

# The effect of chemical additives on the electro-assisted reductive pretreatment of chalcopyrite

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## ABSTRACT

The oxidative leaching of chalcopyrite demands extreme conditions of temperature and solution potential or non-aqueous solvents because of the formation of recalcitrant passivation layers. Chalcopyrite reduction suffers much less from this phenomenon and therefore could provide a starting point as a pretreatment to facilitate the subsequent leach. However, even though the electro-assisted reduction reactions occur at ambient temperature and pressure, the kinetics are slow, and consequently the power requirements are too high, to compete with conventional technology. A further decrease in passivation for a given reduction time should enhance the formation of chalcocite and metallic copper, which should result in an improved copper extraction in the subsequent oxidative leaching stage. This would directly impact the economy of the process.

The use of complexing agents for iron(II), sulfide and copper(I) in sulfuric acid solutions increased the amount of chalcocite and metallic copper formed in the electro-assisted reduction pretreatment of chalcopyrite compared with the same leaching system with only H<sub>2</sub>SO<sub>4</sub>. The improvement in the copper extraction in the subsequent oxidative stage is probably due to the complexation of iron by the carboxylic acids and sulfur by the ethanolamines in the reductive pretreatment, thus avoiding the formation of a pyrrhotite (FeS) passivation layer on the chalcopyrite surface. On the other hand, ethylene glycol stabilizes copper as the cuprous ion, facilitating the chalcopyrite transformation and copper extraction; however, this action alone is not as effective as the carboxylic acids and the ethanolamines in diminishing passivation.

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## 1. Introduction

Sulfide minerals are the main source of base metals. Approximately 70% of world's copper reserves are in the form of chalcopyrite (CuFeS<sub>2</sub>), making it the most profitable copper mineral (Davenport et al., 2001). Currently, copper sulfides are processed mainly by pyrometallurgy and only 15 to 20% of copper production, mostly oxides, is extracted by hydrometallurgical methods. Although there are two types of hydrometallurgical processes, oxidative and reductive, practically all of the processes developed to extract copper from chalcopyrite use the oxidative route, in the leaching stage (Dreisinger and Abed, 2002). However, these last methods require high pressure and temperature or non-aqueous solvents (Muir and Senanayake, 1985) to achieve quantitative chalcopyrite dissolution. The reason for this behavior is that chalcopyrite is passivated by intermediate sulfides, which impede the oxidant from reaching the chalcopyrite surface, thus preventing further reaction (Parker and Muir, 1981; Parker and Power, 1981).

Many research teams in the last 50 years have contributed to the explanation of this passivation phenomenon with the aim of finding ways to diminish its effects. Since the reaction rate depends on the hydrogen

ion concentration [H<sup>+</sup>] (Hiskey and Wadsworth, 1975), the chalcopyrite is usually leached at highly acidic conditions, employing solutions containing concentrated hydrochloric or sulfuric acid. Ferric chloride, copper chloride and hydrochloric acid, as part of the chloride leaching media, lessen the problem, but have the disadvantage of high corrosivity. High pressure leaching and ferric sulfate leaching also offer limited improvement. However, none have been sufficiently successful to lower the leaching temperature to near ambient values, which could permit a more selective copper extraction. Finally, bacterial leaching has the disadvantage of being a slow process.

One option to avoid these problems is to employ the reductive route, specifically electro-assisted reductive pretreatments in which chalcopyrite is transformed into less refractory sulfides (chalcocite and djurleite) or copper metal. Generally, these processes do not show the same degree of passivation as the oxidative ones. However, there is very little information regarding the reduction mechanism.

The nature of the chalcopyrite reduction reaction products is determined by the pH and composition of the electrolytic solution. The thermodynamic data in the form of E<sub>h</sub>-pH diagrams provide a guide to obtain information about the reactions taking place. In particular for chalcopyrite, the products of the reduction reaction under acidic conditions are expected to be hydrogen sulfide (H<sub>2</sub>S) and ferrous ion (Fe<sup>2+</sup>), as well as bornite, chalcocite, and copper metal as solid phases, in that

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order as the potential becomes more negative (Fuentes-Aceituno et al., 2008). In the reduction processes, iron and sulfur are extracted from the mineral, leaving a copper rich sulfide (Biegler and Swift, 1976).



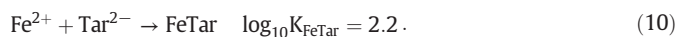
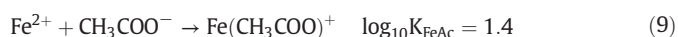
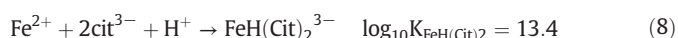
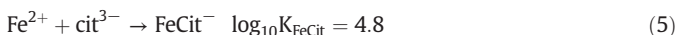
The electrons needed for this reaction may come from a reducing agent or from direct electrolytic reduction (because copper sulfides have semiconducting properties). Metals, such as aluminum, iron, lead or zinc have been used as reducing agents in acidic media (Lapidus and Doyle, 2006). However, the problems of high reagent consumption and toxic  $\text{H}_2\text{S}$  production limit this approach. The electro-assisted reduction process helps minimize these problems, but has not previously been investigated in detail.

