

Electrochemical study of chalcopyrite dissolution in sulfuric, nitric and hydrochloric acid solutions



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ABSTRACT

Electrochemical and surface analyses were carried out to study the leaching of chalcopyrite in acid media, aiming to increase copper extraction from low-grade chalcopyrite ores. Unpublished results include the use of electrochemical impedance spectroscopy (EIS) to characterize the dissolution resistance of chalcopyrite surfaces in 0.1 mol·L⁻¹ of hydrochloric, nitric or sulfuric acids. Potentiodynamic polarization, atomic absorption spectrometry and EIS analysis showed that hydrochloric acid solutions are more efficient leaching agents than nitric and sulfuric acids. The impedance results suggested that the chalcopyrite dissolution is a diffusion-controlled process in hydrochloric and sulfuric acids. The use of Raman spectroscopy and scanning electron microscopy with energy dispersive spectrometers (SEM/EDS) allowed the partial identification of lead and bismuth sulfides as impurities. Two products were identified on the surface of chalcopyrite after anodic polarization, i.e., sulfur in the sulfuric acid only and covellite in all three acids.

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1. Introduction

Chalcopyrite (CuFeS₂) is the Earth's most abundant Cu bearing mineral, and accounts for approximately 70% of the world's copper reserves (Li et al., 2015; Córdoba et al., 2008). The extraction of copper from ore may be conducted using two different processes: the pyrometallurgical and the hydrometallurgical.

The pyrometallurgical process has dominated the copper industry since the late nineteenth century (Dreisinger, 2006; Habashi, 2009). However, this scenario is changing slowly. This process is not suitable for the treatment of complex and low-grade ores, and has high capital for smelting and refining plants, as well as negative environmental impact caused by the generation of sulfur dioxide (SO₂) (Prasad and Pandey, 1998). In contrast, 18% of copper extraction comes from the hydrometallurgical processes. The advantages of hydrometallurgy are the ability to treat complex ores with low copper content, small initial capital expenditure required for the installation of industrial plants, and the viability for small or large plants (Dutrizac, 1992).

The application of the hydrometallurgical process for the production of copper is promising but has not yet been consolidated, as there are several challenges to be overcome. The difficulty of employing such a method for the hydrometallurgical extraction of copper from chalcopyrite is the leaching step, where the copper dissolution from chalcopyrite in an acid medium is slow at low temperatures and tends to decrease with time (Majuste et al., 2012). This slow kinetics is attributed to the formation of a protective layer on the mineral surface, inhibiting continued dissolution (Córdoba et al., 2008). The hindered chalcopyrite dissolution process has also been reported elsewhere (Majuste et al., 2013).

Despite many years of studies, the formation of this layer and its characteristics are not yet fully established. Few studies have used the technique of electrochemical impedance spectroscopy (EIS), which is an important tool for the study of surfaces (Hiroyoshi et al., 2004; Dakubo et al., 2012; Ghahremaninezhad et al., 2012). Hiroyoshi et al. (2004) studied the synergistic effect of cupric and ferrous ions on active-passive behavior during anodic dissolution of chalcopyrite in sulfuric acid solutions, using EIS technique. They reported that a high-resistance passive layer grows on the chalcopyrite surface without cupric and/or ferrous ions, and that coexistence of these ions causes the formation of another product layer and inhibits the formation of intermediate Cu₂S in the active region. Dakubo et al. (2012) investigated the effectiveness of peroxodisulfate for enhancing copper leaching rates from chalcopyrite, using sulfuric acid leaching solutions at pH 2. The

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presence of peroxodisulfate greatly increased copper leaching rates. Ghahremaninezhad et al. (2012) evaluated the surface of chalcopyrite during dissolution in $0.5 \text{ mol} \cdot \text{L}^{-1}$ sulfuric acid solutions using electrochemical techniques. EIS analysis at open circuit potential proved the existence of a thin surface layer on the electrode. This layer was stable up to 100 mV vs. mercury/mercury sulfate electrode (MSE) and was assumed to be $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2$. By increasing the potential to the range of 100–300 mV (MSE), the previously formed layer partially dissolved and a second layer ($\text{Cu}_{1-x-z}\text{S}_2$) was formed on the surface. Both layers showed the characteristics of passive layers at a low scan rate ($0.05 \text{ mV} \cdot \text{s}^{-1}$) but acted like pseudo-passive layers at high scan rates ($\geq 50 \text{ mV} \cdot \text{s}^{-1}$). However, in the potential range of 300–420 mV (MSE), both surface layers dissolved and active dissolution of the electrode started (Ghahremaninezhad et al., 2012).

