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

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ABSTRACT

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, ($CuFeS_2$), 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 $Cu^{+}Fe^{3+}S_2^{2-}$ (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.

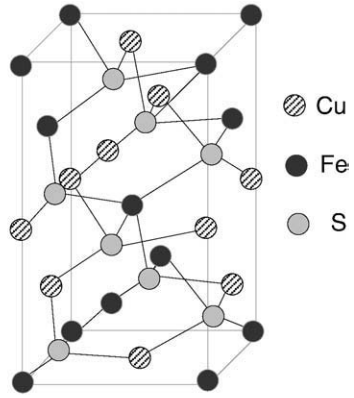

Fig. 1. Chalcopyrite crystal lattice (Betejtin, 1977).

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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 Río 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 $CuFeS_2$–H_2O 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 (Cu_5FeS_4, CuS, Cu_2S), 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):

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^{\circ} \quad (1)$$

$$CuFeS_2 + 4Fe^{3+} + 3O_2 + 2H_2O \rightarrow Cu^{2+} + 5Fe^{2+} + 2H_2SO_4 \quad (2)$$

Several researchers have reported the stoichiometry of chalcopyrite leaching. Chronologically, Traill 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 $FeCl_3$:

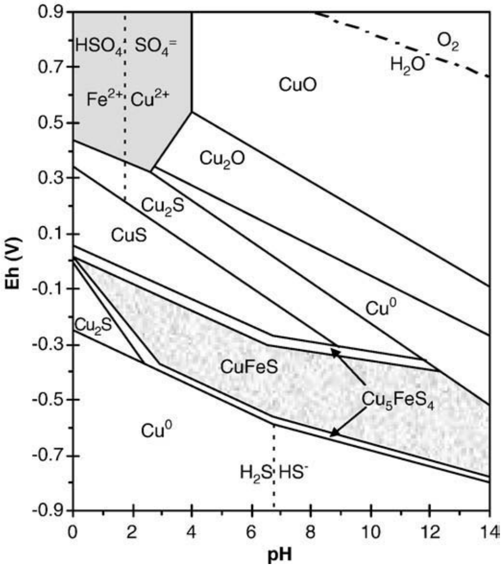

Fig. 3. Pourbaix diagram for the $CuFeS_2$–H_2O system at 25 °C (Garrels and Christ 1965).

$$CuFeS_2 + 3FeCl_3FeCl_3 \rightarrow CuCl + 4FeCl_2 + 2S^{\circ} \quad (3)$$

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 S° (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.

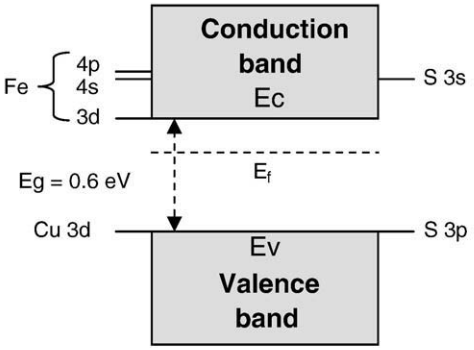

Fig. 2. The energy band diagram for chalcopyrite (Torma, 1991).

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