 2 week intervals to determine the transformation rate and the behavior of As. For all experiments, solid-phase As was greater than 99.5% during the entire period of observation (at least 84 days). The fraction of As(V) adsorbed on the solids was estimated from the desorption amount of As with 1.0 M phosphate solution at pH 5.0.[6] Fe and As K-edge XAFS of the solid samples were obtained at the beamline BL01B1 in SPring-8 (Hyogo, Japan). The XAFS data was analyzed by REX2000 (Rigaku) and FEFF7.0.[7] The experimental details are provided in the Supporting Information (SI).[14]

The Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra and the Fourier transforms (FTs) of the solid samples are shown in Figures S1 and S3 in SI,[14] respectively. The intensity of the second-neighbor shell in the FT gradually increases with time, indicating an increase in the Fe–Fe coordination number (CN), which is consistent with longer Fe–Fe linkages in the structure. The observations in the FT could be interpreted as a phase transformation of the metastable ferrihydrite to goethite and hematite, which is also supported by X-ray diffraction (XRD) data (Figure S2 in SI[14]). The amount of each mineral in the solids was determined using a least-squares fitting using reference EXAFS spectra (Figure 1). At an As/Fe ratio of 0.001, most of the ferrihydrite was converted to goethite and hematite after 40 days. On the other hand, at an As/Fe ratio of 0.01, about 30% of the ferrihydrite remained over the same period. This result suggests that the transformation is retarded at higher As(V) loadings. Previous studies have also reported a similar retardation of the transformation in the presence of As(V).[8] Ford suggested that As(V) on the surface inhibits the dissolution of ferrihydrite and stabilizes the metastable phase, because the transformation proceeds by the dissolution of ferrihydrite and the precipitation of the new phase.[8]

On the transformation, the phosphate-unextractable fraction of As increases from 40 to 50% in the initial stage to about 80–90% after 84 days for all As/Fe ratios (Figure 2), which indicates an immobilization of As into solid phase during the transformation. These findings imply that (1) As(V) is incorporated into the transformed products or As(V)-coprecipitated

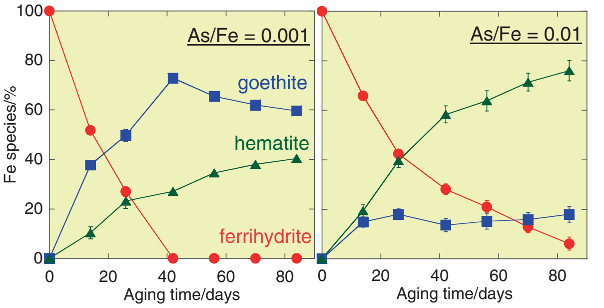

Figure 1. Fraction of each mineral (ferrihydrite, goethite, and hematite) estimated by quantitative fitting analysis using Fe EXAFS spectra.

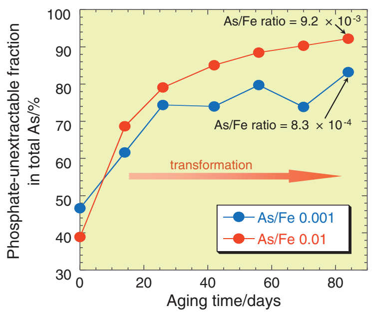

Figure 2. Phosphate-unextractable fraction of As. Uncertainties are smaller than the sizes of the symbols at both As/Fe molar ratios.

ferrihydrite with the aging and/or that (2) As(V) generates other phases bearing As and Fe (such as scorodite, $FeAsO_4$). Regarding the latter species, no separate As phases were detected in both XAFS and XRD as expected considering the low As content.

