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Leaching of chalcopyrite with ferric ion. Part I: General aspects

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A B S T R A C T

This paper presents a review of the literature on chalcopyrite leaching with ferric sulphate in acid medium. The effects of several parameters (ferric salt anion, oxidant concentration, pH and temperature) are examined and possible explanations are offered for the passivation of this sulphide during dissolution. The main theories related with chalcopyrite passivation point to the formation of a diffusion layer surrounding the chalcopyrite during dissolution, consisting of: bimetallic sulphide, copper polysulphide with a deficit of iron with respect to chalcopyrite, and elemental sulphur. Recent studies suggest that ferric ion plays two important and opposite roles in this process: as a mineral oxidizing agent and as the agent responsible for chalcopyrite passivation.

1. Introduction

Chalcopyrite, \( \text{CuFeS}_2 \), is the most abundant copper mineral in nature (Dutrizac, 1978) counting for about 70% of copper reserves in the world (Rivadeneira, 2006). In metallurgical applications it is mainly subjected to pyrometallurgical treatment after concentration by a flotation process. Hydrometallurgy, as an alternative to pyrometallurgy, presents important advantages such as the possibility of treating low-grade ores (increasingly more abundant in the case of copper) and easier control of waste, with the attendant benefits to the environment.

At present, approximately 18% of world copper production is treated by hydrometallurgy (Bravo, 2006). The process involves static leaching in heaps followed by solvent extraction and electrolytic precipitation of copper. Despite that, the only existing industrial processes for the treatment of chalcopyrite concentrates at present are pyrometallurgical. Chalcopyrite is highly refractory under hydrometallurgical conditions, due to surface transformations which render products very stable under oxidizing conditions (Burkin, 1969). Nevertheless, different hydrometallurgical processes have been investigated on both laboratory and pilot scales in attempts to implement these technologies at industrial level.

Any proposal for an economically viable hydrometallurgical process for the treatment of chalcopyrite should take into account basic studies that elucidate the chemical and electrochemical aspects governing leaching. This review presents information on the fundamental aspects of chalcopyrite leaching and the problems associated with low copper recoveries from this mineral.

2. Chalcopyrite crystal structure

The chemical formula that best describes chalcopyrite is \( \text{Cu}^{2+}\text{Fe}^{2+}\text{S}^2^- \) (De Filippo et al., 1988; Boekema et al., 2004; Mikhlin et al., 2004). The crystal structure consists in a relatively simple tetragonal lattice, close to cubic (Betejtin, 1977; Sand et al., 2001), with each sulphur ion surrounded by four metal ions of copper and iron located on tetrahedron angles and in a certain order in each plane (Fig. 1).

In the first and fifth planes, corresponding to the lower and upper faces of the tetragonal prism, Fe ions are located at the square angles and Cu ions in the middle. In the third plane, at the prism centre, the order is the reverse. In the second and fourth planes, two Cu ions bond two Fe ions, but there are iron ions underneath copper cations in the second plane, and vice versa in the fourth plane.

Fig. 1. Chalcopyrite crystal lattice (Betejtin, 1977).
Although chalcopyrite presents a crystal structure essentially characterized by covalent metal–sulphide bonds, its semiconducting properties indicate that not all bonding electrons correspond to simple covalent crystals (Forward and Warren, 1960).

The substitution of copper and iron by other metal atoms in the crystal lattice of natural chalcopyrites leads to the formation of n- and p-type semiconductor structures. Fig. 2 shows a simplified energy band diagram for n-type semiconductor chalcopyrite with an energy gap around 0.6 eV (Torma, 1991). While the electronic character of the lower part of the conduction band is given by Fe 3d orbitals, the upper part of the valence band is given by Cu 3d and S 3p orbitals.

3. Chemical leaching of chalcopyrite with ferric ion

The leaching of copper from sulphide ore bodies occurs naturally, releasing copper and iron. In ancient times, copper was recovered by cementation with metal iron and iron in the form of ferrous sulphate by evaporation of the solution. The first reference to the application of ferric acid sulphate solutions to the leaching of copper minerals is dated 1752, at Rio Tinto (Huelva, Spain). At that time, mineral heaps were irrigated with acid solutions and copper recovered by cementation with metal iron. Nevertheless, the development of chalcopyrite leaching processes using ferric solutions has been limited, chiefly because the slow kinetics makes for an incomplete mineral attack.

