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Improvement of Cu Recovery in Chalcopyrite Bioleaching System via Microbial Redox Potential Control

Yusei Masaki, Tsuyoshi Hirajima, Keiko Sasaki, Hajime Miki, and Naoko Okibe*
Department of Earth Resources Engineering, Kyushu University, Fukuoka 819-0395, Japan
**Correspondence*

Abstract
Development of copper (Cu) extraction techniques from low-grade refractory sulfides, such as chalcopyrite, has been actively studied to maximize its Cu recovery in bioleaching system. Since involvement of chalcocite as an intermediate has recently been proposed during chemical leaching at low-redox potentials and the solution redox potential level was found to strongly affect Cu extraction efficiency, the potential of microbiological control of solution redox potentials during chalcopyrite bioleaching was investigated in this work. Two different mixed cultures were used for bioleaching test; *Acidithiobacillus caldus* KU (sulfur-oxidizer) mixed with either *Sulfobacillus* sp. YTF1 (weaker iron-oxidizer; "mixed culture A") or *Acidiplasma* sp. Fv-Ap (strong iron-oxidizer; "mixed culture B"). Recovery of Cu in mixed cultures A and B, reached 75 and 49%, respectively, at day 70. The difference in final Cu recovery in the two mixed cultures can be attributed to the solution redox potential levels during bioleaching: E_{normal} values in the former were in the range of $0<E_{normal}<1$, whereas those in the latter were $1<E_{normal}$.

1. Introduction

Copper (Cu) is one of the most essential elements for our society with a number of industrial usages. However, we have been facing the problem with a lack in high grade secondary copper sulfides. This has motivated many research groups to develop efficient Cu extraction techniques from refractory primary copper sulfides such as chalcopyrite ($CuFeS_2$), via chemical leaching and bioleaching. Hiroyoshi et al. (2000, 2001) reported that chalcopyrite dissolution proceeds via formation of chalcocite (Cu_2S) as an intermediate, and is strongly affected by solution redox potentials [1, 2]: The formation (Eq. 1) and oxidation (Eq. 2) of chalcocite was found to facilitate dissolution of chalcopyrite as follows:

$$CuFeS_2 + 3Cu^{2+} + 4e^- = 2Cu_2S + Fe^{2+} \quad \text{(Eq. 1)}$$

$$Cu_2S = 2Cu^{2+} + S^0 + 4e^- \quad \text{(Eq. 2)}$$

Okamoto et al. (2004) defined "E_{normal}" to evaluate optimal redox potential levels for the chalcopyrite leaching system, and proposed that chalcopyrite dissolution can be maximized at the E_{normal} value of 0.43 [3].

$$E_{normal} = (E - E_{ox}) / (E_c - E_{ox}) \quad \text{(Eq. 3)}$$

, where E, E_{ox}, and E_c indicate the solution redox potential, oxidation potential for chalcocite, and critical potential of chalcocite formation, respectively.

Owing to several advantages with bioleaching techniques (e.g., applicable to refractory lower Cu grade ores, with relatively low cost) for the practical Cu extraction process, chalcopyrite bioleaching has been actively studied to improve its efficiency. However, the effect of the redox potential level on the chalcopyrite bioleaching system has yet been studied in detail. This study thus aimed to investigate how solution redox potentials affect Cu recovery efficiency in bioleaching systems.

2. Materials and Methods

All the bioleaching tests were conducted in 500 mL Erlenmeyer flasks containing 200 mL HBS media (pH 2.0 with H_2SO_4) supplemented with 0.01% (w/v) S^0, 5 mM Fe(II), trace elements [4], and 1% (w/v) chalcopyrite concentrate. Two mixed cultures A (KU + YTF1) and B (KU + Fv-Ap), were prepared with the initial cell densities of 2.0×10^7 cells/mL in total (1.0×10^7 cells/mL of each strain). Yeast extract (0.01% (w/v)) was added to mixed culture B only. All the media were maintained at 45°C on an orbital rotary shaker at 150 rpm. Samples were regularly taken to monitor cell density, pH value, solution redox potential value, and concentrations of Fe(II) (*o*-phenanthroline method), total soluble Fe, and total soluble Cu (ICP-OES). All the experiments were carried out in duplicates.

