Research Article

On the Mechanism of Chalcopyrite Bioleaching with Thermophiles

Javier Vilcáez*

Boone Pickens School of Geology, Oklahoma State University, USA

*Corresponding author: Javier Vilcáez, Boone Pickens School of Geology, Oklahoma State University, Stillwater, OK 74078, USA

Abstract

Although various features of the thermophilic bioleaching of chalcopyrite have been elucidated, others remain unclear and require further research. That is the case of the inhibitory effect of PbS on the growth of *A. brierleyi*, *S. metallicus* and *M. Sedula*. A chalcopyrite mineral containing PbS has been found to leach at faster rates than a pure chalcopyrite concentrate, suggesting that partial inhibition of Fe^{2+} oxidation by thermophiles leads to ORP levels around 450 mV where the leaching rate of chalcopyrite is known to be highest. Another important factor which has been found it can affect negatively the copper extractions yields from chalcopyrite is temperature. Higher copper extractions were obtained with chemical leaching than with thermophilic bioleaching at 85°C. This research highlights the necessity of including the effect of mineral composition and temperature in kinetics models of chalcopyrite bioleaching with thermophiles.

Keywords: Chalcopyrite bioleaching; Thermophiles; PbS inhibition

Introduction

Chalcopyrite ($CuFeS_2$) is the most abundant copper-bearing mineral counting for about 70% of the world reserve [1]. However, chalcopyrite is highly refractory under hydrometallurgical conditions, due to surface transformations which render products very stable under oxidizing conditions [2]. Approximately 18% of world copper production is obtained by hydrometallurgy of other sulfide copper-bearing minerals such as chalcocite, (Cu_2S) and covellite (CuS), and/or oxides copper-bearing minerals [3]. For copper production from chalcopyrite at plant scale to become a reality, new hydrometallurgy technologies need to be developed.

The minimum pollution caused by hydrometallurgy and low operational costs in comparison to pyrometallurgy has given born to a new branch in mineral processing technology called biohydrometallurgy. This new technology combines principles of hydrometallurgy and biotechnology to bioleach ore minerals. A wide variety of iron and sulfur oxidizing bacteria and archaea isolated from natural leaching environments such as acid mine drainage are employed to bioleach copper bearing minerals. At present, mesophilic iron and sulfur oxidizing bacteria such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillusthiooxidans* are employed to bioleach copper from copper oxides and secondary copper sulfides [4]. However, chalcopyrite has been shown to be refractive to bioleaching with mesophiles. Typically copper extractions obtained with mesophiles are within the range of 30–40%. One effective way of increasing the copper extraction yields from chalcopyrite consists in the use of thermophilic archaea. Cooper extractions obtained with thermophiles are within the range of 80–100% [5]. This high copper extraction yields has motivated a number of studies to understand the factors that control the bioleaching of chalcopyrite with thermophiles.

Studies on biological and physicochemical factors involved in the bioleaching of chalcopyrite with thermophilic archaea (*Sulfolobusmetallicus, Metallospherasedula, and Acidianus Brierleyi*) have led to the conclusion that the bioleaching of chalcopyrite is controlled by both biological factors such as a probable enzymatic direct attack of thermophiles to chalcopyrite [6,7], as well as physicochemical factors such as temperature, pH and ORP [8]. Although, some thermophiles such as *Acidianus Brierleyi* seems to have the ability to attack chalcopyrite through its enzymes, it is now known that the most controlling variable in chalcopyrite bioleaching is the oxidation reduction potential (ORP) that results from combined biotic and abiotic reactions. Chalcopyrite has been proven to have an optimum ORP level around 450 mV where the leaching rate of copper is highest. This optimum ORP level has been found can be reached with a leaching solution of pH 1.0, in which case the leaching rate of chalcopyrite is higher than in bioleaching with thermophiles [7]. Therefore, contrary to one might expect, the presence of bioleaching microorganisms in the leaching solution does not always enhances the leaching of copper from chalcopyrite, but it may result in lower leaching rates than in chemical leaching at ORP levels of 450 mV and pH of 1.0.