More recently, most research on chalcopyrite dissolution has been directed at elucidating reaction mechanisms and improving the leaching rate with ferric sulphate.

3.1. Thermodynamics and stoichiometry of the chalcopyrite dissolution

The Pourbaix diagram for the CuFeS₂–H₂O system (Fig. 3) (Garrels and Christ, 1965) shows that the dissolution of chalcopyrite in acid medium takes place through a solid transformation in different intermediate sulphides (Cu₅FeS₄, CuS, Cu₂S), increasingly richer in copper (Biswas and Davenport, 1976). According to this diagram, a pH lower than 4 and an oxidizing redox potential higher than +0.4 V is required to dissolve copper from chalcopyrite. These conditions are achieved using oxidizing agents, the most common being ferric ion as a sulphate or chloride.

Chalcopyrite dissolves in the presence of ferric ion according to the following reactions (Dutrizac and MacDonald, 1974):

\[
\begin{align*}
\text{CuFeS}_2 + 4\text{Fe}^{3+} &\rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0 \\
\text{CuFeS}_2 + 4\text{Fe}^{3+} + 3\text{O}_2 + 2\text{H}_2\text{O} &\rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{H}_2\text{SO}_4
\end{align*}
\]

Several researchers have reported the stoichiometry of chalcopyrite leaching. Chronologically, Trail and McClelland (1926) were the first to study the dissolution of chalcopyrite with concentrated ferric chloride (70 g/L) at high temperature (95°C); they obtained a copper yield of 90% after 5 h of leaching and only 60–70% of Fe, probably because it hydrolysed and precipitated during the process. In that study, the recovery of elemental sulphur was as low as 5%, confirming that the reaction is stoichiometric (2). In 1933, Sullivan investigated dissolution of chalcopyrite concentrates in both ferric chloride and ferric sulphate, concluding that around 75% of chalcopyrite dissolves according to reaction (1) and the remaining by reaction (2). The lower rate of sulphate formation was attributed to the presence of dissolved oxygen more than to the action of ferric ion. Ichikuni (1960) established that ferric sulphate dissolved chalcopyrite according to reaction (1); he found only slight deviations of the Cu/Fe molar ratio in solution during the initial stage of leaching with ferric chloride and concluded that there was a preferential dissolution of Fe from the chalcopyrite lattice. Dutrizac et al. (1969) studied the dissolution process of chalcopyrite-sinterized discs in acid ferric sulphate. The stoichiometry of chalcopyrite dissolution was described by reaction (1) and the rate-controlling step was assumed to be the transport of ferric sulphate through a sulphur layer, in constant growth, surrounding the chalcopyrite surface. Then, in 1971, Haver and Wong (1971) proposed a third reaction to describe chalcopyrite dissolution with FeCl₃:

\[
\text{CuFeS}_2 + 3\text{FeCl}_3\text{Cl}_2\rightarrow \text{CuCl} + 4\text{FeCl}_2 + 2\text{S}^0
\]

These authors found that around 70% of the sulphur was oxidized to elemental sulphur and the remainder to sulphate, and they proposed that copper was dissolved in the monovalent form (Cu⁺).

Dutrizac (1989) established that during chalcopyrite leaching with ferric sulphate at 95 °C the sulphide sulphur was practically all oxidized to S²⁻ (94%). More recently, in 1995, Hackl et al. (1995) found that during leaching of chalcopyrite with ferric sulphate at high temperature and an oxygen pressure of 0.69 MPa, the oxidation of sulphide sulphur to sulphate increased from 28 to 100% when the temperature rose from 110 to 200 °C. This was associated with an increase in oxygen consumption.

These results indicate that although both reactions (1) and (2) can take place during the leaching of chalcopyrite, the formation of sulphate is limited by the availability of oxygen in the leaching medium.

