



# Study of chalcopyrite leaching from a copper concentrate with hydrogen peroxide in aqueous ethylene glycol media

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## ABSTRACT

The use of polar aqueous solvents, such as acetone, methanol and ethylene glycol, together with hydrogen peroxide and sulfuric acid solutions, have been shown to increase chalcopyrite dissolution. However, the reason for this improvement is not clear, especially in the case of ethylene glycol. The objective of the present study is to investigate the nature of chalcopyrite leaching, with and without the presence of ethylene glycol (EG), and to understand the role of this polar solvent in the modification of the characteristic behavior involved. For this purpose, a relatively pure chalcopyrite concentrate was leached at 20 °C and atmospheric pressure (79 kPa, México City) with hydrogen peroxide in aqueous sulfuric acid solutions, with and without EG. The results showed that, in the absence of EG, the decomposition of 99% of the initial hydrogen peroxide in 24 h, was catalyzed by the  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions (Fenton reagents) present as a consequence of the leach itself. Furthermore, after the first six hours, the copper and iron dissolution effectively ceased (44 and 37%, respectively). In contrast, in the presence of EG, the  $\text{H}_2\text{O}_2$  consumption was minimal (~16%) in the same time period and mostly due to the oxidation reactions. The final extractions for copper and iron were 90 and 71%, with an ascendant tendency. It was suggested that hydroxyl radicals, product of the Fenton-type reactions, are the driving force for peroxide decomposition and, these were shown to be absent in solutions containing ethylene glycol.

Chalcopyrite dissolution kinetics in the presence of ethylene glycol, are well described by the reaction-controlled shrinking particle model. The kinetic expression is a first order function of the hydrogen peroxide concentration and is not dependent on the  $\text{H}^+$  concentration, although peroxide decomposition slightly increased at higher pH values. The reaction controlling the dissolution process was determined to be the conversion of the chalcopyritic sulfide to elemental sulfur; this was followed by its oxidation to sulfate, although apparently did not affect the leaching kinetics.

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## 1. Introduction

Chalcopyrite ( $\text{CuFeS}_2$ ) is the most abundant copper-containing mineral in nature and the primary source for copper production (Córdoba et al., 2008a; Rivadeneira, 2006). It is usually processed by high temperature pyrometallurgical methods. However, these procedures are only cost-effective for high grade concentrates (greater than 20% Cu) due to their limited selectivity.

One of hydrometallurgy's advantages is that low grade ores or concentrates may be economically processed and generally allows easier handling of the generated waste. Although current day hydrometallurgical routes cannot completely substitute the smelting/conversion sequence, several hydrometallurgical processes, such as the high-pressure CESL process developed by Teck Resources Limited, have proven to be technically sound, transforming chalcopyrite into cupric sulfate,

hematite and elemental sulfur (Defreyne et al., 2006). Despite their relative success, these process routes are problematic, due to their inclusion of chloride as a catalyst, and lack of specificity for copper sulfides.

As has been observed by numerous research teams, chalcopyrite is highly refractory in acid media due to superficial chemical transformations, which generate compact, stable and electrically resistive products (Liddicoat and Dreisinger, 2007; Córdoba et al., 2008a). These entities, known as passive layers, limit mineral dissolution. Their chemical nature depends on diverse factors, which include redox potential, concentration and type of oxidant, as well as of the acid employed (Nava and González, 2006; Córdoba et al., 2008a), although the general consensus is that the passivation resides in the formation of an iron-deficient polysulfide layer (Ammou-Chokroum et al., 1977; Hackl et al., 1995).

Chalcopyrite dissolution in aqueous acid media takes place through solid transformations into different intermediaries, such as bornite ( $\text{Cu}_5\text{FeS}_4$ ), covellite ( $\text{CuS}$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ), finally producing  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  at solution potentials (ORP) above 0.4 V vs SHE. This state may be achieved using one of many oxidants, such as oxygen, ozone, hydrogen peroxide, Caro's acid, ferric sulfate and chloride.

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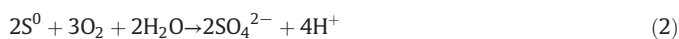
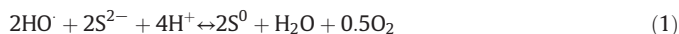
Córdoba et al. (2008a, 2008b, 2008c) published a review of the principal studies in the ferric chloride and sulfate systems, the most common systems for chalcopyrite leaching. They showed that, while the dissolution in ferric chloride showed a linear tendency, copper extraction was basically slower with parabolic-type kinetics in the sulfate system. This verifies the advantage of chloride, which complexes the cuprous ion, although in ferric chloride media, the dissolution is still limited by passivation. An important drawback of the chloride ion is its corrosive nature, which is an important consideration for the scale-up of the process.

Among the less toxic oxidants, hydrogen peroxide has received the most attention since it satisfies the oxidation potential criterion ( $E^{\circ} = 1.77$  vs SHE) and has been successful in the oxidation of other refractory sulfides, such as sphalerite (ZnS) and pyrite (FeS<sub>2</sub>) (Antonijević et al., 1997; Antonijević et al., 2004). However, hydrogen peroxide easily decomposes in the presence of metallic ions, especially, iron and copper, whose concentrations increase as the leach progresses.