In this paper a reaction mechanism of chalcopyrite leaching is discussed on the basis of new experiments aimed to analyze the effect of the presence of PbS in chalcopyrite minerals and high temperatures.

Proposed Reaction Mechanism

A mechanism that explains high leaching yields of chalcopyrite observed at ORP levels around 450mV has been proposed by Hiroyoshi et al. [9]. In this mechanism, chalcopyrite is reduced by ferrous (Fe^{2+}) and cupric (Cu^{2+}) ions to form chalcocite (Cu_2S) which is subsequently oxidized by ferric ions (Fe^{3+}) to release Cu^{2+}. This mechanism does not account for the effect of pH on the leaching of chalcopyrite. A mechanism that accounts for the effect pH on the leaching of chalcopyrite through the reductive formation of Cu_2S with protons (H^+) has been proposed by Nicol and Lázaro [10]. In this

mechanism, although the enhancing effect of low pH levels is taken into account, the enhancing effect of low ORP levels on the leaching of chalcopyrite is not considered. In this mechanism, the formation of Cu_2S is controlled by pH rather than by the availability Fe^{2+}.

Experimental results on the bioleaching of chalcopyrite with thermophiles at temperatures within $60-80^0C$ are not in accordance neither with the leaching mechanisms proposed by Hiroyoshi [9] nor with the leaching mechanism proposed by Nicol and Lázaro [10]. The bioleaching yields of chalcopyrite with thermophiles dependents on the ORP as well as on the pH level of the leaching solution. Initial amounts of Fe^{2+} and Cu^{2+} are not necessary to trigger the leaching reaction of chalcopyrite as one might expect according to the mechanism proposed by Hiroyoshi et al. [9].

In the following, a mechanism of chalcopyrite bioleaching is proposed to explain the leaching behavior of chalcopyrite observed with thermophiles.

In the absence of initial amounts of Cu^{2+}, if initial amounts of Fe^{3+} are available in the leaching solution, the leaching of chalcopyrite follows an anodic oxidation reaction with Fe^{3+} being the oxidant (r1):

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0$$
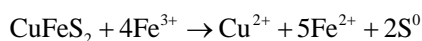
If initial amounts of Fe^{3+} are not available, the initial leaching reaction may be expressed by a non-oxidative reaction with protons being the leaching agent (r2):

$$CuFeS_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2H_2S$$
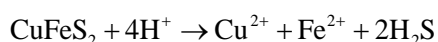
The occurrence of r1 is of general acceptance and r2 has been proposed by Nicol and Lázaro [10]. Once enough Fe^{2+} and Cu^{2+} have being accumulated in the leaching solution, depending on the amounts of Fe^{3+} in solution, the leaching reaction may proceed in two ways. At high $[Fe^{3+}]/[Fe^{2+}]$ levels (high ORP), chalcopyrite reacts anodically with Fe^{3+} being the oxidant (r1), whereas at low $[Fe^{3+}]/[Fe^{2+}]$ levels (low ORP), chalcopyrite reacts cathodically with Fe^{2+} and Cu^{2+} being the reductants (r3):

$$CuFeS_2 + Fe^{2+} + Cu^{2+} + 2H^+ \rightarrow Cu_2S + 2Fe^{3+} + H_2S$$

The formed Cu_2S, regardless of the pH of the leaching solution is subsequently anodically oxidized by Fe^{3+} (r4):

$$Cu_2S + 4Fe^{3+} \rightarrow 2Cu^{2+} + S^0 + 4Fe^{2+}$$
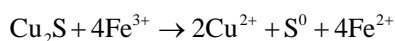
Whereas the formed H_2S in the non-oxidative reaction (r2) at low pH levels (<1.5), reacts with Fe^{3+} to form Fe^{2+} (r5):

$$H_2S + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + 2H^+$$
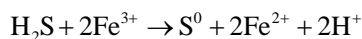
The occurrence of this reaction (r5) benefits the leaching reaction by reducing the $[Fe^{3+}]/[Fe^{2+}]$ level in the leaching solution.

