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Effects of initial Fe^{2+} concentration and pulp density on the bioleaching of Cu from enargite by *Acidianus brierleyi*

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ABSTRACT

To maximize Cu recovery and minimize As release during the bioleaching of enargite (Cu_3AsS_4) by *Acidianus brierleyi* at 70 °C, the initial Fe^{2+} ion concentration and pulp density were investigated in batch tests. A maximum Cu recovery of 91.0 ± 0.5% was obtained with an initial Fe^{2+} ion concentration of 1.8–2.7 g/L and a pulp density of 1.0%. As the immobilization of As depended on the formation of scorodite ($FeAsO_4 \cdot 2H_2O$) and cupric arsenate, a more rapid and stable As immobilization was achieved with an initial Fe^{2+} ion concentration of 2.7 g/L. Thus the initial Fe^{2+} concentration of 2.7 g/L and 1.0% pulp density provided for a combination of As precipitation and >90% Cu recovery. When the initial Fe^{2+} concentration was increased, K-jarosite ($KFe_3(SO_4)_2(OH)_6$) precipitated, leading to passivation of the enargite surface. When the initial Fe^{2+} concentration was lowered, the Cu recovery was incomplete due to insufficient oxidation. Elevating the pulp density to 2.0% showed that the increase in Eh significantly lagged behind the exponential phase in the planktonic cell growth curve. Pulp density also clearly affected the makeup of secondary minerals in solid residues after the bioleaching of enargite. There is a tendency for dissolved Fe^{3+} ions to readily precipitate as potassium jarosite at relatively smaller pulp densities and as scorodite at relatively larger pulp densities.

1. Introduction

Enargite (Cu_3AsS_4) is a representative copper-arsenic sulfide mineral similar to tennantite. Although enargite is also a valuable copper resource, the arsenic in the mineral makes it potentially environmentally toxic in metallurgical processing because of the emissions associated with smelting (Dutré and Vandecasteele, 1995). This scenario makes enargite a good candidate for beneficiation through bioleaching processes. In general, the bioleaching of sulfide minerals is strongly dependent on biochemical engineering factors such as microorganisms, culture history, inoculum size, carbon and oxygen supply, toxic metals, pH, temperature, and pulp density (Bosecker, 1997; Tshilombo et al., 2002). Many of these factors have been tested in efforts to maximize the bioleaching of valuable metals. Previous publications on the bioleaching of enargite have focused on the bioleaching of Cu by mesophilic bacteria (Acevedo et al., 1998; Corkhill et al., 2008; Escobar et al., 2000; Watling 2006) and thermophilic bacteria and archaea (Escobar et al., 2000; Muñoz et al., 2006).

In the case of enargite, it is also necessary to consider minimizing the As release in addition to maximizing the Cu recovery. The predominant mechanism of immobilization of As in the bioleaching of enargite with the thermophilic iron-oxidizing archaeon, *Acidianus brierleyi*, is the formation of scorodite ($FeAsO_4 \cdot 2H_2O$) (Takatsugi et al., 2011). In this process, the Fe^{3+} ions serve two functions: (i) as oxidants of enargite, and (ii) as a source of secondary Fe(III) precipitates, including jarosite and scorodite. Since both Fe and As are components of scorodite, the initial Fe^{2+} concentration and pulp density of enargite in the bioleaching system are important controlling factors of the bioleaching and secondary mineral formation. The present work focused on these two variables, the initial Fe^{2+} concentration and pulp density, in experiments to improve Cu recovery and immobilize As released from enargite.

2. Materials and methods

2.1. Mineral

The museum-grade specimen of enargite was obtained from Jinguashi Mines, Taipei, Taiwan. The sample was ground to the −77 to +38 μm size range inside a glove box that was purged with 99.999% nitrogen gas. The elemental composition of enargite was (per g): 422 mg Cu; 171 mg As; 288 mg S; 35.4 mg Si; 3.91 mg Sb; 4.59 mg Fe; 13.7 mg Al; 34.2 mg Na; 4.62 mg K; 1.34 mg P; 1.25 mg Zn; and 19.9 mg others. This corresponds to a Cu:As:S mol ratio of 2.91:1.00:3.94. The enargite purity was estimated to be 88.1%, assuming that all Cu was

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associated with enargite. Enargite was the predominant sulfide mineral in the sample, as also confirmed by X-ray diffraction (XRD).

