

AC-catalyzed enargite bioleaching using moderately thermophilic bacteria

Keishi Oyama, Naoko Okibe

Department of Earth Resources Engineering, Graduate School of Engineering, Kyushu University

Email: o.keishi8219@gmail.com

Abstract: *The catalytic effect of activated carbon (AC) was evaluated in the bioleaching of enargite concentrate using moderately thermophilic bacteria. Rapid pyrite dissolution began at the beginning of the experiment in the absence of AC, which was increasingly delayed by addition of 0.1% and 0.2% AC. Suppression of pyrite dissolution was likely the result of the lower Eh level. While final copper (Cu) recovery was improved by the addition of AC, this was not much contributed by the galvanic interaction between enargite and AC. A kinetic study using the shrinking core model revealed that Cu dissolution continued steadily at lower Eh under suppression of pyrite dissolution, improving the final Cu recovery. Addition of AC also facilitated the arsenic (As) immobilization. However, re-solubilization of once-immobilized As was observed coincided with rapid iron (Fe) dissolution, which might trigger the re-solubilization of As-precipitates.*

Keywords: Copper; Arsenic; Bioleaching; Activated Carbon; Enargite

1. INTRODUCTION

Due to the decrease in the Cu grade of ores, the contamination of As as an impurity increasingly becomes a serious problem. Although enargite (Cu_3AsS_4), known as one of the major As-bearing copper sulfides, is considered as a hazardous material, its potential usage as the Cu resource is not negligible, requiring a novel process which enables selective extraction of Cu from enargite. Bioleaching is expected to be one of the promising techniques and high-temperature (70°C) bioleaching was indeed shown to be effective (>90% Cu extraction; Takatsugi et al., 2011). On the other hand, it still needs to be improved under low-temperature (25-30°C) conditions (<5% Cu extraction; Sasaki et al., 2010), indicating the necessity of the reaction catalyst for further improvement.

As a catalyst to solubilize refractory minerals, AC has been tested by some studies. Its effectiveness on the bioleaching of chalcopyrite (CuFeS_2) has already been confirmed, achieving >70% Cu recovery (Liang et al., 2010). Basically, the mechanism of AC-catalyzing effect on chalcopyrite dissolution have been reported as electrochemical galvanic reaction. However, its effect on enargite bioleaching has yet been clarified. Some studies have been carried out, which imply that the presence of AC modify the surface of enargite, while the discussion have yet been reached consensus.

The objective of this study was therefore set to evaluate the effect of AC on the bioleaching of enargite and to elucidate its mechanisms for further improvement of the Cu extraction technique.

2. MATERIALS&METHODS

The enargite concentrate used for this study was derived from Peru, mainly containing enargite (Cu_3AsS_4 ; 37.4%) and pyrite (FeS_2 ; 47.3%). Elemental composition of the concentrate is as follows: S 39%, Fe 22%, Cu 20%, As 7.1%, Zn 0.39%, Sb 0.32%, Al 0.22%.

Mixed culture of three moderately thermophilic bacteria (*Acidimicrobium ferrooxidans* ICP, *Sulfobacillus sibiricus* N1, and *Acidithiobacillus caldus* KU) was utilized for bioleaching experiments. The initial cell density of each strain was set to 1.0×10^7 cells/mL (3.0×10^7 cells/mL in total). Bioleaching tests were carried

out in 500 mL Erlenmeyer flasks containing 200 mL of heterotrophic basal salts media (Oyama et al, 2018; pH adjusted to 2.0 with H_2SO_4) with 2.0% (w/v) enargite concentrate and 5 mM Fe(II) (as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Different concentrations of AC (0-0.3% (w/v)) were added as a catalyst. The flasks were incubated shaken at 150 rpm and 45°C for 60 days. Liquid samples were regularly withdrawn to monitor cell density, pH, Eh (vs. SHE), Fe(II) concentration (o-phenanthroline method), As(III) concentration (molybdenum blue method), and total soluble Fe, Cu and As concentrations (ICP-OES). Leaching slurry sample was also obtained to clarify the microbial diversity during the bioleaching test by Real-Time PCR. Leaching residues were freeze-dried overnight and analyzed by XRD and EPMA. In order to understand the effect of galvanic reaction, an electrochemical analysis was also carried out.

3. RESULTS&DISCUSSION

3.1 Suppression of Pyrite Dissolution by AC

In the absence of AC, rapid dissolution of Fe from pyrite began at day 7, readily reaching >80% Fe solubilization by day 40. Addition of 0.1 and 0.2% AC increasingly delayed pyrite dissolution to day 25 and 35, respectively. At 0.3% AC, pyrite dissolution was suppressed almost completely until day 60. This trend was accompanied by lower Eh levels during bioleaching, and it took 7 (0% AC), 25 (0.1% AC), and 35 days (0.2% AC) to reach 700 mV: Since it has been reported that rapid dissolution of pyrite begins at 700 mV in bioleaching cultures (Gu et al., 2012), AC likely played a role in this study to maintain the lower Eh level to delay unwanted pyrite solubilization. The preliminary experiment confirmed that sulfur (S)-ion species such as $\text{S}_4\text{O}_6^{2-}$ are oxidized on the surface of AC coupled with Fe(III) reduction. This suggests that lower Eh was the result of Fe(III) reduction on the AC surface coupled with the oxidation of RISCs (reduced inorganic sulfur compounds) deriving from sulfide minerals. Microbial population analysis by Real-Time PCR revealed that the abundance of S-oxidizer, *At. caldus* KU, decreased from 71% (0% AC) to 62% (0.1% AC) and 30% (0.2% AC), implying that the consumption of RISCs on the AC surface led to depletion of the energy source

for this S-oxidizer.

