

Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy

ANDREA L. FOSTER,^{1,*} GORDON E. BROWN JR.,^{1,2}
TRACY N. TINGLE,^{1,3†} AND GEORGE A. PARKS¹

¹Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

²Stanford Synchrotron Radiation Laboratory, Stanford, California 94309, U.S.A.

³Center for Materials Research, Stanford University, Stanford, California 94305-4045, U.S.A.

ABSTRACT

X-ray absorption fine structure spectroscopy (XAFS) was used to determine arsenic (As) oxidation state, local coordination (to a radius of ≈ 7 Å around As), and the relative proportion of different As species in model compounds and three California mine wastes: fully oxidized tailings (Ruth Mine), partially oxidized tailings (Argonaut Mine), and roasted sulfide ore (Spenceville Mine). Mineralogy was characterized by Rietveld refinement of X-ray powder diffraction patterns. The spatial distribution of As in the mine wastes (at several micrometers spatial resolution) was determined by electron microprobe analyses. X-ray absorption near edge structure (XANES) analysis indicates that As⁵⁺ is the dominant oxidation state in the mine samples, but mixed oxidation states (nominally As⁰ and As⁵⁺) were observed in the Argonaut Mine waste. Non-linear, least-squares fits of mine waste EXAFS (Extended XAFS) spectra indicate variable As speciation in each of the three mine wastes: As⁵⁺ in the Ruth Mine sample is sorbed on ferric oxyhydroxides and aluminosilicates (probably clay) in roughly equal portions. Tailings from the Argonaut Mine contain $\approx 20\%$ As bound in arsenopyrite (FeAsS) and arsenical pyrite (FeS_{2-x}As_x) and $\approx 80\%$ As⁵⁺ in a precipitate such as scorodite (FeAsO₄·2H₂O); however, no precipitate was detected by X-ray diffraction or microprobe analysis, suggesting that the phase is poorly crystalline or has low abundance (total As in sample = 262 ppm). Roasted sulfide ore of the Spenceville Mine contains As⁵⁺ substituted for sulfate in jarosite [KFe₃(SO₄)₂(OH)₆] or incorporated in the structure of an unidentified Ca- or K-bearing phase, and As⁵⁺ sorbed to the surfaces of hematite or ferric oxyhydroxide grains. Determination of solid-phase As speciation in mine wastes by XAFS spectroscopy is a valuable first step in the evaluation of its bio-availability, because the mobility and toxicity of As compounds vary with oxidation state. As bound in precipitates, as in the Argonaut mine sample, is considered to be less available for uptake by organisms than when sorbed on mineral surfaces or coprecipitated with poorly crystalline phases, as found for the Ruth and Spenceville mine wastes.