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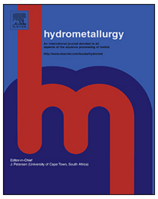

A study of the electro-assisted reductive leaching of a chalcopyrite concentrate in HCl solutions. Part I: Kinetic behavior and nature of the chalcopyrite reduction

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ABSTRACT

This first part of research presents an analysis of the electro-assisted reductive leaching (ERL) of refractory chalcopyrite ($CuFeS_2$) performed in HCl media using an electrolytic cell operated at room temperature and pressure. This is as an alternative approach to decrease the passivation phenomenon observed in the ERL process with sulfuric acid, which favored the chalcopyrite reduction kinetics at pulp densities $> 10\,g/L$. Different variables were optimized to understand the electro-reduction kinetics of chalcopyrite such as: acid concentration, current density and pulp density. The reaction mechanism proposed was complemented with the electrochemical techniques, and SEM-EDS and X-ray diffraction analyses. The results revealed that electro-reduction of chalcopyrite performed in HCl at a pulp density of 100 g/L present a higher reduction rate than that of the sulfuric acid system. From a mechanistic viewpoint, chalcopyrite can be sequentially reduced to chalcocite and metallic copper, respectively. The latter is a very reactive species which can be easily oxidized in the presence of air and remaining hydrochloric acid, to cuprous hydroxychloride or atacamite species ($Cu_2Cl(OH)_3$) and cuprite (Cu_2O) when the solid residue is withdrawn from the reactor. These copper species are highly soluble in aqueous solutions which can permit the recovery of copper. From an energetic viewpoint, the energy consumption of the HCl electrolytic system is lower than that of the H_2SO_4 electrolytic system.

1. Introduction

About 70% of the world copper resources are present as chalcopyrite ($CuFeS_2$) (Wang, 2005), which is commonly processed by smelting (Najdenov et al., 2012). Recently it has been reported that over 80% of known copper is in porphyry copper and sediment-hosted copper deposits (Singer, 2017). It is important to develop alternative green processes for the recovery of copper from chalcopyrite, due to the high production costs and pollution in the conventional smelting processes. Therefore, scientists and engineers have considered hydrometallurgy as an alternative. In general, the two types of hydrometallurgical methods for the recovery of copper from the chalcopyrite are based on the oxidative and reductive processes, which have mostly been studied at laboratory scale. The oxidation of chalcopyrite has been studied by several authors (Burkin, 1969; Ammou-Chokroum et al., 1977; Muñoz et al., 1979; Prince and Warren, 1986; Nicol and Lázaro, 2003; Córdoba et al., 2008; Yang et al., 2015; Hao-dan et al., 2012; Crundwell et al., 2015; Khoshkhoo et al., 2014; Nicol, 2017; Nicol et al., 2017; Nicol and Basson, 2017). However, its main limitation relates to the passivation of chalcopyrite due to the formation of elemental sulfur, polysulfide species or iron hydroxysulfate species (Burkin, 1969; Córdoba et al., 2008; Ammou-Chokroum et al., 1977; Muñoz et al., 1979; Habashi and Toor, 1978; Yoo et al., 2010; Nicol, 2017). In order to decrease such passivation, inorganic acids such as nitric acid, sulfuric acid and hydrochloric acid, have been studied (Al-Harahsheh et al., 2008). It is reported that the chalcopyrite dissolution kinetics is higher in the oxidative systems containing chloride species or hydrochloric acid than in those containing sulfate species (Almeida et al., 2016; Nicol, 2017; Habashi and Toor, 1978; Yoo et al., 2010; Liddicoat and Dreisinger, 2007; Yévenes, 2009).

Chemical reductive processes have been considered an alternative to decrease the passivation of chalcopyrite commonly found in oxidative processes. In these processes, chalcopyrite is predominantly reduced to less refractory copper sulfide species such as chalcocite. The

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reduction of chalcopyrite has been assessed in the presence of sulfate or chloride media and chemical reducing agents such as: iron, copper, lead, aluminum, H_2 and SO_2 (Hiskey and Wadsworth, 1975; Avraamides et al., 1980; Sohn and Wadsworth, 1980; Hackl et al., 1987; Chae and Wadsworth, 1979; Shirts et al., 1974, Dreisinger and Abed, 2002; Lapidus and Doyle, 2006). In terms of efficiency, the chloride chemical-reductive systems present higher chalcopyrite reduction kinetics than the sulfate reductive systems (Dreisinger and Abed, 2002).

Chalcopyrite is considered a semi-conductor that can be electrolytically decomposed (Biegler, 1977) producing bornite (Cu_5FeS_4), chalcocite (Cu_2S) and metallic copper (Cu^0) (Biegler and Constable, 1977; Warren et al., 1985; Fuentes-Aceituno et al., 2008a, 2008b).

There are a few references related to the electroreduction of chalcopyrite slurries in electrolytic cells (Biegler and Constable, 1977; Fuentes-Aceituno et al., 2008a; Martínez-Gómez et al., 2016). In many of these investigations sulfuric acid was used as the electrolytic medium, while only one reference (Biegler and Constable, 1977) reported the use of 4 M HCl to perform the continuous electrolytic reduction of a chalcopyrite slurry. However, electroreduction of chalcopyrite slurries in HCl with electrolytic cells has not been studied systematically, particularly the complete characterization of solid products formed in this system is not presented.

