

THE STRUCTURE AND AGEING OF As-RICH 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 its biogeochemical cycle. It has been classified as one of the priority pollutants, contested in its toxicity only by few other elements. In this work, we have been investigating the formation process, the structure, and ageing of As-rich ferrihydrite from the Pezinok deposit. At this site, As-ferrihydrite serves as a transport medium for As contamination.

The abandoned Sb deposit Pezinok lies in the in Malé Karpaty Mts in western Slovakia. The deposit is located in carbonaceous and actinolite schists and amphibolites and contained abundant stibnite and smaller amounts of other Sb minerals. In addition to the Sb minerals, pyrite and arsenopyrite were also common. The mineralization occurred as quartz-carbonate lenses, veinlets, nests, and impregnations in the host rocks. The ores were milled and Sb minerals were collected by flotation. The waste was then deposited in two large tailing impoundments.

The fine-grained waste is currently slowly weathering and releasing the toxic elements into the surrounding soils and streams. The principal weathering product is As-rich ferrihydrite, a mineral almost amorphous to X-rays. Because of the lack of long-range order, techniques other than X-ray diffraction (XRD) had to be used to describe this mineral.

Using X-ray absorption near-edge structure (XANES) spectroscopy, we have determined that all probed elements (Fe, As, S) are present in their highest oxidation states. Thus, the material escaping from the impoundments is already fully oxidized, and no further changes in its oxidation state should be expected.

Extended X-ray absorption fine-structure (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 de-

polymerized. 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 AsO_4 tetrahedra are attached to the iron oxide particles in a binuclear-bidentate fashion. Our results agree well with previous conclusions of WAYCHUNAS *et al.* (1993), obtained on a chemically similar synthetic material.

Selected samples were kept at 60 °C in a wet state for a period of almost 4 months and the changes in the samples were monitored by XRD, leaching and chemical analysis of the leachates, and EXAFS spectroscopy. Essentially no changes were observed in the XRD patterns. On the other hand, leaching the samples with 0.5 M NaHCO_3 solution showed that the amount of extractable Fe decreased and the amount of extractable As increased as a function of ageing time. Therefore, the samples are indeed changing, but these changes cannot be detected by XRD. Fe EXAFS spectra have documented clearly an increase in the number of Fe neighbours 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 unfavourable 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.

Reference

WAYCHUNAS, G.A., REA, B.A., FULLER, C.C. & DAVIS, J.A. (1993): *Geochimica et Cosmochimica Acta*, 57: 2251–2269.