X-Ray Absorption Fine Structure Spectroscopy Study of Arsenate Adsorption on Schwertmannite

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Abstract. We studied arsenate adsorption on schwertmannite by means of XAFS. Our results show that arsenate is bound to one or two iron octahedra and individual iron octahedra in schwertmannite become more regular after the adsorption. At the same time there is an increase of disorder in polymeric chains of iron octahedra. This suggests that the release of local strain is related to the overall stability of arsenate-adsorbed schwertmannite.

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INTRODUCTION

Schwertmannite is a poorly crystalline iron oxyhydroxysulfate that is stable under highly acidic conditions and at high $\text{SO}_4^{2-}$ concentrations. It has strong affinity and a large reactive surface area for arsenate and yields natural attenuation process in acid mine drainage [1]. The structure of schwertmannite and the adsorption mechanism are not fully understood. Bigham et al. proposed a structure similar to akaganeite [2]. Akaganeite has double chains of FeO$_3$(OH)$_3$ octahedra which share corners and run parallel to the b-axis forming tunnel structure, where anions such as Cl$^-$ occupy and stabilize its structure. In schwertmannite, sulfate plays the same role as these anions. Using IR spectroscopy, Bigham et al. suggested that sulfate forms bidentate bridged complexes inside its tunnel structure. This geometrical constraint severely distorts the structure and leads to poor crystallinity. Excess sulfate is adsorbed on surface sites and arsenate is easily substituted for them [3] and it stabilizes the schwertmannite phase. There are several studies about the arsenate adsorption site using EXAFS. Arsenate mainly adsorbs on the outside of crystallites forming a bidentate complex [4, 5, 6, 7]. In order to obtain insight about the mechanism of the stabilization of schwertmannite by arsenate adsorption, we performed Fe and As K-edge XAFS measurement and discuss the effect of adsorption on the schwertmannite structure.

EXPERIMENTAL AND DATA ANALYSIS

Schwertmannite samples were synthesized by the method described in [2]. The samples were particles of 100~200 nm. Individual particles were aggregates of needle-like crystals. According to the adsorption isotherm of arsenate [8] we obtained two samples with different amount of arsenate. Goethite and akaganeite samples were also synthesized as references. The samples were characterized by XRD and IR measurements. XAFS measurements were performed with a laboratory XAFS equipment (EXAC820, Technos Co., Ltd.) in transmission mode. EXAFS data were analyzed by FEFFIT [9]. Atomic background was subtracted using AUTOBK. In order to obtain EXAFS signals from the oxygen shell properly, theoretical standard was used in the background subtraction. EXAFS curve fitting were performed in R-space, using parameters calculated by FEFF8 [10].

RESULTS AND DISCUSSION

Figure 1 shows the magnitude of Fourier transformed EXAFS $k\chi(k)$ spectra using the k range of 3.5~9.6 Å$^{-1}$. The first peak with slightly different shoulders at $\sim$ 1.5 Å corresponds to the first neighbor Fe-O shell in Fe octahedra. The small change in the spectra implies possible structural changes upon arsenate adsorption. Features at 2~3.5 Å correspond to Fe-Fe single-scattering paths in connected Fe octahedra. We performed least-square fitting in R-space in the range of 0.7~3.7 Å. The first peak was treated as a double shell in order to describe the distortion in the Fe octahedra. Third order cumulants ($C_3$) were taken into account. The results are shown in Table 1. The difference between the two Fe-O distances becomes shorter after arsenate adsorption. Non-zero $C_3$ was obtained only for the sample before arsenate adsorption. These results indicate that the Fe octahedra in schwertmannite approach regular octahedra upon arsenate adsorption. Moreover, the distribution of Fe-O distances becomes more symmetric, indicating that the in-
Figure 1. Fe K-edge EXAFS $k^2\chi(k)$ and the Fourier transforms of $\chi(k)$. Solid lines are experimental data, dashed lines are least-square fits.

Table 1. Structural parameters of schwertmannite and akaganeite. R: bond distance (Å), $\sigma^2$: Debye-Waller factor (Å²), $C_3$: Third order cumulant (Å³). Coordination number of Fe-O: 2(shorter) and 4(larger), Fe-Fe: 2(shorter) and 2(larger).

![Table 1](image)

Figure 2. Fe K-edge XANES spectra and pre-edge region.

Figure 3. Fe K pre-edge spectra and integrated area of "peak1" and "peak2": 0:goethite, 1:akaganeite, 2:schwertmannite(As/Fe=0), 3:(As/Fe=0.0693) and 4:(As/Fe=0.1490).

The pre-edge peak is about 1 eV, which was not resolved here. We fitted these pre-edge spectra with two Gaussians as shown in Fig. 3. The peak at lower energy can be interpreted as the ligand-field multiplet. According to previous work [13], the intensity of the feature at higher energy "peak2" increases with increasing degree of polymerization of FeO$_x$(OH)$_y$ octahedra. Figure 3 also shows the area of these two peaks. Intensity of peak2 decreases upon arsenate adsorption, indicating that the degree of polymerization of Fe octahedra is reduced by arsenate adsorption. This is in agreement with the increase of Debye-Waller factor of Fe-Fe paths seen in the Fe EXAFS.
are least-square fits.

The k range used in the transform is \( k \sim 1.1 \) Å. For the 2E model were not identified in our data. We identified contributions from Fe atoms. Possible models of the adsorption structure are shown in Figure 5 [7]. As-Fe single-scattering paths give a peak at 3.0, 3.6 and 2.3 Å for the 2C, 1V and 2E models, respectively. Contributions of the 2E model were not identified in our data. We performed least-square fitting in R-space using the data range 0.7~4.2 Å. As shown in Table 2, the As-O distance and coordination number are almost the same among the three samples: arsenate adsorbed in schwertmannite keeps tetrahedral coordination. The feature around 3.6 Å was well described by the As-Fe path in the 2C model. In the region around 3.6 Å where the 1V model has the dominant contribution, the As-Fe, As-O-Fe and As-O-Fe-O multiple-scattering paths were taken into account. From our data, the 2C and 1V models were found to be appropriate as an adsorption model.

In conclusion, we found from the present XAFS analysis that individual iron octahedra in schwertmannite become more regular after arsenate adsorption, while polymeric chains of iron octahedra become more disordered. The stabilization due to such local strain release, in spite of the reduced crystalline order of iron octahedra, would likely be the cause of the overall stability of the schwertmannite phase after arsenate adsorption.

**REFERENCES**