Note that the summation of r3, r4, and r5 gives r1, and that in this mechanism the addition of Cu^{2+} as stated with Hiroyoshi et al. [9] is not necessary to cathodically reduce chalcopyrite. One mol of Cu^{2+} will always be available to react with one mole of chalcopyrite. In this way the important role of Fe^{2+} and pH, as well as the necessity of having Fe^{3+} in the leaching solution to enable the cathodic reduction of chalcopyrite is considered.
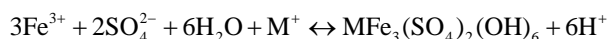
The catalytic effect of thermophiles rest on their ability to form Fe^{3+} (r6):

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$
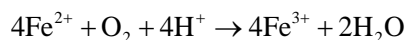
and remove the elemental sulfur (S^0) layer deposited on the surface of the mineral (r7):

$$S^0 + 3/2O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}$$
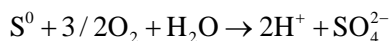
The formed sulfate ions (SO_4^{2-}) also serve to remove Fe^{3+} from the leaching solution through the formation of jarosite (r8):

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

In the following sections new experimental results on chalcopyrite bioleaching with thermophiles and chalcopyrite chemical leaching are discussed in the context of the proposed mechanism.
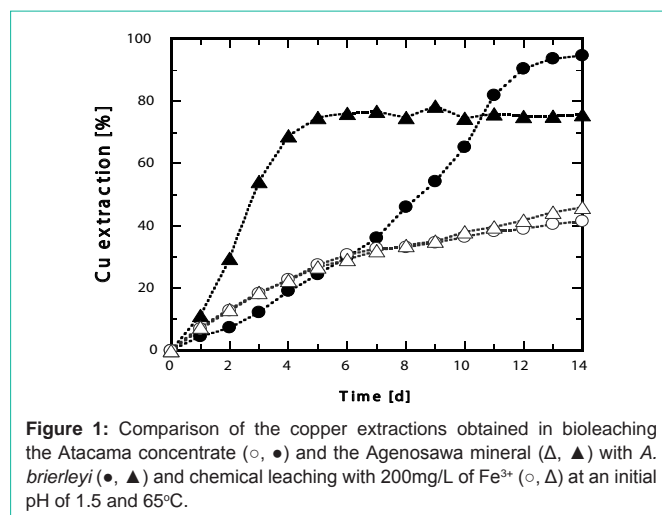
Material and Methods

The detailed experimental procedure is described elsewhere [6]. Briefly, the bioleaching of chalcopyrite was carried out in 200 ml Erlenmeyer flasks containing 100 ml of leaching solution at a pulp density of 1%. Chalcopyrite concentrates as well as chalcopyrite ore minerals have been employed. However, only the data obtained from bioleaching the Atacama concentrate and Agenosawa mineral will be considered for the purposes of this paper. X-ray diffraction characterization of both chalcopyrites showed that the Atacama chalcopyrite concentrate (28.9 wt% Cu) was pure chalcopyrite, whereas the Agenosawa chalcopyrite mineral (20.5 wt% Cu) contained other impurities including pyrite (FeS_2) and galena (PbS). Three thermophile strains were employed: *Acidianus brierleyi*, *Sulfolobusmetallicus* and *Metallosphaerasedula*. Their characteristics and cultivation are described elsewhere [6]. The initial biomass concentration in all experiments was 1.2×10^8 cells/ml.

Chemical leaching experiments were performed at the same conditions as in the bioleaching experiments, except that the leaching solution was not inoculated with the thermophiles, instead Fe^{3+} was supplied at a concentration of 200 mg/L.

