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Technical note

Solid-phase controls on lead partitioning in laboratory bioleaching solutions

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ABSTRACT

The purpose of the work was to examine the co-precipitation of Fe(III) and Pb(II) in *Acidithiobacillus ferrooxidans* cultures under ambient temperature conditions. The competitive formation of plumbojarosite ($PbFe_6(SO_4)_4(OH)_{12}$) and anglesite ($PbSO_4$) was of particular interest with respect to defining the phase(s) controlling Pb solubility. The medium contained no K^+ and a low level of 6.06 mM NH_4^+. Precipitates were prepared in two phases. In the first phase (8 days), *A. ferrooxidans* cultures oxidized ferrous iron to ferric iron (pH 2.4), which partially precipitated as schwertmannite ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$). In the second phase, lead nitrate (up to 100 mmol Pb/l) was added to the schwertmannite-containing culture solutions, and the suspensions were held for an additional 22 days. X-ray diffraction analysis indicated that lead precipitated as anglesite, and ferric iron was associated with schwertmannite and hydronium jarosite. No characteristic X-ray diffraction peaks for plumbojarosite were evident.

1. Introduction

Galena (PbS) is found in sulfide ores, and minor amounts of Pb can be present in other mineral phases such as zinc sulfides. Under aerobic conditions, the S-entity in galena can be oxidized to sulfate by acidophiles such as *Acidithiobacillus ferrooxidans* with the concomitant precipitation of anglesite ($PbSO_4$) (Bang et al., 1995; Chaudhury and Das, 1987; Garcia et al., 1995; Guo et al., 2010; Tipre and Dave, 2004). Because of anglesite ($PbSO_4$) precipitation, the concentration of dissolved lead is usually low under bioleaching conditions (Guo et al., 2010; Wang et al., 2013), and lead inhibition of microorganisms in bioleaching solutions is minimized. Bioleaching may also produce elemental S on galena surfaces. The further oxidation of sulfur to sulfate can sequester lead as anglesite and result in mineral surface passivation (da Silva, 2004; Guo et al., 2010; Olulambi, 2009).

Under acid and sulfate-rich bioleaching conditions (pH ~1.5-2.5), ferric iron is released from a variety of host minerals and partially precipitates due to hydrolysis, resulting in the formation of iron oxides, oxyhydroxides and hydroxysulfates. Among the most common phases are schwertmannite and jarosite-group minerals. Schwertmannite (solubility product K_{sp} 10^{-18}) is a relatively poorly crystalline secondary mineral ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$), whereas jarosites are well crystalline phases formed usually by incorporation of monovalent ions ($M = K^+$, NH_4^+, H_3O^+, or Na^+) into $MFe_3(SO_4)_2(OH)_6$. The K_{sp} values for end members are in the range of $10^{-5.3}$ for Na-jarosite, $10^{-5.4}$ for H_3O-jarosite, and $10^{-9.2}$ for K-jarosite (Parkhurst and Appelo, 1999).

Some divalent metals can replace monovalent cations in jarosites (Dutrizac and Kaiman, 1976). For example, Pb has been reported to precipitate with ferric iron as plumbojarosite, $PbFe_6(SO_4)_4(OH)_{12}$, in sulfate-rich solutions (Eary, 1998; Forray et al., 2010; Gaboreau and Vieillard, 2004; Szymanski, 1985). Plumbojarosite has also been found in solid residues from pressure leaching systems (Dutrizac and Dinardo, 1983; Dutrizac and Kaiman, 1976). Gericke et al. (2008) claimed the formation of plumbojarosite at 45 °C during the bioleaching of a polymetallic sulfide concentrate, but no data were shown to support the presence of this secondary phase. Likewise, Cortez et al. (2009) speculated that lead released during bioleaching of old mine tailings formed plumbojarosite. Steemson et al. (1997) reported that lead occurred in solid residues as anglesite rather than Pb-jarosite upon the bioleaching of a Zn-concentrate, but specific data were not provided to evaluate this finding.

