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Effect of pH reduction and ferric ion addition on the leaching of chalcopyrite at thermophilic temperatures

Javier Vilcáez *, Ryoichi Yamada, Chihiro Inoue

Graduate School of Environmental Studies, Tohoku University, Aoba 6-6-20, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

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ABSTRACT

Up to now various methods including bioleaching with thermophilic archea have been studied to enhance the leaching of chalcopyrite. However, the combined effect of pH and low ORP values at thermophilic temperatures (65–80 °C) has attracted little attention. Therefore, in this work, various chalcopyrites including two concentrates and two ore minerals were leached to study the combined effect of pH and ORP. It was found that a temperature of 65 °C at an initial pH of 1.0 can lead to copper extractions comparable to those obtained in bioleaching with *A. brierleyi* and *S. metallicus*. Furthermore, at an initial pH of 1.0, the addition of Fe^{3+} (200 mg/L) at concentration much lower than the usually employed (e.g. 5000 mg/L), where formation of iron salt precipitates could be avoided and low ORP values (<450 mV) could be induced, higher leaching yields than in thermophilic bioleaching were obtained. In addition to the low ORP values derived from the presence of low amounts of Fe^{3+}, the notable enhancement is attributed to the generation of sufficient amounts of Fe^{3+} that resulted from the oxidation of Fe^{2+} by oxygen at an initial pH of 1.0 and 65–80 °C without the aid of thermophiles. The oxidation of Fe^{2+} by oxygen only took place under the presence of sulfides such as Cu_2S or CuS.

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1. Introduction

The successful results obtained in bioleaching sulfide minerals such as chalcocite have motivated extensive research to extend the use of bacteria to bioleach chalcopyrite. However, the copper extraction yields obtained in bioleaching chalcopyrite with mesophilic bacteria are still unsatisfactory. Subsequent researches on thermophilic bioleaching have shown that the copper extraction yields are notably enhanced if archea with a preference for oxidizing sulfur rather than ferrous ion are employed instead of conventional mesophilic bacteria.

However, contrary to the case of mesophilic bioleaching, the contribution of temperature in thermophilic bioleaching should not be underestimated. The reactions involved in the leaching of chalcopyrite can be grouped into acid generation (Eqs. (3) and (4)), acid consumption (Eq. (2)), ferric ion generation (Eq. (2)) and ferric ion consumption (Eq. (1)) reactions.

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \tag{1}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{2}$$

$$S^0 + 3/2O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \tag{3}$$

$$3Fe^{3+} + 2SO_4^{2-} + 6H_2O + M^+ \Leftrightarrow MFe_3(SO_4)_2(OH)_6 + 6H^+ \tag{4}$$

Eq. (1) demonstrates the necessity of ferric ion to leach chalcopyrite. Eq. (2) concerns the feasibility of recycling the ferrous ion released from chalcopyrite to generate the ferric ion required to oxidize the chalcopyrite, Eq. (3) the possibility of generating acidity to counterbalance the acid consumption reactions, and Eq. (4) the feasibility of the formation of iron salts such as jarosite which can passivate the leaching of chalcopyrite.

Although the main contribution of thermophiles is believed to rest on their capacity to catalyze the formation of ferric ion (Eq. (2)) and to remove the sulfur accumulated on the mineral surface (Eq. (3)) (Jordan et al., 2006), a doubt remains as to whether high temperatures alone can induce the formation of sufficient amounts of ferric ion at pH lower than that usually employed in bioleaching. On the other hand, since the feasibility of sulfur oxidation without the aid of thermophiles at high temperatures has been proved feasible (Jones, 1977), the contribution of thermophiles might be less than is commonly believed.

Therefore, as an attempt to elucidate the uncertainties regarding the contribution of temperature to the leaching of chalcopyrite, the feasibility of enhancing the leaching of chalcopyrite in sulfuric acid media containing additional ferric ion at low pH, without the aid of thermophiles, is evaluated against the leaching of chalcopyrite with thermophiles.

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* Corresponding author. Tel./fax: +81 22 795 7404.
E-mail addresses: vilcaez@er.kankyo.tohoku.ac.jp, vilcaez@hotmail.com (J. Vilcáez).

