New information on the chalcopyrite bioleaching mechanism at low and high temperature

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Abstract

The chalcopyrite bioleaching mechanism was studied to determine its direct or indirect nature. At the same time, a study of possible causes that diminish the dissolution rate and inhibit the attack of this sulphide mineral was carried out. An electrochemical study of the mineral was also performed, which included the elimination or dissolution of possible diffusion barriers formed on the mineral surface.

Results of these studies showed that the oxidation state of the dissolved iron (Fe^{3+}) was fundamental to chalcopyrite bioleaching because Fe^{3+} controlled the relative rate of the oxidation reactions. In addition, the attack of chalcopyrite was controlled by elemental sulphur and intermediate, nonstoichiometric, copper sulphides forming on the chalcopyrite surface, which are less reactive than the original sulphide. Intermediate sulphides caused an important barrier effect at low temperature (35 °C). At higher temperature (68 °C), these intermediate sulphides do not constitute a diffusion barrier due to their dissolution.

Microbial attachment to the pyritic phase of the copper ore was related to the dissolution rate of the mineral due to the liberation of Fe^{2+} after the attack of the pyrite by contact bioleaching.

It was concluded that the bioleaching of chalcopyrite concentrate is a cooperative effort involving the simultaneous contact bioleaching of the pyritic phase of the mineral, possibly by an indirect mechanism via thiosulphate, and the indirect bioleaching of chalcopyrite, probably by a mechanism by way of polysulphide and elemental sulphur.

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1. Introduction

Microbial oxidation of copper sulphides is fundamental for copper extraction from low-grade concentrates. Bioleaching processes are particularly suitable for the treatment of secondary copper sulphides but are very inefficient for attacking chalcopyrite (CuFeS₂), due to the refractory nature of this mineral to chemical and biological leaching, resulting in low dissolution rates. The main reason for this refractory character is the formation of a solid passive layer on the mineral surface, which limits both reagent contact and diffusion. This slows the sulphide attack and eventually halts the attack altogether. Although it is known that the passive layer is responsible for the refractoriness of
chalcopyrite the exact nature of this passive layer is debatable. Also disputable is the exact role of microorganisms in the bioleaching of this mineral.

Review of the technical literature on the chalcopyrite bioleaching reveals concurrence on some important aspects of this phenomenon although there is far from total agreement on the subject and there is no universally accepted theory on the mechanism of chalcopyrite bioleaching.

The first attempt to explain a possible mechanism of bioleaching was carried out by Silverman and Ehrlich in 1964. They established two possible bioleaching routes, which they called: direct and indirect. After years of study, the indirect mechanism via polysulphide and elemental sulphur production proposed by Sand et al. (1995, 1999) and Schippers and Sand (1999) is the most coherent attempt to explain the true bioleaching mechanism. The mechanism proposed by Sand et al. entails several steps, which start with the dissolution of mineral sulphides with protons present in the bioleaching medium. This first step liberates metals in their ionic form and produces hydrogen sulphide. Hydrogen sulphide is transformed by the oxidation with Fe$^{3+}$ and subsequent dissociations and dimerizations in the polysulphide. As a result of the combined actions of acidity and Fe$^{3+}$, elemental sulphur is the final product. The reactions of the polysulphide mechanism are depicted as follows:

\[
MS + \text{Fe}^{3+} + n\text{H}^+ \rightarrow \text{M}^{2+} + n\text{H}_2\text{S}_n + \text{Fe}^{2+} \quad (n \geq 2) \\
0.5\text{H}_2\text{S}_n + \text{Fe}^{3+} \rightarrow 0.125\text{S}_8 + \text{Fe}^{2+} + \text{H}^+ \\
0.125\text{S}_8 + 1.5\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{bacteria}} \text{SO}_4^{2-} + 2\text{H}^+ 
\]

According to this mechanism proposed by Sand et al. (1995, 1999) and Schippers and Sand (1999), the role of microorganisms during the bioleaching of metallic sulphides is to generate sulphuric acid to provide protons to the medium for the mineral hydrolysis and to maintain the iron in the maximum oxidation state, Fe$^{3+}$, for the oxidizing attack of the mineral.