2.2. Culture conditions

Acidianus brierleyi (DSM 1651), a thermophilic and acidophilic archaeon, was obtained from the German Collection of Microorganisms and Cell Cultures (Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH), Braunschweig, Germany. It was subcultured in modified DSM 150 medium containing (per L): 3.0 g $(NH_4)_2SO_4$, 0.1 g KCl, 0.5 g K_2HPO_4, 0.5 g $MgSO_4 \cdot 7H_2O$, 0.01 g $Ca(NO_3)_2 \cdot 4H_2O$, 0.2 g yeast extract, and 0.9 g Fe^{2+} (added as $FeSO_4 \cdot 7H_2O$) at pH 1.5 and 70 °C.

2.3. Bioleaching

In the bioleaching experiments, enargite (0.5 g) was placed in 200-mL conical flasks with 50 mL of 9 K basal medium that contained (per L) 3.0 g $(NH_4)_2SO_4$, 0.1 g KCl, 0.5 g K_2HPO_4, 0.5 g $MgSO_4 \cdot 7H_2O$ and 0.01 g $Ca(NO_3)_2 \cdot 4H_2O$) (Silverman and Lundgren, 1959). To investigate the influence of the initial concentration of Fe^{2+} on the bioleaching of enargite, batch tests were carried out with different initial Fe^{2+} concentrations. The required amounts of $FeSO_4 \cdot 7H_2O$ were added into the medium to adjust the initial concentrations of Fe^{2+} to 0.9, 1.8, 2.7, and 3.6 g/L. *A. brierleyi* was inoculated to a cell density of 1.0×10^7 cells/mL. The flasks were incubated in a water bath shaker (Sanki Seiki Co. Ltd, Osaka, Japan) at 100 strokes (70 mm each)/min and at 70 °C. A range of pulp densities from 0.5% to 2.0% was also investigated with an initial Fe^{2+} concentration of 2.7 g/L. At intervals, samples were removed for pH and Eh (vs. NHE) measurements and planktonic cell counts. Cell counts were determined in leach solutions microscopically at 600× with a counting chamber. Samples were filtered (0.20 μm) for the determination of Cu and As concentrations with inductively coupled plasma atomic emission spectrometry (ICP-AES, Vista-MPX, SII, Chiba, Japan) and total dissolved Fe and Fe^{2+} concentrations by the 1,10-phenanthroline method (Tamura et al., 1974). The concentration of dissolved As^{3+} (arsenite) species from enargite was determined with HPLC (TOSOH DP-8020, Tokyo, Japan) coupled with ICP-mass spectrometry (ICP-MS, Agilent 7500ce, Hachioji, Japan).

The solid residues were sampled at the end of each time course. They were recovered by filtration and freeze-drying overnight before analysis by XRD using a Rigaku Multi Flex (Akishima, Japan) with CuKα 40 mA and 20 kV, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) using a Keyence VE-9800 (Osaka, Japan) and Genesis XM2 (Osaka, Japan), and X-ray photoelectron spectroscopy (XPS) using a PHI 5800 ESCA system (Chanhassen, MN). The collected XP spectra were analyzed with Casa XPS software (Ver. 2.3.12). Background corrections were made using the Shirley method for O 1 s, C 1 s, Cu 2p, S 2p and As 3 d spectra (Shirley, 1972). Peak shapes were defined using a Gaussian-Lorentzian mixed function. The C-C binding energy, E_B[C 1 s], from the vacuum pump oil in the apparatus has a well-defined value at 284.6 eV, which was used as a reference peak to correct for differential charging effects. The speciation of As in the residues was also analyzed by X-ray absorption near-edge structure (XANES) after dilution with boron nitride (Wako Chemicals, special grade, Osaka, Japan). The As K-edge XANES spectra for the residues and several standards were collected at beam line BL12C in the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. For transmission electron microscopy (TEM) observation, the powdery solid residues were fixed in epoxy resin and sliced with a Reichert Ultracut C Ultramicrotome to thin sections with a 100 nm thin section before examination using an FEI Tecnai-20 transmission electron microscope (TEM, Phillips, Netherlands) coupled with EDS.