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2. Background

2.1. Passivation of the leaching reaction

Although bioleaching of chalcopyrite with thermophiles has led to copper extractions close to 100%, in the cases where lower copper extractions were obtained, the precipitation of ferric ion as jarosite is generally agreed to cause the passivation of the leaching reaction (Stott et al., 2000; Parker et al., 2003; Sandström et al., 2005). However, the formation of jarosite appears to be inherent to the utilization of thermophiles. Thermophiles readily oxidize the elemental sulfur formed on the mineral surface to soluble sulfate (Eq. (3)). In the pH range of 1.5–2.5, and temperatures within the range of 60–80 °C, where thermophiles are active, the sulfate formed readily precipitates with ferric ion to form jarosite (Eq. (4)).

Passivation of the chalcopyrite leaching has been more frequently reported in chemical leaching than in bioleaching. Studies on the leaching behavior of chalcopyrite in acidic sulfate media at temperatures between 60 and 95 °C suggested that complete copper extractions were not possible because of the passivation caused by the accumulation of intermediates such as copper polysulfide (Barriga et al., 1987), sulfide (or polysulfide) (Hackl et al., 1995), or elemental sulfur (Munoz et al., 1979; Majima, 1995).

Although the gradual accumulation of intermediate products on the mineral surface appears to passivate the chemical leaching of chalcopyrite more than does the sudden precipitation of jarosite that occurs in chalcopyrite bioleaching, the question remains as to whether the passivation that occurs in leaching chalcopyrite using acidic ferric sulfate solutions can be attenuated by reducing the pH to facilitate the oxidation of the sulfide (or sulfur) intermediates to sulfate.

2.2. The oxidation–reduction potential (ORP)

Studies on the leaching behavior of chalcopyrite in acid ferric sulfate solutions have shown that the oxidation rate of chalcopyrite changes suddenly at a critical potential around 450 mV, denoted the critical potential (Kametani and Aoki, 1985). The validity of this finding has been confirmed in a series of studies carried out at ambient temperatures (Hiroyoshi et al., 2000, 2001, 2007). Although studies comparing the catalytic effect of thermophiles against the enhancing effect of low ORP values at thermophilic temperatures are as yet unavailable, recent studies have revealed that the apparent catalytic effect of thermophiles is enhanced at low ORP values rather than at high ORP values (Sandström et al., 2005; Petersen and Dixon, 2006; Vilcáez et al., in press-a). Therefore, the question remains as to whether the increase of temperature above 60 °C and reduction of the ORP below 450 mV alone can lead to copper extractions similar to those obtained in thermophilic bioleaching.

2.3. Additional ferric ion

Extensive research has been carried out to elucidate the role of additions of ferric ion in chalcopyrite leaching at temperatures between 60 and 95 °C (e.g.: Munoz et al., 1979; Majima, 1995; Dutrizac, 1981). It is generally agreed that ferric ion above about 0.01 M (Dutrizac, 1981; Hirato et al., 1987) does not affect the kinetics of the reaction. A similar conclusion was obtained in bioleaching chalcopyrite. While some studies reported that additional ferric ion (0.08 M, 0.125 M; Vilcáez et al., in press-b) only enhances the initial leaching rates but not the final leaching yields, other studies reported that additional ferric ion (0.013 M, 0.026 M; Konishi et al., 2001) makes negligible contribution to the bioleaching of chalcopyrite.

Interestingly, high ferric ion concentrations were used in most studies related to the leaching behavior of chalcopyrite in acidic ferric sulfate media at high temperatures (60–95 °C) (0.125 M, 0.015 M; Munoz et al., 1979; 0.02 M; Majima, 1995; 1.62 M; Barriga et al., 1987; 0.09 M; Hackl et al., 1995; 1 M; Kametani and Aoki, 1985; 0.4 M; Dutrizac, 1981). These ferric ion concentrations, in the absence of enough ferrous ion in solution, apparently resulted in high ORP values (>600 mV) which avoided any probable enhancement promoted by low ORP values (<450 mV). Taking into consideration the relevance of the ORP and temperature in the leaching kinetics of chalcopyrite, the effect of adding lower concentrations of ferric ion at thermophilic temperatures (65 °C) is yet to be evaluated.