This proposed mechanism is based on interdisciplinary studies involving mineralogical and semiconducting properties of chalcopyrite (CuFeS$_2$), sphalerite (ZnS), galena (PbS), hauerite (MnS$_2$), orpiment (As$_2$S$_3$) and realgar (As$_4$S$_4$). All of these sulphides have valence bands formed by atomic orbitals from both metallic and sulphur atoms. The result is that these sulphides can be attacked not only by Fe$^{3+}$ but also by protons, which can produce the same effect (Tributsch and Bennett, 1981a,b; Vaughan and Craig, 1978; Crundwell, 1988). Additionally, other studies show substantial formation of elemental sulphur (>90%) and minor production of sulphates and polythionates during the chemical oxidation of these ores with Fe$^{3+}$ (Schippers and Sand, 1999).

Tributsch (1999) performed a review of the existing proposals for chalcopyrite bioleaching and based on this review proposed three different bioleaching strategies:

1. Indirect bioleaching, whereby the microbial action is restricted to the renewal of the bioleaching reagent, Fe$^{3+}$;

2. Contact bioleaching, which entails attachment of microorganisms to the mineral surface and these organisms prepare the medium and facilitate the mineral attack through an electrochemical dissolution involving Fe$^{3+}$ contained in the microbe’s extracellular polymeric substances (EPS); and

3. Cooperative bioleaching, which entails cooperation between microorganisms attached to the mineral surface and free bacteria in solution. The attached microbes, through contact bioleaching, release chemicals to the solution that constitute the energy source for the organisms that are free in solution.

The principal aim of the present work is to study the mechanism involved in chalcopyrite dissolution. For this, a chalcopyrite concentrate was bioleached at two different temperatures (35 and 68 °C) and parameters such as the Fe$^{3+}$ concentration produced during the bioleaching process. Also, Cu and Fe dissolution kinetics, microbial attachment to the mineral surface, and the electrochemical behaviour of the mineral were examined. In addition, the decrease in the dissolution rate of copper during bioleaching was studied through the removal of possible diffusion barriers formed on the mineral surface; this removal of diffusion barriers was fol-
2. Materials and methods

2.1. Ores

A copper sulphide flotation concentrate supplied by Rio Tinto Metal (Huelva, Spain) was used. Chemical analysis of the sample was: 18.9% Cu; 34.6% Fe; 0.01% Zn; and 36.8% S. X-ray diffraction analysis of the ore showed chalcopyrite as the major component (54.6%), pyrite (FeS₂) (33.1%) as the minor one, and small amounts of silica and dolomite. Over 65% of the ore had a size between 44 and 149 μm.

2.2. Experimental conditions

The microorganisms used, the conditions and procedure of their culture, the description of the bioleaching tests, the microbial attachment control, the electrochemical measures, and the two-step bioleaching tests are described in a paper published in this same issue of Hydrometallurgy entitled: “New information on the pyrite bioleaching mechanism at low and high temperature”. Before carrying out the second bioleaching test, the chalcopyrite residues from the first bioleaching test were washed with a CS₂ solution to dissolve possible diffusion layers, mainly S⁰, formed during the process.

3. Results and discussion

3.1. Leaching kinetics

The results obtained during the chalcopyrite bioleaching at 35 and 68 °C are shown in Fig. 1 and Table 1.

The copper dissolution curves show that both the kinetics and the efficiency of leaching were directly related to the Fe³⁺ and H⁺ concentrations in solution. In the test with thermophilic microorganisms, the Fe³⁺ concentration increased more quickly, achieving higher kinetics and copper leaching efficiency. In all the experiments, the H⁺ concentration decreased initially due to the consumption of acid during the protonic attack of the chalcopyrite. Later, acidity increased, because of the oxidation of elemental sulphur by sulphur-oxidizing microorganisms (Fig. 2).

These observations confirm the importance of indirect bioleaching involving polysulphide and elemental sulphur, as proposed by Schippers and Sand (1999) for chalcopyrite, and the results of other papers, showing a direct relationship between the dissolution rate of chalcopyrite and the Fe³⁺ concentration in the reaction medium (Dutrizac, 1981; Hirato et al., 1987; Rath et al., 1988; Majima, 1995; Howard and Crundwell, 1999).

Mineral dissolution ceased when the microbial growth reached a maximum, corresponding with a decline in capacity of Fe³⁺ regeneration. This cessation of mineral leaching was due to the formation of a passive layer on the chalcopyrite surface, which limited the diffusion of the leaching agent to the solid.

