

Arsenate Sorption Mechanisms in Synthetic Schwertmannites and Natural Schwertmannite from the Chinkuashih Acid Mine Drainage Area, Northern Taiwan

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In order to obtain a basic understanding of the true nature of arsenate sorption on schwertmannite, $\text{Fe}_{16}\text{O}_{16}(\text{OH})_{12-9}(\text{SO}_4)_{2-3.5} \cdot n\text{H}_2\text{O}$, the first run of the EXAFS experiment at the NSRRC 17C1 W20 beam line was focused on synthetic schwertmannite specimens (prepared by three different methods) before and after sorption treatments with various arsenate concentrations. The As K-edge EXAFS analyses of the synthetic schwertmannite (prepared with the mixing solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Na_2SO_4) after arsenate sorption suggests the presence of a 4-fold coordination of As ($\text{As}(\text{O},\text{OH})_4$ tetrahedron) with an As-O bonding distance of 0.168 nm (Figure 1 & Table 1). An ionic distance of 0.322-0.326 nm with a coordination number of 1.74-1.91 in the second sphere As-Fe coordination was also obtained from the analysis. The weak signal at 0.285 nm can be fitted with an As-O-O-As multiple scattering effect. There are no apparent differences between the specimens of different arsenate sorption concentrations. The EXAFS results obtained from the schwertmannite specimens prepared by 3 different methods are similar. The data collectively imply that the sorption mechanism of arsenate on schwertmannite involves a bidentate binuclear ^2C corner-sharing coordination between one $\text{As}(\text{O},\text{OH})_4$ tetrahedron and two neighboring $\text{Fe}(\text{O},\text{OH})_6$ octahedra (Figure 2). The As K-edge EXAFS analysis of a naturally occurring As-bearing schwertmannite specimen collected from the Chinkuashih acid mine drainage area produced noisy signals in the high-value range of the k space but gave a spectrum of reasonable quality after arsenate sorption, with a result similar to those obtained from synthetic specimens with a surface and/or tunnel ^2C corner-sharing mechanism (Figure 3).

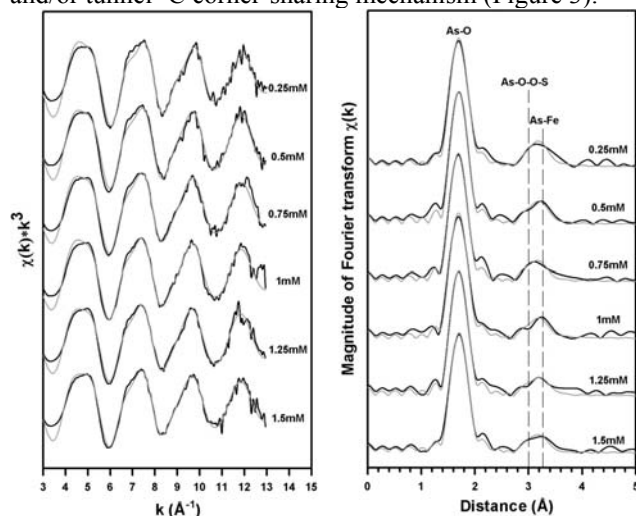


Figure 1. As K-edge EXAFS spectra (acquired with the fluorescence mode) and Fourier transform patterns of schwertmannites prepared by mixing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Na_2SO_4 solutions after sorption with various arsenate

concentrations (see Table 1).

Table 1. EXAFS parameters for spectra of Figure 1 (σ^2 = Debye-Waller factor).

Initial [As] (mM)	As/Fe	S/Fe	As-O shell			As-O-O-As MS			As-Fe shell		
			R_o (nm)	N_o	σ^2	R_{Fe} (nm)	N_{Fe}	σ^2	R_{Fe} (nm)	N_{Fe}	σ^2
0.25	0.026	0.029	0.169	3.95	0.0018	0.307	11.84	0.0018	0.325	1.78	0.0082
0.50	0.053	0.044	0.169	4.12	0.0022	0.307	12.35	0.0022	0.325	1.87	0.0073
0.75	0.080	0.058	0.168	4.07	0.0022	0.306	12.21	0.0022	0.325	1.91	0.0095
1.00	0.106	0.071	0.169	4.05	0.0023	0.307	12.15	0.0023	0.327	1.75	0.0087
1.25	0.123	0.081	0.169	3.94	0.0022	0.307	11.82	0.0022	0.327	1.78	0.0099
1.50	0.142	0.095	0.169	3.91	0.0024	0.307	11.74	0.0024	0.325	1.78	0.0105

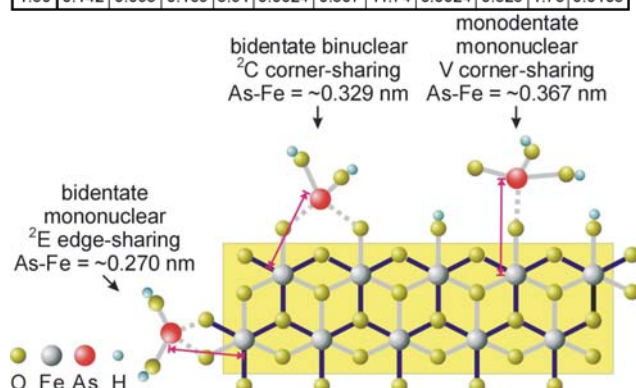


Figure 2. Different modes of surface complexation of arsenate tetrahedra to iron oxyhydroxide.

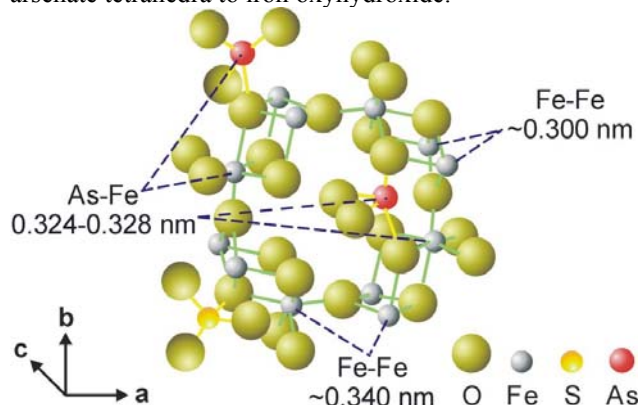


Figure 3. A structural model of schwertmannite with surface bonding of arsenate and sulfate tetrahedra and coordination of an arsenate tetrahedron in the structural tunnel.