3.2 Enhancement of Cu Dissolution by AC

In sterile controls, final Cu recovery at day 60 was improved from 11% to 23% by the addition of 0.3% AC. A similar effect was observed in bioleaching cultures; Cu recovery at day 60 was improved from 36% (0% AC) to 46% (0.1% AC) and 53% (0.2% AC). In order to confirm the possible galvanic effect on Cu dissolution, electrochemistry of the pyrite-enargite system and the AC-enargite system were examined. At higher Eh (>800 mV), a relatively high galvanic current was observed, indicating that galvanic reaction could significantly facilitate enargite dissolution (Fig. 1). However, under lower Eh conditions (<700 mV), where relatively fast Cu dissolution was observed in the actual bioleaching experiment, the galvanic current was less than 1 μ A and only minor difference between the pyrite-enargite system and the AC-enargite system was seen (Fig. 1). These results showed that contribution of the galvanic effect on enargite dissolution is negligible in AC-assisted bioleaching systems.

In order to explain the reason why final Cu recovery was improved by the addition of AC, a kinetic study using the shrinking core model was carried out. Increasing the AC concentration led to a decrease in the rate constant value, but prolonged the period of surface chemical reaction as the rate-limiting step from 7 days (0%) to day 25 (0.1%), 35 (0.2%), and 60 days (0.3%). Since the surface chemical reaction period ended by the initiation of rapid pyrite dissolution, preventing pyrite dissolution by AC addition was shown to be the key to support longer and more stable Cu dissolution for greater final Cu recovery.

3.3 Immobilization of As and its Re-solubilization

The amount of As re-immobilization was facilitated by AC addition from 3.1 mM (0% AC at day 10) to 6.9 mM (0.2% AC at day 40, corresponding to 77% of dissolved As). However, once-immobilized As began to re-solubilize at day 10, 30, and 40 in the presence of 0, 0.1, and 0.2% AC, respectively. Since this As re-solubilization was coincident with the initiation of rapid Fe dissolution, it is possible that high dissolved Fe concentrations have the effect of triggering re-solubilization of As-precipitates. EPMA analysis revealed that ferric arsenate (Ferric arsenic) was selectively precipitated on the surface of enargite grains before the As re-solubilization started.

4. REFERENCES

- [1] Takatsugi, K. et al., Hydrometallurgy, 109 (2011) 90-96.
- [2] Sasaki, K. et al., Hydrometallurgy, 109 (2011) 153-160.
- [3] Liang, C. et al., Hydrometallurgy, 105 (2010) 179-185.
- [4] Oyama et al., Hydrometallurgy, 177 (2018) 197-204.
- [5] Gu et al., Transactions of Nonferrous Metals Society of China, 22 (2012) 1250-1254.

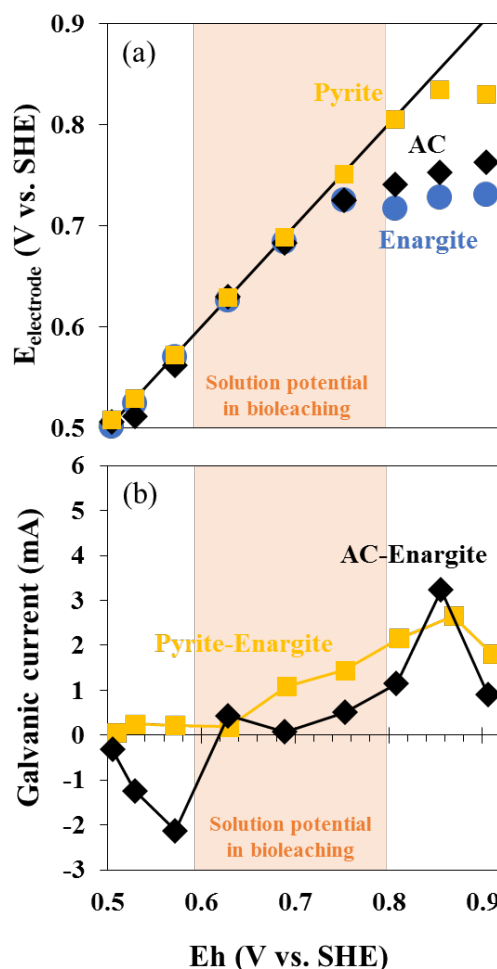


Fig. 1 Electrode potentials in the enargite-pyrite system and the enargite-AC system (a), and the galvanic current in each of the two systems (b) tested in various Eh solutions.