Enhancing effect of thermophiles on chalcopyrite bioleaching

Figure 1 compares typical copper extractions obtained with thermophilic bioleaching and chemical leaching of chalcopyrite at 65^OC. As expected, higher copper extractions were obtained with

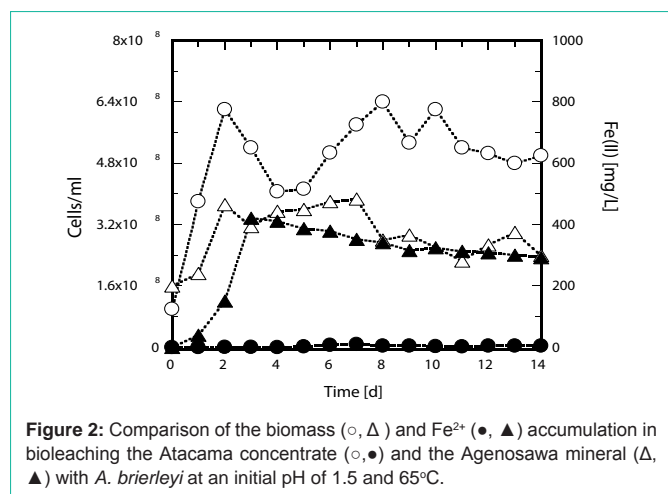**Figure 1:** Comparison of the copper extractions obtained in bioleaching the Atacama concentrate (○, ●) and the Agenosawa mineral (Δ, ▲) with *A. brierleyi* (●, ▲) and chemical leaching with 200mg/L of Fe^{3+} (○, Δ) at an initial pH of 1.5 and 65ºC.

Figure 2: Comparison of the biomass (○, Δ) and Fe^{2+} (●, ▲) accumulation in bioleaching the Atacama concentrate (○,●) and the Agenosawa mineral (Δ, ▲) with *A. brierleyi* at an initial pH of 1.5 and 65°C.

bioleaching than with chemical leaching. With chemical leaching at 65°C and 200 mg/L of Fe^{3+}, only 42% and 45% of copper could be extracted from the Agenosawa mineral and the Atacama concentrate, respectively. Whereas copper extractions of 75% (Agenosawa mineral), and 95% (Atacama concentrate) were obtained using thermophilic bioleaching at 65°C.

However, unexpectedly the bioleaching rate of the Agenosawa mineral was much faster than the bioleaching rate of the Atacama concentrate. The rate of copper extraction from the Agenosawa mineral was approximately three times faster than the copper extraction rate from the Atacama concentrate. Usually, chalcopyrite minerals are faster to bioleach than chalcopyrite concentrates. This apparent incoherency can be explained in terms of the reaction mechanism described above. According to this mechanism, thermophiles enhance the leaching of chalcopyrite mainly through the regeneration of Fe^{3+} (r6) and removal of S^0 from chalcopyrite (r7). A low rate of Fe^{3+} regeneration leads to the accumulation of Fe^{2+} which results in low ORP values enabling the reductive formation of Cu_2S (r3). In accordance to this mechanism, Figure 2 shows that higher amounts of Fe^{2+} accumulated in bioleaching the Agenosawa mineral than in bioleaching the Atacama concentrate. Thus, the Agenosawa mineral is leached at faster rates than the Atacama concentrate due to the poor ability of *A. brierley* to catalyze the oxidation of Fe^{2+} to Fe^{3+} or due to the inhibition of *A. brierley* by the presence of PbS in the Agenosawa mineral. Figure 2 also compares the biomass concentration of *A. brierley* over time in bioleaching both, the Agenosawa mineral and the Atacama concentrate. The biomass concentration in bioleaching the Agenosawa mineral remains lower than the biomass concentration in bioleaching the Atacama concentrate through the duration of the reaction. Suggesting that the presence of PbS might have benefited the bioleaching reaction of the Agenosawa mineral by partially inhibiting the growth of *A. Brierley*.