Plumbojarosite has been found in old tailings, sometimes in association with argentian species (Viñals and Núñez, 1988) due to the co-occurrence of Pb and Ag in sulfide ores. For example, the Rio Tinto gossan is known to contain minor amounts of plumbojarosite (Viñals et al., 1995). From an environmental perspective, geochemical and mineralogical zonation of high-sulfide mine wastes has been observed at both mineral (Davis et al., 1994) and landscape levels (e.g., Harris et al., 2003; Sidenko et al., 2005) so that the bioavailability of Pb is controlled by the precipitation of secondary mineral phases such as anglesite and plumbojarosite. Reported solubility constants for anglesite ($K_{sp} = 10^{-7.7}$) and plumbojarosite ($K_{sp} = 10^{-24.3}$–$10^{-28.4}$) indicate

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that both minerals are relatively insoluble (Eary, 1998; Forray et al., 2010; Gaboreau and Vieillard, 2004).

To this end, Davis et al. (1994) observed that Pb-bearing phases associated with mine wastes in the Butte mining district, Montana, USA consisted of galena grains altering to anglesite and plumbojarosite. In studies of the waste dump at the Montalbion silver mine in Queensland, Australia, Harris et al. (2003) reported that anglesite comprised up to 9 vol.% and plumbojarosite up to 3 vol.% of the mine waste. Both occurred as efflorescent minerals in close proximity to parent sulfides. Mine drainage from the site was acidic (pH 2.6–3.8) and led to the formation of Fe-rich precipitates (schwertmannite and goethite) with surface sorbed metals. Recently, Wang et al. (2006) described the formation of schwertmannite and its transformation to jarosite in the presence of acidophilic iron-oxidizing bacteria. Consequently, the potential exists for plumbojarosite to form both as a primary and as a secondary alteration product of Pb-sulfides in bioleaching and environmental systems. Thus, the purpose of this study was to address the possible competitive formation of anglesite and plumbojarosite in solutions simulating bioleaching conditions. The results could have important implications for solid-phase control on the mobility of Pb in the environment.

2. Materials and methods

A mixed culture of *A. ferrooxidans*, a composite of four iron-oxidizing enrichments from boreal mine sites, was used in this study. The culture was grown with 160 mmol/l Fe^{2+} (added as $FeSO_4 \cdot 7H_2O$) in mineral salts media (3.0 mmol $(NH_4)_2SO_4$, 1.6 mmol $MgSO_4 \cdot 7H_2O$, 14.7 mmol H_3PO_4, and 2.5 mmol H_2SO_4 per liter) at initial pH 2.0–2.2. The culture was incubated for 8 days in shake flasks at 22 ± 2 °C and 150 rev/min. Under these conditions, as ferrous iron was oxidized, part of the ferric iron precipitated as schwertmannite. The culture with schwertmannite precipitates was subsequently divided into aliquots that received 0.5, 10, 50, or 100 mmol Pb/l (added as $Pb(NO_3)_2$) followed by further incubation on the shaker for 22 days. The control sample (0 Pb) was further incubated for 20 days. The precipitates were harvested by centrifugation, washed with dilute (50 mmol/l) H_2SO_4 and distilled H_2O, and air dried. Chemical analyses of aqueous Fe or Pb were not undertaken in this study.

Subsamples of the air dried precipitates were oven dried (110 °C) and then dissolved in aqua regia using microwave assisted pressure bombs. Soluble Fe and Pb in the digests were analyzed with inductively coupled plasma spectroscopy. Sulfur was determined by iodometric titration of SO_2 following combustion of the dried samples at 800 °C in a LECO 521 induction furnace (LECO Corporation, St. Joseph, MI). The color of the precipitate samples was recorded in Munsell color notation (Hue, Value and Chroma) using a Minolta CR-300 Chroma Meter (Konica Minolta Photo Imaging, Mahwah, NJ). Mineralogical composition was determined by X-ray diffraction (XRD) using a Philips PW 1316/90 diffractometer (Philips Electronics, New York, NY) with CuKα radiation. The samples were packed into a zero background quartz sample holder and step-scanned from 3 to 70° 2θ using a step interval of 0.05° 2θ and a counting time of 4 s.

3. Results and discussion

Shake flask cultures of *A. ferrooxidans* oxidized 160 mmol Fe^{2+}/l within 2 days, but the cultures were held on the shaker for a total of 8 days to promote the formation of any solid-phase hydrolysis products. Yellowish-red, poorly-crystalline schwertmannite and <5% wt/wt of a jarosite type mineral were formed under these conditions (Fig. 1, Table 1). Presumably, the jarosite phase was hydronium jarosite because the mineral salts solution lacked K^+ and Na^+ for the formation of K-jarosite and Na-jarosite, respectively, and the level of NH_4^+ in the medium, 6.06 mmol NH_4^+/l, was too low to produce ammoniojarosite exclusively (Gramp et al., 2008). Majzlan and Myneni (2005) have also reported that schwertmannite and hydronium jarosite are the phases that control the solubility and short-term availability of Fe and SO_4 in acid sulfate waters deficient in other monovalent cations.

