

# Formation, Composition, Structure, and Ageing of As-ferrihydrite From Pezinok, Slovakia

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Arsenic is permanently attracting significant attention from the viewpoint of its negative influence on the human health, transport through the trophic chain, and consequently on its biogeochemical cycle. Here we have investigated the formation process, the composition, structure, and ageing of As-ferrihydrite from the Pezinok deposit in Slovakia.

The minute grains (10-100  $\mu\text{m}$ ) of sulfide minerals in the mining waste slowly weather and release the As and Sb into the surrounding aqueous phase. The weathering is accompanied by formation of thin Fe-rich rims that act as scavengers of As and Sb from the aqueous phase. Micro-XANES spectroscopy showed that As is pentavalent in these rims; no indication of trivalent As was found.

EXAFS spectroscopy gave valuable evidence about the structure of As-ferrihydrite. EXAFS spectra at the Fe K edge have shown that the particles in the studied material are extremely depolymerized. The octahedra  $\text{Fe}(\text{O},\text{OH},\text{OH}_2)_6$  are connected almost exclusively by edges, forming short polyhedral chains. EXAFS spectra at the As K edge indicate that the  $\text{AsO}_4$  tetrahedra are attached to the iron oxide particles in a binuclear-bidentate fashion.

Ageing of the waste was simulated by maintaining the samples at 60 °C in a wet state for a period of almost 4 months. Essentially no changes were observed in the XRD patterns. Fe EXAFS spectra documented an increase in the number of Fe neighbors in the second coordination shell. In other words, the small particles polymerize during ageing and probably evolve toward a goethite-like structure. The polymerization and recrystallization of the Fe oxide particles is accompanied by the release of As.

The results presented here have important consequences for the remediation effort at this and other sites. As-ferrihydrite is an excellent medium for capturing As, but an unfavorable choice for the long-term storage of this toxic element. When As-ferrihydrite ages, it releases the arsenic back into the solution. Thus, care must be taken when the As-ferrihydrite is disposed.