![Fig. 1. Chalcaldrite bioleaching efficiency using mesophilic (a) and thermophilic (b) microorganisms.](image-url)
According to other researchers, the passive layer on the ore surface could be formed by:

1. Jarosite precipitated in the presence of high concentrations of ferric iron and sulphates as a consequence of the pH increase (Howard and Crundwell, 1999; Kingma and Silver, 1980; Boon and Heijnen, 1993);

2. Intermediate copper sulphides less reactive than the original chalcopyrite (Biegler and Horne, 1985; Johansson et al., 1999); or

3. A sulphur layer formed as a by-product during the copper–iron sulphide dissolution (Hirato et al., 1987; Dutrizac, 1990; Saxena and Mandre, 1992).

The copper leaching efficiency achieved with thermophilic microorganisms was higher than that obtained with mesophilic bacteria. Other authors have observed these differences between thermophilic and mesophilic microorganisms as well (Johansson et al., 1999; Barr et al., 1992; Jordan et al., 1993; Rubio et al., 1994; Norris et al., 1996; Clark and Norris, 1996; Le Roux and Wakerley, 1988; Konishi et al., 1999). A SEM study of residues from thermophilic bioleaching showed the presence of substantial amounts of jarosites; jarosite was not detected in the tests with mesophilic microorganisms. In the tests at 68 °C, the attack on the mineral was greater than at 35 °C. No diffusion barriers were noted at 68 °C, but they were observed in the presence of mesophilic microorganisms. Therefore, it can be stated that jarosites did not participate in the ore passivation with the thermophilic microorganisms. These observations coincide with the conclusions of Johansson et al. (1999) on chalcopyrite bioleaching using the GEOCOAT™ process.

An EDS analysis carried out on several particles of chalcopyrite previously attacked by bioleaching detected sulphur concentrations higher than that corresponding to the chalcopyrite composition; this sulphur can be associated with either the presence of a thin layer of elemental sulphur on the ore or the formation of intermediate copper sulphides enriched in sulphur.

The differences found in the bioleaching process at 68 and 35 °C could be related to the high sulphur-oxidizing activity of the thermophilic culture and, possibly, to a microbial selection of iron-oxidizing microorganisms in the mesophilic culture. This was confirmed by TEM studies of the microbial popula-

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Table 1

<table>
<thead>
<tr>
<th></th>
<th>Mesophilic microorganisms (35 °C)</th>
<th>Thermophilic microorganisms (68 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu dissolved (%) after 40 days</td>
<td>9.5</td>
<td>56</td>
</tr>
<tr>
<td>Fe dissolved (%) after 40 days</td>
<td>6.2</td>
<td>41</td>
</tr>
<tr>
<td>K (h⁻¹)</td>
<td>1.4E-06</td>
<td>9.2E-05</td>
</tr>
<tr>
<td>Kₐ (mL/Cell-h)</td>
<td>1.7E-10</td>
<td>1.2E-08</td>
</tr>
<tr>
<td>Fe₃⁺ max. (g/L)</td>
<td>1.1</td>
<td>4.8</td>
</tr>
</tbody>
</table>

a K, bioleaching kinetic constant.
b Kₐ, attachment kinetic constant.
c Maximum concentration of Fe³⁺ during the process.

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![Figure 2](image_url)
tions. The selection likely occurred at the beginning of the process, because the cells found sufficient concentration of soluble Fe\(^{2+}\) but no S\(^0\) in the original inoculum solution. So, under these conditions, survival of sulphur-oxidizing microorganisms was difficult. In the case of *Acidithiobacillus ferrooxidans*, which oxidize both Fe\(^{2+}\) and S\(^0\), they probably used Fe\(^{2+}\) preferentially as electron donor because this was the more accessible energy source.

It can be concluded from these observations that the differences between thermophilic and mesophilic microorganisms were consistent with a greater chemical dissolution of the mineral with increasing temperature and a higher Fe\(^{3+}\) concentration achieved through microbial oxidation of Fe\(^{2+}\). At 68 °C, the high sulphur-oxidizing capacity of the culture led to the oxidation of most of the elemental sulphur formed on the mineral surface; this in turn, increased the acidity in the medium.