Inhibitory effect PbS on the thermophilic bioleaching of chalcopyrite

The fact that the biomass concentration in bioleaching the Agenosawa mineral remained lower than in bioleaching the Atacama concentrate (Figure 2) suggested that impurities such as PbS contained in the Agenosawa mineral but not in the Atacama concentrate, might have partially inhibited the growth of thermophiles facilitating
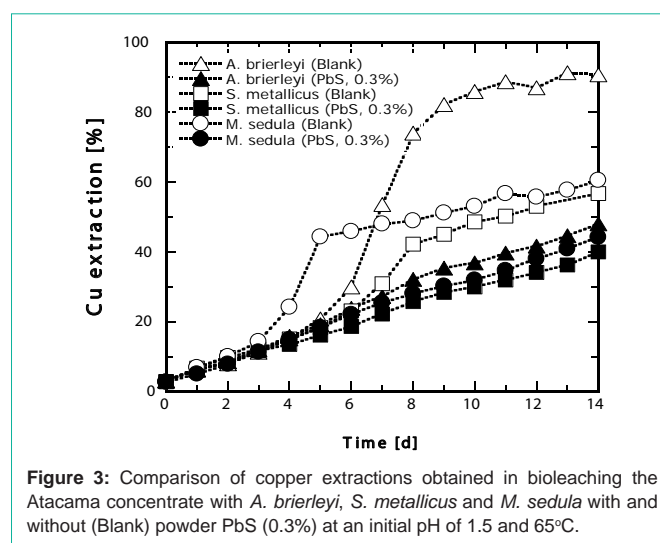
the accumulation of Fe^{2+}. If that is truth, the use of powder PbS in bioleaching the Atacama concentrate should accelerate the rate of copper extraction. In order to prove this hypothesis, experiments have been performed using three types of thermophiles (*A. brierleyi*, *S. metallicus* and *M. Sedula*) with and without the addition of powder PbS at a concentration of 0.3%.

Figure 3: Comparison of copper extractions obtained in bioleaching the Atacama concentrate with *A. brierleyi*, *S. metallicus* and *M. sedula* with and without (Blank) powder PbS (0.3%) at an initial pH of 1.5 and 65°C.

The results of that experiment are shown in Figure 3. Although the biomass concentration was lower than in bioleaching without the addition of PbS (result not shown), the addition of PbS did not accelerate the leaching rate of the Atacama concentrate with all three thermophiles. On the contrary, the addition of PbS resulted in a decrease in copper extraction yields. Copper extractions of 90%, 60% and 58% obtained from bioleaching the Atacama concentrate with *A. brierleyi*, *S. metallicus* and *M. Sedula*, respectively decreased to 48%, 45% and 40% due to the addition of PbS (0.3%).

These results reveal two important facts: 1) PbS inhibits the growth of *A. brierleyi*, *S. metallicus* and *M. Sedula* thermophiles, and 2) the high leaching rates observed in bioleaching the Agenosawa mineral (Figure 1) maybe related to the inhibitory effect of PbS. Apparently,
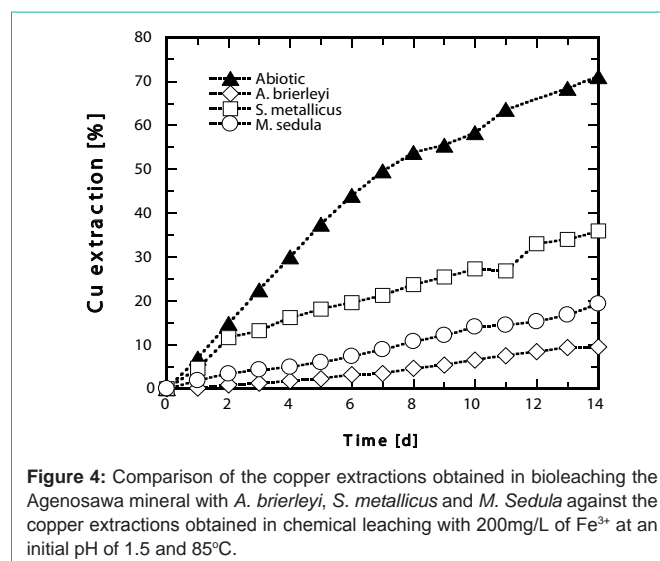