3. Results and Discussion

Sulfobacillus sp. YTF1 is a moderately thermophilic acidophile with relatively weak Fe(II)-oxidizing capability compared with *Acidiplasma* sp. Fv-Ap. The two Fe(II)-oxidizers were selected in this study in order to establish two different E_{normal} ranges during the bioleaching test; $0<E_{normal}<1$ (mixed culture A) or $1<E_{normal}$ (mixed culture B). Yeast extract was added to mixed culture B (KU + Fv-Ap), in order to maximize Fe(II)-oxidizing capability of strain Fv-Ap.

Recovery of Cu in mixed cultures A (KU + YTF1) and B (KU + Fv-Ap), reached 75 and 49%, respectively, at the end of the experiment (day 70), while that in sterile controls was 20% (Fig. 1). The difference in final Cu recovery was likely due to a difference in the solution redox potential level (E_{normal} values) in the two mixed cultures and sterile controls. In mixed culture A (KU + YTF1), the solution redox potentials gradually increased up to around 620 mV (vs. SHE) until day 29, and remained stable until day 70, owing to the relatively weak Fe(II)-oxidizing capability of strain YTF1. On the other hand, a sudden increase in solution redox potentials up to around 770 mV was observed at day 10 in mixed culture B (KU + Fv-Ap), owing to the stronger Fe(II)-oxidizing activity of strain Fv-Ap. Consequently, the E_{normal} values in mixed culture A stayed stable at around 0.5 after day 16 until the end of the experiment, while those in mixed culture B were kept high (over 1) throughout the bioleaching test.

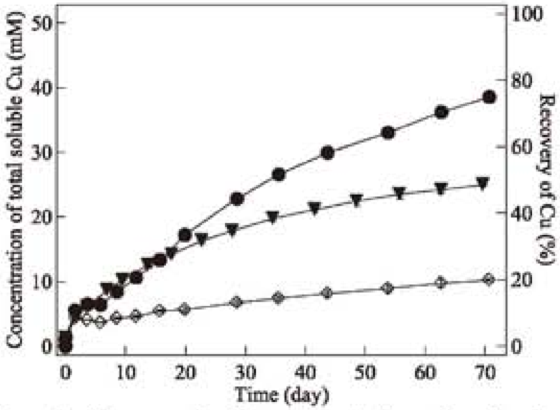

Figure1. Changes in Cu concentrations in mixed cultures A (KU + YTF1; ●), B (KU + Fv-Ap; ▼), and sterile controls (◇).

Chalcopyrite dissolution can be promoted via formation of intermediate chalcocite, when the E_{normal} values are maintained in the range; $0<E_{normal}<1$, with the optimum of 0.43 [3]. Therefore, two different E_{normal} levels in mixed cultures differently affected Cu extraction behaviors: Fifty percent improvement in final Cu recovery in mixed culture A compared with B was found since E_{normal} values in the former were well at the middle of the range $0<E_{normal}<1$, whereas those in the latter were out of the range. Although E_{normal} values in sterile controls were always maintained at the lower level of the range $0<E_{normal}<1$, Cu recovery was not effective since oxidation of chalcocite might not have been promoted. The efficiency of chalcopyrite bioleaching was found to be improved in the specific E_{normal} range between 0-1, especially at the middle of the range: The use of relatively weak microbial Fe(II) oxidizing ability was shown to be effective for maximization of bioleaching efficiency.

4. Conclusions

The effect of the microbiological control of solution redox potentials on the chalcopyrite bioleaching efficiency was investigated using mixed cultures; *At. caldus* KU with either *Sulfobacillus* sp. YTF1 (weak Fe(II)-oxidizer) or *Acidiplasma* sp. Fv-Ap (strong Fe(II)-oxidizer). Recovery of Cu in mixed cultures A and B reached 75 and 49%, respectively, at day 70, owing to different levels of E_{normal} values: Final Cu recovery in the former mixed culture was readily improved by maintaining the optimal E_{normal} levels within the range $0<E_{normal}<1$. Effectiveness of redox potential control by naturally-occurring microbial Fe(II)-oxidizing ability was proposed for maximization of Cu recovery from refractory chalcopyrite.

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Email: y-masaki11@kyushu-u.ac.jp

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