### 3.2. Microbial attachment

Microbial attachment to the mineral surface during the first hours of the test (Fig. 3) occurred rapidly; this is in agreement with the results published by other authors (Das et al., 1999). When data from the periods of greatest microbial attachment (Table 1) were fitted to Zobell’s (1943) model, a direct relationship between microbial attachment and the dissolution rate of Cu and Fe was observed. Also noted was the kinetics of cellular attachment, which was faster for the thermophilic microorganisms \((K_a=1.2E-08 \text{ mL/Cells-h})\) than for the mesophilic microorganisms \((1.7E-10 \text{ mL/Cells-h})\). The higher attachment kinetics for the thermophilic microorganisms correlates with a higher dissolution rate in this test \((K=9.2E-05 \text{ h}^{-1})\).

According to studies performed by others, the electrostatic force between the mineral surface and the microorganisms is the fundamental factor in the initial attachment. As electrostatic repulsion increases, attachment decreases (Van Loosdrecht et al., 1990a,b; Devasia et al., 1993). Solari et al. (1992) measured electrophoretic mobility of *A. ferrooxidans* as a function of pH and found an electrostatic attraction between the microorganisms and pyrite at pH<2.2, whereas with chalcopyrite under the same conditions an electrostatic repulsion was observed. The copper concentrate used in our study contained 33% pyrite. Microbial attachment to our concentrate occurred on the pyritic phase and pyrite leaching was the result of the indirect bioleaching mechanism via thiosulphate (Sand et al., 1995, 1999; Schippers and Sand, 1999). This indirect bioleaching of the pyrite phase released iron necessary for chemical dissolution of the chalcopyrite.

Microbial attachment during the entire bioleaching period occurred in three distinct steps (Fig. 4):

1. an initial step of maximum attachment (66%);
2. a second step in which the proportion of newly attached cells decreased with respect to free cells in solution; and
3. a final step in which an equilibrium between attached and free cells (25%) was reached.

These results are similar to those obtained with pyrite (see the results in this same issue of Hydrometallurgy) and the interpretation is exactly the same in that the active sites on the mineral surface influences the attachment of the microorganisms to the mineral and the Fe\(^{2+}\) concentration in solution affects the population density of microorganisms in solution. As in the case with pyrite, chalcopyrite bioleaching takes place in two steps. In the first step, pyritic phase dissolution occurs by the attack of microorganisms initially attached to the pyritic phase via the mechanism of contact bioleaching (Sand et al., 1995; Tributsch, 1999), and the chalcopyrite mineral phase is attacked by ferric ions and protons present in the

![Fig. 3. Microbial attachment to chalcopyrite.](image-url)
medium. In the second step, indirect bioleaching involving ferric iron regenerated by free microorganisms in solution and the action of the sulphur-oxidizing microorganisms are the key factors in the chalcopyrite dissolution. Therefore, during the attack of the copper concentrate two bioleaching mechanisms (indirect and contact mechanism) coexist, and one or the other of these mechanisms is favored depending on the degree of microbial attachment and the concentration of iron- and sulphur-oxidizing organisms in the medium. In this manner, a cooperative bioleaching takes place in which the attached organisms as well as the free organisms in solution participate.

3.3. Electrochemical study

The anodic chalcopyrite polarization curves at 35 and 68 °C from the rest potential (+327 mV) (Fig. 5a and b) showed the typical peaks and electroactive zones of this mineral. The small peak at +500 mV (peak A) was related to chalcopyrite transformation to intermediate products (prewave zone). This initial chalcopyrite oxidation leads to the formation of a passive layer of growing thickness, possibly bornite and elemental sulphur, which is further oxidized to nonstoichiometric copper sulphides (Biegler and Horne, 1985; Warren et al., 1982; Holliday and Richmond, 1990). This layer decreases the rate of electron transfer to the oxidizing agent (Fe$^{3+}$) as well as the ionic transport. There is some controversy regarding the nature of this passive layer, which could be formed by: CuS and S$^0$ (Biegler and Horne, 1985; Holliday and Richmond, 1990); a sulphide with a nonstoichiometric composition enriched in sulphur (Stancovic, 1986); or a polysulphide (Parker et al., 1981). According to Fig. 5b, the prewave reaction seems to be more favored at low temperature (35 °C) than at high (68 °C) temperature. This perhaps explains the low chalcopyrite dissolution with mesophilic microorganisms. There is a dramatic increase of current density in the zone of +700 to +1000 mV (peak B). This zone corresponds to the massive dissolution of chalcopyrite to Cu$^{2+}$, Fe$^{3+}$ and S$^0$ and to the breaking of the passive layer associated with the prewave.

