



Formation and characterization of ternary (Na, NH₄, H₃O)-jarosites produced from *Acidithiobacillus ferrooxidans* cultures

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ABSTRACT

The purpose of this study was to characterize a series of (Na, NH₄, H₃O)-jarosites produced with various combinations of NH₄⁺ + Na⁺ in cultures of *Acidithiobacillus ferrooxidans* that simulated acid solutions from bio-leaching systems. The solution concentrations utilized were 6.1, 80, 160 and 320 mM for NH₄⁺ and 0, 50, 100, 250 and 500 mM for Na⁺ as their respective sulfates. Media at pH 2.2 were inoculated with iron-oxidizing *A. ferrooxidans* and incubated in shake flasks at 22 ± 2 °C. As the bacteria oxidized ferrous sulfate, ferric iron hydrolyzed and precipitated as schwertmannite (idealized formula Fe₈O₈(OH)₆(SO₄)_nH₂O) and/or as solid solution jarosites [(Na, NH₄, H₃O)-Fe₃(SO₄)₂(OH)₆] depending on the relative and absolute concentrations of NH₄⁺ and Na⁺. The precipitates were characterized by elemental analysis, X-ray diffraction, specific surface area, and Munsell color. Schwertmannite was the dominant mineral product at low combinations of Na⁺ (≤50 mM) and NH₄⁺ (≤80 mM) in the media after 2 weeks of aging. At higher single or combined concentrations and with aging for 6 and 11 weeks, the formation of yellowish, solid solution jarosites was enhanced. Precipitation of jarosite-group minerals was favored by NH₄⁺ relative to Na⁺. Color (Munsell hue) was a useful tool for assessing sample mineralogy after extended aging, but the presence of abundant, poorly crystalline schwertmannite tended to mask the color of admixed jarosite-group minerals after only 2 weeks of contact with the culture media. The purest samples of jarosite-type minerals had specific surface areas < 1.0 m²/g. Unit cell edge lengths and cell volume calculations from powder XRD data indicated that the jarositic phases produced were ternary (Na, NH₄, H₃O)-solid solutions. Most products also appeared to be deficient in structural Fe, especially at low NH₄ contents. Thus, ferric iron precipitation from the simulated bioleaching systems yielded solid solutions of jarosites with chemical compositions that were dependent on the relative concentrations of Na⁺ and NH₄⁺ in the synthesis media. No phase separations involving discrete, end-member Na-, NH₄-, or H₃O-jarosites were detected.

1. Introduction

Jarosite group minerals have the general formula (AFe₃(SO₄)₂(OH)₆), where A = Ag⁺, K⁺, Na⁺, NH₄⁺, Rb⁺, Tl⁺, H₃O⁺, Pb²⁺, Ca²⁺, Cu²⁺, Zn²⁺, and Hg²⁺ (Dutrizac and Jambor, 2000). (Note: Hereafter, the appropriate “A” site cation will be used to reference specific minerals within the group so that “jarosite” *sensu stricto* will be referred to as K-jarosite. When the “A” site cation is unspecified or a generic reference to the group or minerals within the group is intended, A-jarosite will be used). A-jarosite group minerals are typically found in acidic, iron- and sulfate-rich environments such as acid mine drainage impacted sediments, acid sulfate soils, and precipitates from bioleaching systems (Bigham and Nordstrom, 2000; Deveci et al., 2004; Blodau, 2006; Fitzpatrick et al., 2017). Most minerals within the group

are relatively stable under natural conditions in the approximate pH range of 1.5–3.0 but are rarely found as pure, end-member species in the environment because of solid solution in the “A” cation sites. Phases dominated by K, Na, NH₄, and Ag are most common and can be synthesized in Fe³⁺-SO₄²⁻ systems that simulate bioleaching solutions (Wang et al., 2007; Gramp et al., 2008; Mukherjee et al., 2016). Under proper hydrothermal conditions (e.g., 140 °C with pressure) the “A” position in these common A-jarosite group minerals can have full occupancy of K, Na, or NH₄ (Basciano and Peterson, 2007a,b; 2008); however, in most synthetic and natural specimens formed under ambient or mildly thermal (up to 70 °C) conditions, “A” position vacancies exist and charge balance is accomplished by H₃O substitution (Brophy and Sheridan, 1965; Basciano and Peterson, 2007a; Casas et al., 2009; Jones et al., 2014). End member H₃O-jarosite is generally formed only

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at elevated temperatures of > 100 °C in alkali deficient systems (Dutrizac and Kaiman, 1976; Driscoll and Leinz, 2005).