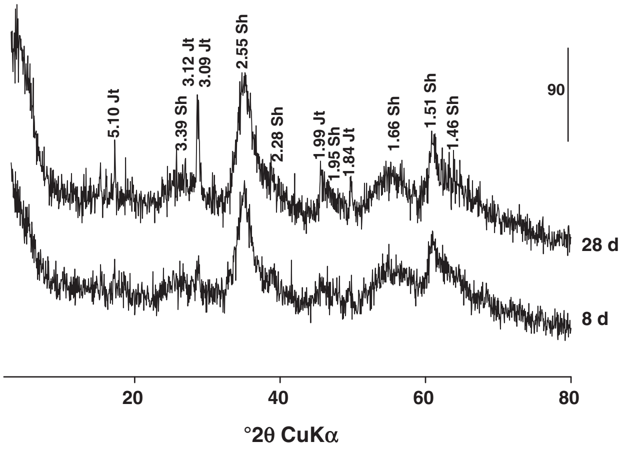

Fig. 1. X-ray diffractograms of precipitates formed in the absence of Pb-nitrate. Schwertmannite is the dominant phase in both 8 day and 28 day Pb-free samples. Peaks due to schwertmannite and a jarosite phase are identified as Sh and Jt, respectively. Numerical values are *d* spacings in Ångstrom units. The vertical bar indicates the scale of relative counts.

The schwertmannite-containing cultures were divided into aliquots, which received 0.5, 5.0, 10, 50, and 100 mmol Pb/l, followed by further incubation for 22 days (i.e., total 30 days of incubation) before the precipitates were harvested and dried. The 0 Pb culture was incubated for a total of 28 days (i.e., 8 days + 20 days) before the second sampling. Schwertmannite remained the dominant Fe mineral after aging in the absence of lead, but diagnostic peaks for the jarosite phase became more intense in the aged, 0 Pb sample (Fig. 1).

Well crystalline anglesite ($PbSO_4$) was formed in all preparations that received Pb-nitrate (Fig. 2). Calculations from the solid-phase chemical compositions indicated the presence of 5–85% (wt/wt) anglesite in these samples (Table 1). Although no mineral phases other than anglesite were detected in the 100 mmol Pb/l preparation, the presence of Fe (10% wt/wt) and the ochreous color of this specimen (Table 1) confirmed the presence of an Fe-bearing mineral that was most likely schwertmannite, already present from the prior culture. The broad, diagnostic peaks for schwertmannite would be easily masked in the background due to a scaling effect from the co-associated, high-intensity peaks for anglesite. The most intense peaks for a jarosite phase at 3.09–3.13 Å (28.9–28.5° 2θ) should have been visible at concentrations approaching 3% wt/wt in this sample, but none were detected.

The primary schwertmannite peak at approximately 2.55 Å was still discernible after 22 days of contact with 0.5, 5.0 and 10 mmol Pb/l, but was lost in the background due to the intense anglesite peaks at higher Pb concentrations (Fig. 2). A jarosite mineral was also easily detected in those samples prepared with 0–50 mmol Pb/l (Fig. 2), and calculations from the bulk chemical analyses suggested these samples contained 3–10% of this phase (Table 1). The intense ($I/I_o = 67$) and interference-free plumbojarosite peak at 11.22 Å (7.85° 2θ) (see ICDD pattern 01-073-1653) was absent (Fig. 2); therefore the phase produced was hydronium jarosite with perhaps some solid solution replacement of H_3O^+ by NH_4^+ since the culture solution contained 6 mM NH_4^+. The mean unit cell parameters for hydronium jarosite occurring in the 0.5, 5, and 10 mmol/l Pb samples were 7.337 ± 0.002 Å and 17.090 ± 0.023 Å for a_0 and c_0, respectively. These parameters and the calculated axial ratios ($c_o/a_o = 2.33$) and unit cell volumes (797 $Å^3$) are consistent with those previously observed for hydronium jarosites from bacterial samples (Wang et al., 2007).

The absence of plumbojarosite, especially in the high Pb preparations, is interesting but perhaps not surprising. Reference plumbojarosites