2.4. pH

The leaching of chalcopyrite consists of acid consumption reactions. Thus, as the leaching reactions progress, the pH increases. One consequence of the increased pH is the formation of iron salt precipitates (Eq. (4)) which can passivate the leaching reaction. Passivation of the reaction in leaching with acidic ferric sulfate solutions can be avoided by providing excess sulfuric acid concentrations. However, in bioleaching chalcopyrite, since most thermophiles are not resistant to pH lower than 1.0, excess sulfuric acid concentrations, which could prevent the formation of iron salt precipitates such as jarosite precipitation, cannot be employed.

3. Material and methods

3.1. Chalcopyrite samples

Leach tests were carried out on various chalcopyrite types including two chalcopyrite ores and two chalcopyrite concentrates. The chalcopyrite concentrates were obtained from the Atacama copper mine located in Chile, and from the Hanaoka copper mine located in Japan. The chalcopyrite minerals were obtained from the Agenosawa and Hanaoka mines located in Japan. The ground minerals were sieved to obtain the size fraction of 25–35 µm and then washed three times consecutively with HNO_3 (1 mol/L), once with distilled water and once with pure ethanol. The washed mineral particles were then dried at room temperature in a vacuum desiccator. The Atacama concentrate contained 28.9 wt.% Cu, 31.9 wt.% S, 28.9 wt.% Fe, 1.76 wt.% Si, 0.63 wt.% Al, 0.5 wt.% Zn, and other impurities. The Hanaoka concentrate contained 28.3 wt.% Cu, 28.6 wt.% Fe, 4.58 wt.% Zn, and 3.20 wt.% Pb. The Agenosawa mineral contained 20.5 wt.% Cu, 12.8 wt.% Zn, and 1.7 wt.% Pb. The Hanaoka mineral contained 11.61 wt.% Cu, 31.39 wt.% Fe, 2.62 wt.% Zn, 5.73 wt.% Pb. Except for the Atacama chalcopyrite all chalcopyrites contained pyrite (Fig. 1).

3.2. Acidophilic thermophiles

Two thermophile strains were selected: *Acidianus brierleyi* DSM 1651 and *Sulfolobus metallicus* DSM 6482 both of which were obtained from the German Collection of Microorganisms and Cell Cultures (DSMZ). The thermophiles were grown aerobically at 65 °C in the appropriate media described in the DSMZ online catalogue. These strains were gradually adapted to modified media supplemented with 1% $CuFeS_2$ concentrate at an initial pH of 1.8. The leaching medium in the case of *A. brierleyi* contained: 3 g/L $(NH_4)_2SO_4$, 0.5 g/L K_2HPO_4, 0.5 g/L $MgSO_4{\cdot}7H_2O$, 0.1 g/L KCl, and 0.2 g/L Yeast extract (Bacto). In the case of *S. metallicus* the leaching media contained: 1.3 g/L $(NH_4)_2SO_4$, 0.28 g/L KH_2PO_4, 0.25 g/L $MgSO_4{\cdot}7H_2O$; 0.07 g/L $CaCl_2{\cdot}2H_2O$, 0.02 g/L $FeCl_3{\cdot}6H_2O$, and 0.2 g/L Yeast extract (Bacto), as well as 1 ml of a tracer element solution: 1.8 g/L $MnCl_2{\cdot}4H_2O$, 0.45 g/L $Na_2B_4O_7{\cdot}10H_2O$, 0.022 g/L $ZnSO_4{\cdot}7H_2O$, 0.005 g/L $CuCl_2{\cdot}H_2O$, 0.003 g/L $Na_2MoO_4{\cdot}2H_2O$, 0.003 g/L $VOSO_4{\cdot}2H_2O$, and 0.001 g/L $CoSO_4$.

3.3. Leach tests

All leaching tests were carried out in 250 ml Erlenmeyer flasks containing 100 ml of the leaching solution at a pulp density of 1%. The

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