Several investigations have been undertaken to evaluate the ability of hydrogen peroxide to leach chalcopyrite in sulfuric acid media. For instance, Adebayo et al. (2003) studied the kinetics in a wide range of conditions (323–353 K, 10–20% weight H<sub>2</sub>O<sub>2</sub> and 0.1–6 M H<sub>2</sub>SO<sub>4</sub>) and reported that the increase in peroxide and acid concentrations favored the process, achieving almost complete dissolution in 30 min at 323 K. Despite these excellent results, substantial hydrogen peroxide decomposition was inevitable due to the presence of copper and iron cations, especially significant at higher temperatures where thermal decomposition also contributed to the problem.

Excessive peroxide depletion by the metallic cations, and the subsequent termination of chalcopyrite dissolution after 60 min, was also observed by Olubambi and Potgieter (2009), and independently by Agacayak et al. (2014), at elevated concentrations of peroxide. These last authors also found that the decomposition accelerated at higher temperatures.

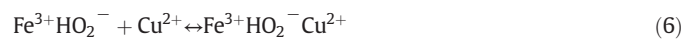
The explanation of the aforementioned behavior can be found in the nature of the resulting solutions. The Fenton reactions, discovered over 100 years ago, consist of the reaction of iron salts with hydrogen peroxide to form hydroxyl radicals, which have a redox potential superior to that of peroxide alone (Neyens and Baeyens, 2003). This combination is frequently used to destroy toxic organic contaminants (Yoon et al., 2001). In this direction, Lin and Luong (2004) found that hydroxyl radicals oxidize sulfide ions, first to elemental sulfur and later, in the presence of oxygen, can transform these to sulfate, according to the following reactions:



Fenton-type reactions, and their effect on the decomposition of hydrogen peroxide, have been the subject of much research (Barb et al., 1951; Eary, 1985; Kremer, 1962, 2006). Especially important for this study is the work by Kremer (1962 and 2006), who studied the influence of the cupric ion, in the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup>, on the decomposition of hydrogen peroxide in acidic solutions. According to this author, hydrogen peroxide reacts with the ferric ion in the following manner:



And in the presence of Cu<sup>2+</sup>, the destruction of the Fe<sup>3+</sup>HO<sub>2</sub><sup>-</sup> complex is hastened, according to the following sequence, which favors the decomposition of peroxide to oxygen:



The problem of hydrogen peroxide decomposition changed considerably when Mahajan et al. (2007) found, in the presence of small amounts of ethylene glycol, the oxidative dissolution of chalcopyrite was possible, with acidic solutions of relatively low concentrations of H<sub>2</sub>O<sub>2</sub>. The authors attributed this improvement to the stability of hydrogen peroxide in aqueous solutions of ethylene glycol. Solis-Marcial and Lapidus (2013) also observed increased chalcopyrite leaching in the presence of acetone, methanol, 2-propanol and ethylene glycol; however, solvent mineralization and excessive H<sub>2</sub>O<sub>2</sub> consumption were detected in the case of acetone, but not with the other organics.

Neither Mahajan et al. (2007) nor Solis-Marcial and Lapidus (2013) studied the stoichiometry of the chalcopyrite dissolution reaction or, in greater detail, of the hydrogen peroxide decomposition reactions in these polar organic solvents, especially ethylene glycol. Furthermore, a distinct approach to enhance copper extraction from chalcopyrite is to modify the leaching medium, in order to prevent or diminish formation of the passive layer. The use of polar organic solvents together with acidic aqueous solutions was found to enhance chalcopyrite dissolution at near ambient conditions in the case of other oxidants, besides hydrogen peroxide (Solis-Marcial and Lapidus, 2012, 2013, 2014). However, the role played by the solvent has not been sufficiently explained and

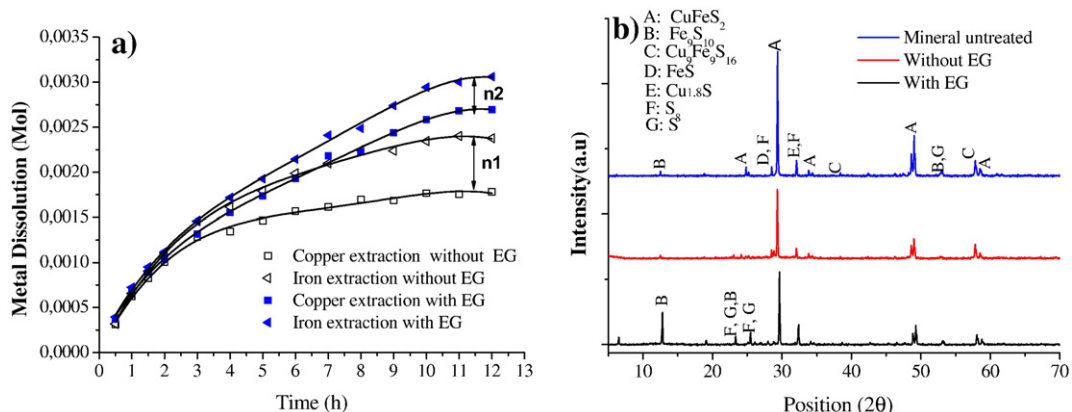


Fig. 1. Chalcopyrite leaching with and without ethylene glycol (EG): (a) moles of copper and iron extracted in each case (b) X-ray diffractograms of the residues after the 24-h leach. Conditions: [ethylene glycol] = 0 & 3.5 M, [H<sub>2</sub>SO<sub>4</sub>] = 0.7 M, [H<sub>2</sub>O<sub>2</sub>] = 1.0 M, [Mineral] = 3.75 g/L.

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