In the absence of or with low concentrations of compatible “A”-site cations, ferric iron hydrolysis often produces schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)_n\text{H}_2\text{O}$), a poorly crystallized metastable mineral (Bigham et al., 1994; Majzlan and Myneni, 2005). Schwertmannite may alter to A-jarosite minerals if equilibrated in the presence of structurally compatible cations (Wang et al., 2006), but it more commonly transforms to goethite ($\alpha\text{-FeOOH}$) with increasing pH or ageing (Bigham et al., 1996). Elevated temperatures generally enhance these transformations (Wang et al., 2007). In both types of Fe(III)-hydroxysulfates, i.e., schwertmannite and A-jarosite, the structural sulfate can be partially substituted with arsenate, selenate, chromate, and other oxyanions (Dutrizac and Jambor, 2000; Carlson et al., 2002; Dutrizac and Chen, 2003; Regenspurg and Peiffer, 2005; Liao et al., 2009). The solubility product ($\log K_{sp}$) values of common A-jarosite minerals at 25 °C, calculated from the reaction $\text{AFe}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow \text{A}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O}$, are -12.50 and -9.76 for K-jarosite and NH_4 -jarosite, respectively, and -8.56 and -8.67 for Na-jarosite and H_3O -jarosite, respectively (Gaboreau and Vieillard, 2004), suggesting that equilibrium conditions favor the formation of K- and NH_4 -jarosites. Experimental data on the biogenic synthesis of A-jarosite group minerals are compatible with this differential sequence (Gramp et al., 2008; Bai et al., 2012).

Ferric iron can precipitate as A-jarosite solid phases on mineral surfaces during acid and biological leaching of sulfide minerals (Watling, 2006). In extreme cases, secondary mineral formation leads to a passivation effect, whereby the coating forms a diffusion barrier between the reactive mineral surface and the contacting solution phase (Watling, 2006; Zeng et al., 2010). Controlled precipitation of A-jarosite minerals in leach solution recirculation systems can be used to moderate these problems (Nurmi et al., 2010; Kaksonen et al., 2014a,b; Sheng et al., 2017). The precipitation of A-jarosites to remove Fe and other impurities from hydrometallurgical circuits also has application in the zinc industry (Dutrizac, 1982; Dutrizac and Jambor, 2000).

Our earlier work (Wang et al., 2006, 2007; Gramp et al., 2008, 2009) has examined the formation of various A-jarosite group minerals under conditions that simulated acid bioleaching systems at ambient or near-ambient temperatures. More recently, we have also studied the chemistry and mineralogy of ternary (K- NH_4 - H_3O)-jarosites precipitated from mixed solutions of K and NH_4 sulfate (Jones et al., 2014). While complete solid solution among K-, NH_4 -, Na-, and H_3O -jarosites is possible, there is a natural tendency for K-jarosite to precipitate first in mixed solution because of the previously described solubility relationships (Basciano and Peterson, 2007a). Even though the ionic radii of K^+ and NH_4^+ are similar at 1.64 vs 1.67 Å and significantly larger than Na^+ (1.39 Å) and H_3O^+ (1.52 Å) in 12-fold coordination (Basciano and Peterson, 2008; Sidey, 2016), Dutrizac and Jambor (2000) have suggested that NH_4^+ is only slightly superior to Na^+ in the precipitation of A-jarosite phases. For that reason, the purpose of the present study was to synthesize and characterize the mineral products formed by iron-oxidizing cultures of *A. ferrooxidans* from mixed sulfate solutions of the monovalent cations Na^+ and NH_4^+ under ambient conditions. We also attempt to better understand the effect of equilibration time (aging) on the mineral products.

2. Materials and methods

2.1. Bacterial cultures and media for mineral synthesis experiments

An iron-oxidizing bacterial consortium dominated by *A. ferrooxidans* (Gramp et al., 2008) was used throughout this study. The culture was maintained in mineral salts solution with ferrous iron as the source of energy and ambient air for CO_2 and O_2 . The medium was designed to prevent K- or Na-jarosite precipitation because it was devoid of K^+ and Na^+ (0.4 g (NH_4) $_2\text{SO}_4$, 0.4 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.36 g H_3PO_4 per liter of

10 mM H_2SO_4 , with 120 mM Fe^{2+} added as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, pH 2.2–2.4). In addition, the concentration of NH_4^+ (6.1 mM) was sufficient to serve as a nitrogen source for the bacteria but too low for the precipitation of NH_4 -jarosite (Wang et al., 2007).