Nevertheless, recent studies have demonstrated that chalcopyrite transforms into intermediate phases and so reactions (1) and (2) must be considered as overall reactions of the chalcopyrite dissolution process.

3.2. Effect of ferric salt anion

Sullivan concluded that ferric chloride is a better chalcopyrite leaching agent than ferric sulphate and that the effect was more
marked at high temperatures. Dutrizac et al. (1969) found that, in a temperature range between 50 and 100 °C, the chalcopyrite leaching rate was linear in chloride medium and parabolic in sulphate medium. Two years later, Dutrizac and MacDonald demonstrated that the addition of chloride ion sped up chalcopyrite dissolution with ferric sulphate at temperatures higher than 50 °C (Dutrizac and MacDonald, 1971). At lower temperatures there was no effect. Majima et al. (1985) established that the chalcopyrite leaching rate was approximately one order of magnitude lower with ferric sulphate than with ferric chloride. This agrees with the observation made by these authors that the elemental sulphur formed during leaching was more porous with ferric chloride than with ferric sulphate.

These researches support the idea that ferric chloride has greater oxidizing power than ferric sulphate during chalcopyrite leaching. However, several factors restrict the application of ferric chloride on an industrial scale, such as:

- The affinity of this ion towards many elements complicates the process of separating copper from the solution.
- Chloride solutions are extremely corrosive.
- Hydrochloric acid is more expensive than sulphuric acid.

The last factor is of prime importance since pyrometallurgical extraction of copper from chalcopyrite, as in other industries, entails the recovery of large amounts of SO₂ to achieve sulphuric acid production at very low cost.

3.3. Effect of ferric ion concentration

Different researchers have pointed out that the chalcopyrite dissolution rate is strongly affected by ferric ion concentration, but only at low concentrations. At high concentrations, the effect is negligible. Sullivan (1933), Linge (1976), Dutrizac et al. (1969), Muñoz et al. (1979) and Kametani and Aoki (1985), among others, found no clear kinetic effect when the ferric ion concentration exceeded 0.01 M.

A few authors have observed a relationship of dependence between chalcopyrite dissolution rate and ferric ion concentration. Hirato et al. (1987) found that chalcopyrite dissolution improved when the concentration of ferric sulphate was increased from 0.001 to 0.1 M. These authors estimated that the concentration of Fe³⁺ and FeHSO₄⁻² ionic species increased when the total iron concentration increased, up to a limiting value of 0.1 M. Above this value, the most important species was FeSO₄. They concluded that the Fe³⁺ and FeHSO₄⁻² ionic species are responsible for chalcopyrite dissolution in sulphate medium.

3.4. Effect of pH

pH also affects chalcopyrite dissolution. According to Dutrizac et al. (1969), the acid prevents hydrolysis and precipitation of ferric salts, since proton attack is negligible. Some researchers (Lu et al., 2000; Antonijević and Bogdanović, 2004) have reported poor results for chalcopyrite dissolution at low pH (<1.0). The first authors reported that the precipitation of ferric ion as jarosite is possible even at pH 0.9, which shows how readily ferric salts hydrolyse. Antonijević and Bogdanović found that at pH lower than 0.5, the chalcopyrite surface lacks iron and this provokes its passivation. Our results (Fig. 4) show that, in a pH range of 0.5 to 2.0, although increased pH favours hydrolysis and precipitation of the oxidant, dissolution of chalcopyrite with ferric sulphate diminishes with decreasing pH. This is understandable if we consider the speciation diagrams for Fe(III) in sulphate medium. These show that the species responsible for oxidation of the chalcopyrite is not Fe³⁺ proper, but probably Fe(SO₄)₂⁻ since that is the only species to show an increase of concentration in the given pH range.

3.5. Effect of temperature

Table 1 shows the values of activation energy reported by different researchers during chalcopyrite leaching with ferric ion. It also indicates the kinetic control proposed in each study.

