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

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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 ≈20% As bound in arsenopyrite (FeAsS) and arsenical pyrite (FeS2-xAsx) and ≈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 bioavailability, 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.

INTRODUCTION

Arsenic (As) is a common constituent of sulfide deposits, often present at the 2–3 wt% level in copper and lead ores and as high as 11 wt% in gold ores (Cullen and Reimer 1989; Azcue and Nriagu 1994). Chronic As poisoning in humans has been associated with the use of contaminated well water from As-bearing aquifer material (Cebrian 1994; Chen 1994; Singh 1995). In arid mining regions or near active smelters, an additional pathway for As exposure exists by ingestion or inhalation of As-rich particulates (Cebrian 1994). Inadvertent or inappropriate use of mine tailings, coal fly ash, and other As-rich surficial material poses a potential threat to human health (e.g., Greenwald 1995; Vogel 1995).

A realistic evaluation of the risk posed by As-bearing tailings piles depends on accurate determination of As speciation, because its toxicity and mobility varies with oxidation state and chemical environment. For example, in vivo studies indicate that the toxicity of reduced As compounds such as gallium arsenide [and by analogy, elemental arsenic (As0) and arsenopyrite (FeAsS)] are significantly lower than inorganic As compounds containing As3+ and As5+, mainly because of their lower solubility (Yamauchi and Fowler 1994). However, upon ingestion reduced arsenic compounds are slowly converted to inorganic As3+ and or As5+ (Cullen and Reimer 1989). Both As3+ and As5+ form anionic species when in aqueous solution, adsorbed to mineral surfaces, or incorporated into precipitates. As5+ adsors more strongly to mineral surfaces than does As3+, thus is generally less mobile (Frost and Griffin 1977; Korte and Fernando 1991).

The mobility of As released during the microbially mediated weathering of sulfide ore and pyrite-bearing shales is