The solutions for mineral synthesis experiments were prepared with a range of Na^+ concentrations (0, 50, 100, 250, and 500 mM Na^+ added as Na_2SO_4) in combination with 6.1, 80, 160 or 320 mM NH_4^+ added as $(\text{NH}_4)_2\text{SO}_4$. The range of Na concentrations was based on initial screening experiments for Na-jarosite precipitation as a function of $[\text{Na}^+]$. The $(\text{NH}_4)_2\text{SO}_4$ concentrations were based on the same range used in a previous study on the formation of NH_4 -jarosites (Wang et al., 2007). The concentration of Fe^{2+} was increased to 160 mM in order to improve the precipitate yield, and the growing cultures were incubated at 22 ± 2 °C in shake flasks at 120 rev/min. Even though complete oxidation of Fe^{2+} was achieved within 3–4 d, an initial time course of 2 weeks was adopted to enhance yields. This equilibration time was ultimately extended to 6 weeks or 11 weeks for some samples to further boost yields and the formation of A-jarosite group minerals in particular. Precipitates from spent cultures were collected by centrifugation at $15,300 \times g$ for 10 min, followed by washing with 10 mM H_2SO_4 and double distilled H_2O . The samples were air dried at 22 ± 2 °C and stored in a desiccator until analyzed.

2.2. Analytical methods

Total sulfur contents of the precipitates were determined by iodometric titration of SO_2 evolved following sample combustion at 800 °C in a LECO model 521 induction furnace (LECO Corp., St. Joseph, MI). Total Fe, K, and Na were measured by atomic absorption spectroscopy on a SpectrAA-5 instrument (Varian, Palo Alto, CA) following complete dissolution of samples in 6 M HCl over a 24 h period. Total N was determined using a Thermoquest NC 2100 soil analyzer (CE Instruments, Milan, Italy) with atropine as the standard.

Color measurements were performed using a Minolta CR-300 Chroma Meter (Konica Minolta Photo Imaging, Mahwah, NJ). Colors were recorded using Munsell color notations involving hue, value and chroma. Surface area measurements were determined using a Micromeritics Flowsorb II 2300 surface area analyzer (Micromeritics, Norcross, GA). Precipitates were added to U-tube sample holders and dried over P_2O_5 for 24 h before analysis using the single-point Brunauer-Emmett-Teller (BET) method with N_2 as the adsorbate.

Powder X-ray diffraction (XRD) was performed using a Philips PW 1316/90 diffractometer (Philips Electronics, New York, NY) with $\text{CuK}\alpha$ radiation in combination with a diffracted-beam monochromator. All samples were packed into a zero background quartz sample holder and step-scanned from 3 to 80 ° 2θ using a step interval of 0.05 ° 2θ and a counting time of 4 s.

The Bruker DIFFRAC.EVA (Release 2009, Bruker AXS GmbH, Karlsruhe) evaluation software module, part of the DIFFRAC.SUITE software platform for phase identification and X-ray data analysis, was used in scan processing and for obtaining structural parameters as described by Jones et al. (2014). The DIFFRAC.EVA tune cell function enables manual fitting of reference patterns to experimental scans in order to simulate the structural effects of solid solution. Starting parameters from H_3O -jarosite were chosen for these simulations because its c_0 unit cell length is approximately midway between those of NH_4 - and Na-jarosite. A synthetic reference H_3O -jarosite (PDF # 31–0650, S.G. 166, R3m) was selected from the powder diffraction database in the form of a “reduced” scan consisting of a collection of relative intensities and corresponding 2θ angles (Jenkins and Snyder, 1996). Reflections of the reduced H_3O -jarosite reference pattern were overlain onto $\text{K}\alpha_2$ -stripped experimental scans and manually adjusted, thereby yielding a modified reduced pattern with a_0 and c_0 axial cell lengths. Invoking the DIFFRAC.EVA full pattern matching (FPM) utility created a simulated scan built over the modified pattern framework by adjusting peak shape, broadening, asymmetry and position to minimize discrepancies

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