The high values of activation energy found by different authors demonstrate the need for high temperatures in order to break down bonds in the chalcopyrite crystal lattice. Our results (Fig. 5) show that the effect of temperature on chalcopyrite chemical leaching is very pronounced in the range between 35 and 68 °C. In that range, copper extraction increased from <3% to >80% after 13 days of leaching and an activation energy of 130.7 kJ/mol was determined, which is appreciably higher than that reported by other researchers (71–88 kJ/mol) in the range of temperature between 50 and 94 °C using a sulphate medium (Table 1). Thus, the differences observed are presumably due to the different range of temperature tested.

These results agree with the theoretical analysis of Hiskey (1993) who concluded that due to n-type semiconduction of chalcopyrite, the transport of electrons through vacancies is minimum. The first stage in chalcopyrite oxidation, consumes vacancies, which favours the transport of electrons through the crystal lattice. Therefore, the heat consumed in the displacement of ions from the bulk to the surface eliminates vacancies at the surface and promotes the transport of electrons. This means chemical mechanisms control chalcopyrite dissolution; however, as noted earlier, diffusion of the oxidant is also very important in this process.

We would note that there are clear differences when using one or other type of medium (sulphate or chloride). The activation energies

<table>
<thead>
<tr>
<th>Medium</th>
<th>Temperature (°C)</th>
<th>Activation energy (kJ/mol)</th>
<th>Kinetic control</th>
<th>Bibliographic reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric sulphate</td>
<td>50–94</td>
<td>71</td>
<td>Parabolic kinetics Diffusion control</td>
<td>Dutrizac et al., 1969</td>
</tr>
<tr>
<td></td>
<td>60–90</td>
<td>84</td>
<td>Parabolic kinetics Electrochemical control</td>
<td>Muñoz et al., 1979</td>
</tr>
<tr>
<td></td>
<td>50–78</td>
<td>88</td>
<td>Parabolic-linear kinetics Chemical control</td>
<td>Hirato et al., 1987</td>
</tr>
<tr>
<td></td>
<td>35–68</td>
<td>130.7</td>
<td>Parabolic-linear kinetics Chemical control</td>
<td>Córdoba et al., in press</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>60–90</td>
<td>60</td>
<td>Linear kinetics Electrochemical control</td>
<td>Hirato et al., 1986</td>
</tr>
<tr>
<td></td>
<td>55–84</td>
<td>69</td>
<td>Linear kinetics Electrochemical control</td>
<td>Magjima et al., 1985</td>
</tr>
<tr>
<td></td>
<td>50–100</td>
<td>47</td>
<td>Linear kinetics Diffusion control</td>
<td>Dutrizac, 1978</td>
</tr>
</tbody>
</table>
are higher in sulphate than in chloride medium, which is consistent with the lower oxidizing power of ferric sulphate (Section 3.2).

4. Passivation of chalcopyrite during leaching with ferric ion

After almost a century of research into the mechanisms of chalcopyrite dissolution in ferric medium, there is consensus with respect to the formation of a passivating layer on the surface which slows down the oxidation reaction. But in spite of that, the nature of this film is still unknown, although it has been postulated that it must have low porosity and/or be a bad electric conductor. Following is an account of the principal theories on this topic.

In 1969, Burkin (1969) established that the diffusion film surrounding the chalcopyrite during leaching with Fe$^{3+}$ formed by a bimetallic sulphide with chemical and structural properties different from the original raw material, but with the same semiconducting properties. These intermediate products are the result of solid state transformations that favour solubilization of cations from the crystal lattice at different rates. Therefore, the model implies that the reaction takes place preferentially at the interface, within the thickness of a reaction front.

Later, Ammou-Chokroum et al. (1977) suggested that the rate of the dissolution process is controlled by the formation and evolution of a compact diffusion layer of a low-solubility copper polysulphide, less reactive than the original chalcopyrite and with less iron. The thickness of this film is the result of two opposite reactions (Fig. 6): 1) formation of a passive layer, $C_p$, because solid state diffusion is slower in copper than in iron, which obeys a parabolic law; and 2) linear dissolution of the passive layer, producing an outer film of porous sulphur with no controlling effect.

