

Adsorption of toxic oxyanions in poorly crystalline iron mineral and post-behavior

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The understanding of toxic trace metal distribution and cycling in the natural environment is important in predicting the long-term environmental effects of human activities that has released them.

Schwertmannite which forms in acidic sulfide-rich mine waters (Bigham et al., 1994) were documented to uptake significant amounts of arsenic aqueous species from acidic mine waters through sorption onto mineral surfaces. The sorption mechanism has been expounded by Fukushi et al. (2003, 2004) wherein arsenate is taken up by ligand exchange with SO_4 sites on the schwertmannite surface resulting to natural attenuation. However, schwertmannite is a poorly crystalline iron oxyhydroxysulfate mineral that has a limited stability, and eventually transforms to goethite with time (Bigham et al., 1994). This transformation is retarded when arsenate is sorbed because of the enhancement of its stability by sorption processes (Fukushi et al., 2003; 2004).

In this study, sorption of some harmful oxyanion onto schwertmannite has been investigated. These include selenate and chromate which has ill effects on human health, and phosphates that are responsible in the eutrophication of natural waters. Stability of schwertmannite after sorption of harmful oxyanion is further investigated for the aim of prediction of the remediation of contaminated environments.

Synthesized schwertmannite was used in the sorption experiments at room temperature and pH 3.9, 50deg C. The concentration of SeO_4 , CrO_4 , AsO_4 and PO_4 range from 0.0mM-2.0mM. Sampling was performed at several hours interval. The solid was separated from the liquid by filtration and pH is measured. ICP-MS and IC was used to quantify oxyanions and Fe, and SO_4^{2-} concentrations, respectively. The solid was analyzed by XRD to determine the mineralogical transformation. XPS was used in determining surface accumulation of sorbate in the solids.

In the case of arsenate, phosphate and chromate sorption, the adsorption reached to equilibrium within 48 hours. Sulfate in schwertmannite was released to the solution as a response of these oxyanions adsorption. The observations indicate that these oxyanions were incorporated via anion exchange with sulfate in schwertmannite. On the other hand, the maximum adsorption of selenate was low relative to other oxyanions and sulfate was released to solution with time regardless of the selenate adsorption. XRD analyses of reacted solids showed that SeO_4 and CrO_4 sorbed schwertmannite were transformed to goethite after 268 hours and 604 hours, respectively. On the other hand, PO_4 and AsO_4 adsorbed schwertmannite did not show any evidence for the transformation. These observations qualitatively indicate that the transformation rate of schwertmannite decrease with amount of oxyanion adsorption. XPS analyses of reacted solids and pH-Eh diagram using Geochemist's Workbench showed that the speciations of adsorbed species are SO_4^{2-} , CrO_4^{2-} , H_2AsO_4^- and H_2PO_4^- for sulfate, selenate, chromate, arsenate and phosphate.

Oxyanion amount of adsorption in schwertmannite follows the order from highest to lowest: H_2AsO_4^- , H_2PO_4^- , CrO_4^{2-} , SeO_4^{2-} . The ability of each oxyanion adsorbed to retard the transformation to goethite follows the order from highest to lowest: H_2AsO_4^- , H_2PO_4^- , CrO_4^{2-} , SeO_4^{2-} . Waychunas et al. (1995) reported that arsenate forms strong inner-sphere bonding and selenate forms weak outer-sphere bonding, in iron mineral surface. In this study, property of H_2PO_4^- , CrO_4^{2-} were similar adsorption behavior and stability of schwertmannite to property of H_2AsO_4^- . Then, inner-sphere group like H_2AsO_4^- , H_2PO_4^- , CrO_4^{2-} showed amount of high adsorption to schwertmannite. In addition, this tendency linked to delaying of Goethitization. Therefore, schwertmannite was long-term stable sink for inner-sphere oxyanions group.