3. Results and discussion

3.1. Effect of the initial Fe^{2+} concentration on the bioleaching of enargite

Fig. 1(a), (b), and (c) shows the changes in pH, Eh and planktonic cell counts during the bioleaching of enargite with different initial Fe^{2+} concentrations. In all inoculated cultures, the pH gradually decreased due to the production of sulfuric acid during the bioleaching. The Eh and cell counts first increased within 10 days and started to decrease after 35 days of leaching with an initial Fe^{2+} concentration ($[Fe^{2+}]_{ini}$) of 0.9 g/L. No decrease in Eh or cell numbers were observed during the

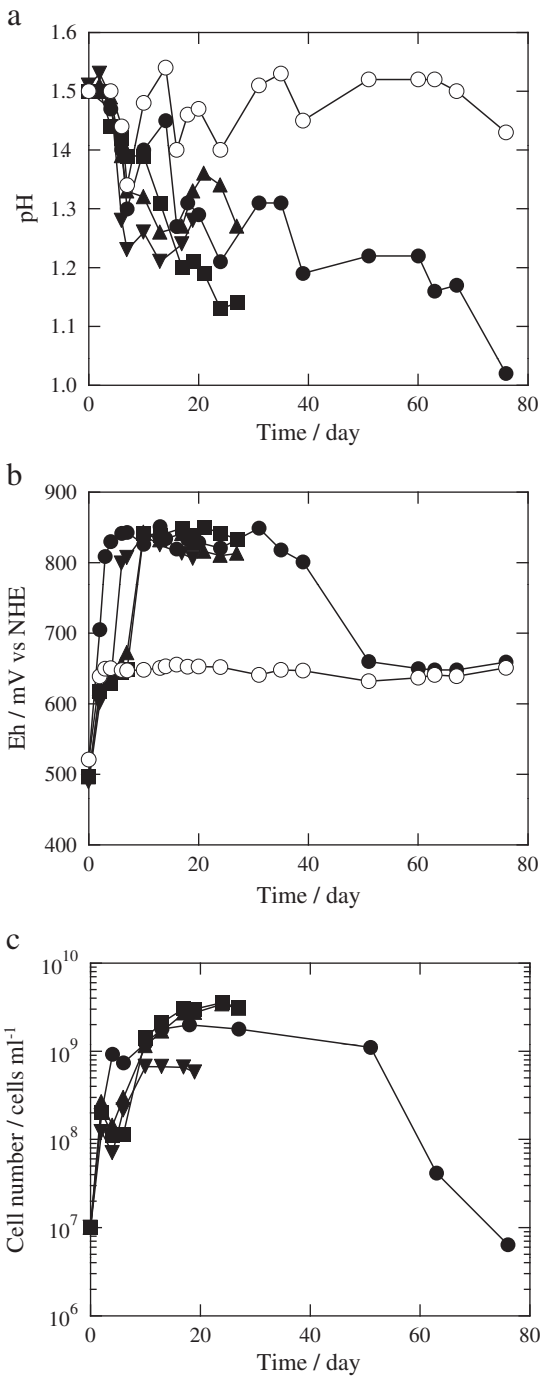

Fig. 1. Changes in (a) pH, (b) Eh, (c) planktonic cell counts, (d) Cu, and (e) As during the bioleaching of enargite by *A. brierleyi* at 70 °C. The initial Fe^{2+} concentrations were 0.9 g/L (● and ○), 1.8 g/L (■), 2.7 g/L (▲), and 3.6 g/L (▼). Solid and open symbols indicate inoculated and sterile samples, respectively.