In 1979, Muñoz et al. (1979) postulated that the limiting step in chalcopyrite dissolution with ferric ion is the transport of electrons, necessary to reduce the ferric ion in the solid–liquid interface, through an insulating film of elemental sulphur (Fig. 7). According to this model, the elemental sulphur affects both anodic and cathodic semi-reactions, limiting the overall redox reaction of chalcopyrite dissolution. This model has been ratified by Dutrizac (1989) and Majima et al. (1985).

In 1995, Hackl et al. (1995) proposed a model mixture of chemical and diffusion control to explain the leaching and passivation of chalcopyrite in sulphate medium. This model complements the model of Ammou-Chokroum et al. (1977). Initially, iron dissolves preferentially to copper forming an intermediate disulphide phase, $Cu_{1-x}Fe_xS_2$, where $y/x > x$ and $x+y = 1$:

$$CuFeS_2 → Cu_{1-x}Fe_xS_x + (x+y)Cu^{2+} + yFe^{2+} + 2(x+y)e^- , \quad y/x > x, \quad x+y = 1$$

In the second stage:

$$Cu_{1-x}Fe_xS_x → Cu_{1-x}Fe_xS_y + 2Cu^{2+} + (1-y)Fe^{2+} + 2(z+1-y)e^-$$

which is slower than the previous stage, the disulphide dissolves to form a copper polysulphide, $Cu_{1-x}S_2$ or $Cu_{x+y}S_y$, where $n = 2/[1 - (x-z)]$. This polysulphide is probably responsible for chalcopyrite passivation. Thus, the rate-controlling step consists of a very slow decomposing of copper polysulphide to cupric ions and porous elemental sulphur, with no effect on chalcopyrite passivation:

$$Cu_{1-x}S_x → (1-x-z)Cu^{2+} + 2S^0 + 2(1-x-z)e^-$$

This model greatly depends on temperature, since the polysulphide dissolution rate increases with temperature. Chalcopyrite passivation does not occur at 200 °C.

In a recent work, Hiroshi et al. (2001) studied the effect of ferrous ion on chalcopyrite oxidation with ferric ions in sulphuric acid and in the absence of oxygen. They discovered that in the presence of high concentrations of cupric ion, the ferrous ion has a very positive effect on copper extraction and the kinetics were controlled by the ratio of Fe$^{3+}$/Fe$^{2+}$ concentrations or by the redox potential of the solution. However, the ferrous ion adversely affected chalcopyrite oxidation at low cupric ion concentrations. To account for these results, they proposed a reaction model involving incomplete reduction of chalcopyrite, according to the following reaction:

$$CuFeS_2 + 3Cu^{2+} + 3Fe^{2+} → 2CuS + 4Fe^{3+}$$

This reaction is followed by oxidation of Cu$S$ (more sensitive to leaching than chalcopyrite) by ferric ion:

$$CuS + 4Fe^{3+} → 2Cu^{2+} + S^0 + 4Fe^{2+}$$

The two reactions (7) and (8) give the overall reaction (1), which traditionally describes the leaching of chalcopyrite in ferric medium. According to this model, the rate-controlling step is the initial reduction of chalcopyrite. This only happens when the redox potential of the solution is below a critical value, which in turn is a function of the concentration of ferrous and cupric ions.
the mechanism of chalcopyrite dissolution by Fe$^{3+}$ has not yet been elucidated. However, the nature of this barrier is still in debate since ferric ions act as a diffusion barrier between the leaching solution and the chalcopyrite that slows down the dissolution rate. Nevertheless, the redox potential of the chalcopyrite surface increases from 0.5 to 0.7 V.

Figure 8. SEM micrograph of a leaching residue at $E_{\text{Initial}}=600$ mV.

The rate-controlling step is electrochemical. The rate of reaction (10) decreases when the redox potential of the chalcopyrite surface is lower than the critical potential of approximately 450 mV vs Ag/AgCl. Then, when the initial redox potential is very high, that tendency to equilibrium favours rapid precipitation of ferric ion as jarosite (Fig. 8) and consequently chalcopyrite passivation.