When the scan direction is reversed towards negative potentials (reduction), the current decreases to +700 mV. A small wave is observed at +400 mV (peak C), which is related to the reduction of ferric to ferrous iron. At +200 mV a new peak (D) associated with the reduction of S$^0$ on the chalcopyrite surface during the previous anodic treatment was recorded. Finally, at about −300 mV the reduction of elemental sulphur resulting from the anodic dissolution of the chalcopyrite and the reduction of the chalcopyrite itself are detected (peak E).

When chalcopyrite, which was biologically attacked, is subjected to polarization (Figs. 6 and 7), some differences in the reactivity of the products formed during the reduction of the treated mineral surfaces are observed. The products formed in the prewave zone at 35 and 68 °C show that the reaction in this potential range was more important at low temperature. That is to say, the barrier effect produced by the products formed at low potentials was more pronounced with mesophilic bacteria. We know this because the electrochemical response of the chalcopyrite (Fig. 7, peak D) attacked at high temperature in the presence of thermophilic microorganisms occurred at more oxidizing potentials (approximately +250 mV). At 68 °C, the products formed at the prewave potentials do not cause the previously discussed barrier. Chemical or biological dissolution of chalcopyrite continues to reach higher efficiencies. These results agree with the conclusions of Johansson et al. (1999), who pointed out that, at high temperature the non-stoichiometric sulphides possibly decompose.

To improve the leaching kinetics, an attempt was made to eliminate elemental sulphur formed on the mineral surface of bioleached residue using carbon disulphide (CS$_2$). However, carbon disulphide was
Fig. 5. (a) Chalcopyrite polarization curves at 35 and 68 °C. (b) Polarization curves of chalcopyrite at 35 and 68 °C considering the zone of low \( i \) values.

Fig. 6. Chalcopyrite polarization curves with (40 days) and without bacterial attack at 35 °C and considering the zone of low \( i \) values.
found to be inefficient in dissolution of the elemental sulphur layer formed under bioleaching conditions. This illustrates that this sulphur is not crystalline but rather is plastic and amorphous as Biegler and Swiff (1979) showed in their studies about the formation of passive sulphur layers on chalcopyrite. Our study demonstrated that during the electrochemical dissolution of chalcopyrite, the morphology of the elemental sulphur formed depended on the magnitude of the applied potential. So, at low potentials (<0.9 V), sulphur has an amorphous and plastic consistency, which is very difficult to dissolve in carbon disulphide; whereas at higher potentials yellow rhombic crystals of sulphur appear, which have a more porous morphology that exerts a lower diffusion control and, in addition, are soluble in CS$_2$.

### 3.4. Two-step experiments

When the dissolution of the sulphur layer was not achieved, chalcopyrite was strongly passivated and the bioleaching tests that were carried out in two steps were very inefficient. Nevertheless, the attack of the pyritic phase continued during the second bioleaching (Fig. 8), since this phase did not present diffusion impediments and the reaction by-product was sulphate instead of elemental sulphur (Sand et al., 1995, 1999; Schippers and Sand, 1999).

### 4. Conclusions

For chalcopyrite leaching, the oxidation state of the dissolved iron (Fe$^{3+}$) was fundamental since it controlled the relative rate of the oxidation reactions involved in the leaching process.

The magnitude of the initial microbial attachment on the pyritic phase of the copper concentrate was related to the dissolution rate obtained during the leaching process. This was due to Fe$^{2+}$ liberation as a consequence of the pyrite attack by contact bioleaching.

Chalcopyrite leaching was controlled by the formation of elemental sulphur and intermediate copper sulphides, both of which are less reactive than the original chalcopyrite. Elemental sulphur and interme-
diate copper sulphides exert a severe barrier effect at low temperature (35 °C), whereas at high temperature (68 °C) these compounds do not affect the reagent diffusion.

Two-step bioleaching showed that pyrite did not present diffusion problems during its attack since the leaching reaction produces sulphate instead of S0. The chalcopyrite phase of the concentrate continued to passivate due to the presence of a strong layer adhering to the mineral surface, and this layer was very difficult to remove.

The bioleaching of the copper concentrate took place by means of a cooperative bioleaching strategy in which the contact bioleaching of the pyritic phase of the concentrate, possibly through the indirect mechanism via thiosulphate, and the indirect bioleaching of chalcopyrite, possibly through the indirect mechanism via polysulphide and elemental sulphur, simultaneously occurred.

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