Electro-assisted reduction of chalcopyrite is possible at ambient temperature and pressure, with an aluminum cathode and a lead-silver alloy anode (Martínez-Jiménez and Lapidus, 2012). According to these authors, the reduction reactions are as follows:



where  $\text{H}\cdot$  is the monoatomic hydrogen produced on the cathode surface. The chalcopyrite to chalcocite reduction (3) is proposed as the rate-limiting step. However, at the reaction boundary, high concentrations of ferrous and sulfide ions can lead to the formation of pyrrhotite ( $\text{FeS}(\text{s})$ ), which probably causes passivation.

In order to favor iron extraction and, consequently, lessen the passivation problem, the addition of carboxylic acids to the reduction pretreatment solution, as ligands for the ferrous ion, has been proposed, (Martínez-Jiménez and Lapidus, 2012). The complexation reactions with citrate, acetate and tartrate ions are as follows (NIST Standard Reference Database 46, 2004):

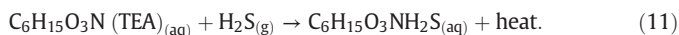


The same authors (Martínez-Jiménez and Lapidus, 2012) reported metallic copper as the main reduction product, which spontaneously reacts to copper oxide when the solids contact air. However the reaction is still quite slow, possibly because of the difficult solid-state transformation.

On the other hand, the copper in chalcopyrite occurs as  $\text{Cu}(\text{I})$ , but the cuprous ion is not stable in sulfate solution, requiring the potential to be high enough to oxidize it to  $\text{Cu}(\text{II})$  state or, in the reduction route, to stabilize it in the cuprous form, and to avoid disproportionation. Nelson et al. (1961) showed that the cuprous ion solubilizes in polar organic solvents. It has been demonstrated that polar organic solvent solutions increase chalcopyrite dissolution under ambient conditions (Muir and Senanayake, 1985; Solís and Lapidus, 2014) by stabilizing the cuprous ion, thereby enhancing copper extraction.

Regarding the chalcopyritic sulfide ion, aqueous solutions of triethanolamine (TEA) are widely employed in the petroleum industry

to remove  $\text{H}_2\text{S}$  from gaseous streams and extract it into the solution, according to the following reaction (Kumar, 1987):



As mentioned earlier, a high  $\text{H}_2\text{S}$  concentration probably causes the formation of pyrrhotite on the surface of the chalcopyrite, which passivates the mineral surface. By diminishing the hydrogen sulfide concentration, the formation of pyrrhotite may be avoided, thus enhancing the chalcopyrite conversion to chalcocite and metallic copper.

In this investigation, the nature of the reactions in the reduction of chalcopyrite is studied, employing the following complexing media: ethylene glycol for  $\text{Cu}(\text{I})$  stabilization, triethanolamine to sequester  $\text{H}_2\text{S}$  and carboxylic acids to complex the ferrous ion.

## 2. Experimental materials and methods

Cyclic voltammetry and chronoamperometry were used to determine the nature of the reactions that take place at the chalcopyrite surface in the different leaching media and to characterize the solid products formed on the surface of the mineral.

Because it has been reported that  $\text{H}_2\text{S}$  plays an important role in the reaction mechanism of the reduction step (Martínez-Jiménez and Lapidus, 2012), electro-assisted reductive pretreatment experiments were carried out with the same mineral to validate the chalcopyrite reactivity shown in the electroanalytical techniques with the different media.

### 2.1. Electrochemical characterization in carbon paste electrodes with voltammetry and chronoamperometry

The electrochemical simulations of the process were performed using cyclic voltammetry and chronoamperometry on chalcopyrite in the form of carbon paste electrodes, in a three-electrode cell. These experiments are the basis for determining the interaction between the chalcopyrite and the different media.

Carbon pastes were prepared using the wet sieved  $-200 + 325$  mesh fraction (44–74  $\mu\text{m}$ ) of a relatively pure chalcopyrite (82.9% chalcopyrite, 11.1% pyrite and 6.0% quartz) from Kidd Creek Mine (Excalibur Mineral Corporation, Inc.), graphite powder (Alfa Aesar 99.99% 2–15  $\mu\text{m}$ ) and silicone oil (Sigma,  $\rho = 0.96$  g/mL) as a binder. 0.4 g of graphite powder and 0.1 g of the chalcopyrite were mixed in an agate mortar with 0.15 mL of the silicone oil to generate a homogeneous paste (Lazaro et al., 1995). The mixture was then placed in a polyethylene syringe (0.7 cm length and 0.2 cm inner diameter) and was compacted using the plunger. A platinum wire welded to a copper wire with silver solder was used to establish electrical contact for electrochemical characterization of the surface reactions.

The carbon paste electrode (working electrode) was submerged in a 100 mL glass cell which contained 50 mL of the electrolyte solution at ambient temperature, which had been previously sparged with nitrogen for 30 min to eliminate  $\text{O}_2$  and  $\text{CO}_2$ . A reference electrode (saturated sulfate electrode, Radiometer Analytical,  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$  saturated, SSE) and a graphite counter-electrode (Alfa Aesar, 99.99%) were placed in the cell as well. The voltammetric and chronoamperometric response were obtained with a PARSTAT potentiostat (model 2373) coupled to a personal computer. The surface of the working electrode was renewed after each voltammogram to remove the products formed. The solutions used in the experiments consisted in 1 M  $\text{H}_2\text{SO}_4$  solution (electrolytic medium) and the following substances: ethylene glycol (20% v/v), tartaric acid (0.5 M), citric acid (0.25 M) and TEA (0.5 M).

### 2.2. Electro-assisted reductive pretreatment and oxidative leaching

The electro-assisted reductive pretreatment experiments were performed in a single chamber electrolytic cell, which consisted of a

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