From a mechanistic viewpoint, chalcopyrite can be electrolytically reduced in acid solutions to bornite or chalcocite, according to Eqs. (1) and (2), respectively (Biegler, 1977; Biegler and Constable, 1977; Biegler and Swift, 1976):

$$5CuFeS_2 + 12H^+ + 4e^- \rightarrow Cu_5FeS_4 + 4Fe^{2+} + 6H_2S \tag{1}$$

$$2CuFeS_2 + 6H^+ + 2e^- \rightarrow Cu_2S + 3H_2S + 2Fe^{2+} \tag{2}$$

Chalcocite can be further electro-reduced to metallic copper, according to Eq. (3) (Biegler and Constable, 1977).

$$Cu_2S + 2H^+ + 2e^- \rightarrow 2Cu + H_2S \tag{3}$$

The global reduction of chalcopyrite to copper can be represented by Eq. (4):

$$CuFeS_2 + 4H^+ + 2e^- \rightarrow Cu + 2H_2S + Fe^{2+} \tag{4}$$

Thermodynamic data for chalcopyrite reduction (Eh-pH diagram) revealed that the stability boundaries of these reduced copper phases are all below the reversible hydrogen potential, which means that their actual formation will depend on kinetic factors, in particular the overpotential of hydrogen evolution (Biegler and Swift, 1976).

Fuentes-Aceituno et al., (2008a), Fuentes-Aceituno, (2010) proposed an alternative reaction mechanism for the electrolytic reduction of chalcopyrite in sulfuric acid medium, i.e., formation of the intermediate monoatomic hydrogen species (reducing agent) on the cathode surface (Eq. (5)). This reducing agent promotes the reduction of chalcopyrite to chalcocite according to Eq. (6).

$$2H^+ + 2e^- \rightarrow 2H\cdot \tag{5}$$

$$2CuFeS_2 + 4H^+ + 2H\cdot \rightarrow Cu_2S + 3H_2S + 2Fe^{2+} \tag{6}$$

Monoatomic hydrogen can recombine through a chemical or an electrochemical event, according to Eqs. (7) and (8), respectively.

$$2H\cdot \rightarrow H_2 \tag{7}$$

$$H\cdot + e^- + H^+ \rightarrow H_2 \tag{8}$$

It is worth mentioning that the number of electrons transferred in Eq. (6) are the same to that transferred in the direct electro-reduction mechanism (Eq. (2)), which suggests that the chalcopyrite reduction mechanism in this type of electrolytic systems can be explained in terms of: a) electrons transferred directly from cathode to the chalcopyrite particles, or b) electrons transferred from monoatomic hydrogen to the chalcopyrite particles. As can be seen the nature of the electron transfer mechanism is a complex problem, which is not intended to be addressed in this paper.

Hydrogen sulfide produced during the reduction of chalcopyrite (Eqs. (1), (2), (3), (4) and (6)) can be electro-oxidized at the anode producing elemental sulfur, which inhibits the hydrogen sulfide emissions (Fuentes-Aceituno et al., 2008a), while ferrous ions produced during the process can be further treated to obtain metallic iron by rapid electrodeposition (Kasper, 1937). It is thus possible to obtain valuable products such as Cu, Fe and S, from the chalcopyrite decomposition. However, recently it has been observed that chalcopyrite electro-assisted reduction kinetics is considerably hindered at the pulp densities higher than 10 g/L in sulfuric acid media (Fuentes-Aceituno et al., 2008a). This renders the process uneconomical. According to Martínez-Gómez et al. (2016), elemental sulfur is produced on the chalcopyrite particles in such a system promoting the passivation of chalcopyrite.

In this research, the electro-assisted reductive leaching of chalcopyrite was studied systematically in HCl solutions with different techniques, in order to elucidate suitable conditions which can accelerate and increase the conversion of chalcopyrite reduction at pulp densities higher than 10 g/L while minimizing the energy consumption. This information is valuable to understand the phenomena occurring in the chalcopyrite electro-reduction using HCl media, and to develop in future an alternate hydrometallurgical reductive process for the recovery of copper from refractory chalcopyrite.

2. Experimental

2.1. Materials

Electrochemical tests were carried out employing a chalcopyrite electrode. For the preparation of the working electrode, a pure chalcopyrite crystal was mounted in a teflon rod in order to obtain a rotating disk electrode with exposed active area of 19.6 mm^2. The elemental analysis or EDS (full) of the chalcopyrite crystal was determined by scanning electron microscopy (SEM, Philips-XL-30-ESEM), which revealed that chalcopyrite has high purity; its chemical composition is shown in Table 1.

Electro-assisted reductive leaching of chalcopyrite was studied employing a chalcopyrite concentrate obtained from Peñoles, Minera el Roble, Cuencamé, Durango, which contains: 68.3% chalcopyrite, 15.4% pyrite, 9.1% sphalerite and 1.5% galena. The particle size distribution in the concentrate is found to be in the range 11 μm to 16 μm with an average size of 13.3 μm.

2.2. Electrochemical tests

The experiments were carried out at room temperature (25 °C) employing a conventional three-electrode electrochemical cell, which comprised of a reference electrode of Ag/AgCl (all potentials presented in this work were changed to the standard hydrogen electrode, SHE), a graphite rod (Alfa Aesar) as the counter-electrode and a massive crystal of chalcopyrite as the working electrode. The cell was connected to a potentiostat/galvanostat (Versastat 4-400, PAR).

The surface of the working electrode was polished with a silicon carbide paper (800, 1200 and 2400) and was then polished in wet to a mirror-like finish employing alumina powder (0.5 μm) for 50 min. The electrode was rinsed with deionized water and was sonicated with

Table 1
Chemical composition of the chalcopyrite working electrode.

Element	wt%	at. %
Cu	34.12	24.62
Fe	30.91	25.38
S	34.97	50.00