To obtain direct information on the host phase of As(V), the local structure of the As was examined using EXAFS. Figure 3 shows the EXAFS and FT spectra of As in ferrihydrite with a 0.01 As/Fe ratio aged for 0, 26, 56, and 84 days. A quantitative simulation analysis shows that the CN of As–O bond in the samples is nearly four with a bond distance of 1.68 Å throughout the aging, which is consistent with As–O tetrahedral linkages (Table S1 in SI). Thus, an isomorphous (structural) substitution of As into the structure of the transformed products during the transition does not occur, because both goethite and hematite are composed of Fe–O octahedron only and do not contain the tetrahedral sites that can readily accommodate As(V).[9] On the other hand, the intensity of the As–Fe shell around 2.6 Å (box in Figure 3) in the FT gradually increases with aging period, and the intensity at 56 and 84 days is significantly higher than that of As(V) adsorbed on ferrihydrite. This suggests that the CN of As–Fe bond increases with transformation of ferrihydrite, which is also supported by the simulation results (Table S1). The increase in the CN may imply an incorporation of As(V) into arsenical ferrihydrite as suggested by Sherman and Randall.[5] In addition, in the As EXAFS spectra, a double-hump feature at $k = 4$–$5\,Å^{-1}$ was observed in the latter periods of aging (arrows in Figure 3). Paktunc et al. reported that this double hump is a characteristic feature of As(V) incorporated into the structure of poorly crystalline ferrihydrite (iron(III) arsenate).[10] Thus, based on our findings and previous reports, it is indicated that As(V) is gradually associated with the poorly crystalline iron hydroxides as adsorbed As decreases with the course of the transformation, which may be a mechanism for As(V) immobilization identified in this study. In fact, there are As(V)-accessible tetrahedral sites in the ferrihydrite structure addition to octahedral sites, according to the structure model reported.[11] Moreover, these findings may explain the higher adsorbed As species at 0.001 As/Fe ratio than at 0.01 observed in the latter period of aging, because most of the ferrihydrite at the As/Fe ratio of 0.001 transformed more rapidly and did not remain in the latter period (Figure 1).

Previous studies with similar experimental pH conditions and As/Fe ratios have also found that the adsorbed As decreases with aging and that As is immobilized in the solid phase after the transformation of ferrihydrite.[8,12] They indicated that As(V) is incorporated into the more crystalline transformed phases.[8,12] However, this has not been confirmed by spectroscopic analysis. Our direct speciation using XAFS spectroscopy indicates that the As(V) is predominantly incorporated into the structure of poorly ordered iron hydroxides. Elements incorporated into the structure are not heavily influenced by factors such as the pH, ionic strength, and concentration of competitive ions compared with adsorbed species accessible to aqueous phase.[13] Thus, our insight would be an important finding for predicting the long-term behavior of As in contaminated soils and Fe precipitates used in industrial water treatments.

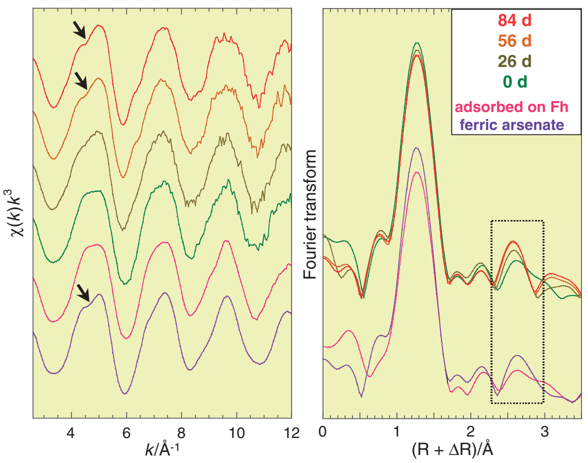

Figure 3. k^3-weighted As K-edge EXAFS spectra (left side) and FT spectra (right side) during the transformation of ferrihydrite coprecipitated with As/Fe ratio of 0.01. "Fh" means ferrihydrite.

The synchrotron experiment was performed with the approval of JASRI (Proposal Nos. 2010B1363 and 2011A1223).

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