Figure 4: Comparison of the copper extractions obtained in bioleaching the Agenosawa mineral with *A. brierleyi*, *S. metallicus* and *M. Sedula* against the copper extractions obtained in chemical leaching with 200mg/L of Fe^{3+} at an initial pH of 1.5 and 85°C.

low concentrations of PbS contained in the Agenosawa mineral favored the bioleaching reaction by attenuating the Fe^{2+} to Fe^{3+} oxidation rate mediated by *A. brierleyi*. Whereas, a high concentration of PbS (0.3%) added to the leaching solutions containing *A. brierleyi*, *S. metallicus* and *M. Sedula*, resulted in an over-attenuation of the Fe^{2+} to Fe^{3+} oxidation rate. This suppressed the formation of sufficient amounts of Fe^{3+} required to oxidize Cu_2S (r4) formed via a reductive reaction of chalcopyrite with Fe^{2+} (r3).

Beside PbS, it was found that high temperatures can also attenuate the thermophilic bioleaching of chalcopyrite. Figure 4 shows the copper extractions obtained in chemical leaching and bioleaching the Agenosawa mineral at 85°C. Higher copper extractions are obtained without thermophiles than with thermophiles in the leaching solution. The reason of this behavior is not clear. It might be that organic materials such as yeast extracts or debris thermophiles itself deposits on the mineral particle inhibiting the leaching reaction.

Conclusion

• The oxidation reduction potential (ORP) in the leaching solution that results from the activity of thermophiles governs the thermophilic bioleaching of chalcopyrite.

• Powder PbS inhibits the growth of *A. brierleyi*, *S. metallicus* and *M. Sedula*.

• Impurities such as PbS contained in chalcopyrite minerals can enhance the bioleaching of chalcopyrite with thermophiles.

• Pure chalcopyrite concentrates do not always leach faster than chalcopyrite minerals containing galena (PbS).

• High temperatures (85°C) in bioleaching with thermophiles can lead to lower copper extractions than with chemical leaching at the same temperature.

References

1. Rivadeneira J. Introduction. Mining innovation in Latin America Reprt. Santiago, Chile. 2006; 6-7.

2. Burkin AR. Solid-state transformations during leaching. Min. Sci Eng. 1969; 1: 4-14.

3. Bravo P. El panorama de la hidrometalurgia. Revista Mineria Chilena, 303. Editec S.A. Santiago, Chile. 2006.

4. Pradhan N, Nathasarma KC, SrinivasRao K, Sukla LB, Mishra BK. Heap bioleaching of chalcopyrite: A review. Minerals Engineering. 2008; 21: 355-365.

5. d'Hugues P, Foucher S, Galle-Cavalloni P, Morin D. Continuous bioleaching of chalcopyrite using a novel extremely thermophilic mixed culture. Int. J. Miner. Process. 2002; 66: 107-119.

6. Vilcáez J, Suto K, Inoue C. Response of thermophiles to the simultaneous addition of sulfur and ferric ion. Minerals Engineering. 2008; 21:1063-1071.

7. Vilcáez J, Yamada R, Inoue C. Effect of pH reduction and ferric ion addition on the leaching of chalcopyrite at thermophilic temperatures. Hydrometallurgy. 2008; 96: 62-71.

8. Vilcáez J, Suto K, Inoue C. Bioleaching of chalcopyrite with thermophiles: temperature-pH-ORP dependence. International Journal of Mineral Processing. 2008; 88: 37-44.

9. Hiroyoshi N, Miki H, Hirajima T, Tsunekawa M. A model for ferrous promoted chalcopyrite leaching. Hydrometallurgy. 2000; 57: 31-38.

10. Nicol MJ, Lázaro I. The role of non-oxidative processes in the leaching of chalcopyrite. In: Riveros PA, editor. Copper 2003, Hydrometallurgy of Copper, Santiago-Chile. 2003; VI: 367–381.