The evidence cited above suggests that passivation of chalcopyrite during leaching is chiefly the result of hydrolysis and precipitation of Fe$^{3+}$ rather than partial transformation of the chalcopyrite surface.

5. Silver-catalyzed chalcopyrite leaching

A way to improve the chalcopyrite dissolution rate is by adding Ag$^+$. In 1976, Pawlek (1976) studied the effect of Ag$^+$ on the leaching of chalcopyrite at 110 °C and 100 kPa. After 30 min, chalcopyrite dissolution was complete in the presence of silver compared with 40% copper dissolution in the absence of silver. In 1979, Miller and Portillo (1979) proposed a model to interpret the catalytic effect of silver ions in the leaching of chalcopyrite with sulphuric acid/ferric sulphate solutions. The authors suggested that in the absence of silver ions, a dense elemental sulphur layer forms on the mineral surface, acting as a diffusion barrier and delaying the oxidative leaching of chalcopyrite with ferric ions. Conversely, in the presence of silver ions the leaching of chalcopyrite takes place according to the following reactions:

$\text{CuFeS}_2 + 4\text{Ag}^+ \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2\text{Ag}_2\text{S}$  \quad (11)

$\text{Ag}_2\text{S} + 2\text{Fe}^{3+} \rightarrow 2\text{Ag}^+ + 2\text{Fe}^{2+} + \text{S}^0$  \quad (12)

The rate of copper extraction is faster in the presence of silver ions since the product layer is formed by a mixture of sulphur and Ag$_2$S, which is porous and does not exert a barrier effect on the chalcopyrite dissolution. Price and Warren (1986) reported that the elemental sulphur obtained under silver catalytic conditions, besides being more porous, presented higher electrical conductivity and hence facilitated the transport of electrons through the chalcopyrite surface.

The model proposed by Miller and Portillo has since been confirmed by Burkini (1982) and Price and Warren (1986), who detected the formation of silver sulphide on the chalcopyrite surface.

At the same time, some authors (Burkin, 1982) have pointed out that silver can substitute copper in the crystal lattice of copper sulphides, given the chemical similarities between copper and silver.

With an excess of Ag, the reaction product on the mineral surface could contain silver and silver sulphate. This is undesirable because of the amount of silver that may be consumed and lost before the objective is achieved — i.e., to diminish the formation of elemental sulphur on the chalcopyrite surface. An excess of silver can also facilitate the sequestering of silver by jarosite (Carranza et al., 1997; Bolorunduro et al., 2003).

The formation of silver jarosite may be represented by reaction:

$\text{Ag}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{AgFe}_2(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+$  \quad (13)

6. Electrochemical characterization and passivation of chalcopyrite

Fig 9a and b shows the electrochemical behaviour of an electrode of massive chalcopyrite at 35 °C.

It is accepted that during anodic polarization of chalcopyrite from its rest potential, there are normally two different electrochemical responses (Biegler and Horne, 1985; Warren et al., 1985; Price and Warren, 1986; Gómez et al., 1996). The first peak, between the rest potential and approximately +740 mV vs. Ag/AgCl, is known as the transpassive zone. The second peak, at higher potentials, is known as the passive zone.

In the passive zone, the chalcopyrite surface transforms into a copper-rich sulphide (CuS) and S$^0$ because of the preferential dissolution of iron from chalcopyrite. The formation of covellite at 35 °C has been justified by reaction (14) (Jones and Peters, 1976), reaction (15) (Biegler and Swift, 1979; Biegler and Horne, 1985) or by the transformation of chalcopyrite in an intermediate phase (bornite).
much a matter of debate, it is unanimously agreed that the leaching of ferric ion in solution affects the process in two ways:

- It favours leaching of the mineral when the ferric concentration is high.
- It causes passivation of the mineral surface and protects it from attack through the formation of intermediate compounds when the ferric concentration is high.

At the same time, the ferrous ion plays an important role in this process by balancing the composition of the leaching solution and delaying the precipitation of ferric ion as jarosite, its nucleation on the mineral surface, and ultimately passivation of the sulphide.

References