Direct leaching of chalcopyrite concentrate includes the use of sulfuric acid, nitric acid, chloride ions, oxygen leaching, ammonia systems, alcoholic acid media, and biological processes (Venkatachalam, 1991; Solís-Marcial and Lapidus, 2014; Ghahremaninezhad et al., 2010; Li et al., 2013; Wang et al., 2014a, 2014b; Feng et al., 2014; Watling, 2014; Zhang et al., 2014; Smith and Sohn, 2014; Abdollahi et al., 2014; Khoshkhoo et al., 2014). The aim of this work was to understand the chalcopyrite dissolution in hydrochloric, sulfuric and nitric acids through an electrochemical study using anodic potentiodynamic tests, EIS, and Raman spectroscopy for the characterization of the chalcopyrite surface after dissolution. The electrochemical parameters such as critical current density, passivation current density, and transpassivation potential were obtained using anodic potentiodynamic polarization tests. The charge transfer resistance and mechanistic information were obtained using electrochemical impedance spectroscopy.

2. Material and methods

The chalcopyrite samples were purchased from Ward's Natural Science, Rochester, N.Y. Chalcopyrite electrodes were prepared as per Majuste et al. (2012). Firstly, massive samples were cut using a diamond wafering blade (Buehler®, n.11-4246), to obtain specimens with 1.0 cm^2 of exposed areas and 0.5 cm thicknesses. The specimens were rinsed with double-distilled water and dried with analytical grade acetone 100% (Synth®). A Cu wire within a glass tube was then attached to each specimen using a conductive silver paint (Dotite®, D-550). The samples were, then, mounted in epoxy resins (Epofix®, Struers); these resin blocks, once dried and hardened, were mechanically wet-polished using SiC papers (grit sizes 1000, 1200 and 2400) and subsequently alumina pastes (1.0 and $0.05 \mu\text{m}$) to obtain fresh and smooth electrode surfaces (Majuste et al., 2012). Next, the electrodes were rinsed with double-distilled water in an ultrasonic bath for 15 min, dried with analytical grade ethyl alcohol 95% (Synth®) and kept under vacuum at room temperature (Majuste et al., 2012). The chalcopyrite samples used were characterized in a previous work (Majuste et al., 2012).

$0.1 \text{ mol} \cdot \text{L}^{-1}$ of hydrochloric, nitric and sulfuric acid solutions were prepared with deionized water and concentrated hydrochloric, nitric and sulfuric acids, all analytical grade reagents (Synth®). Quantitative analysis of iron and copper contents in the leachates was performed using the atomic absorption spectrometer Hitachi-Z8200 coupled to a Hitachi graphite furnace. Atomic absorption spectroscopy analyses of acid solutions were performed before and after polarization tests.

Electrochemical tests were performed in a 150 mL electrochemical cell, using a Versa Stat 2 Princeton Applied Research potentiostat, and Versa Studio software. All experiments were carried out without stirring. The reference electrode used was Ag/AgCl, KCl (sat) and the counter electrode was platinum.

The anodic potentiodynamic polarization and EIS were performed at room temperature $25\text{--}27 \pm 0.05 \text{ }^\circ\text{C}$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$ of hydrochloric, nitric and sulfuric acid solutions. The anodic polarization was performed in the potential range of 0.1 to 1.3 V (Ag/AgCl), at a scan rate of $0.05 \text{ V} \cdot \text{s}^{-1}$.

For the EIS analysis, the potential amplitude and frequency range were 10 mV and $10^5\text{--}10^{-2} \text{ Hz}$, respectively. The treatment and equivalent circuit simulation were carried out using the Zview™ software.

The surface of the chalcopyrite electrode was analyzed using a scanning electron microscope (JEOL, JSM 6360 LV) with energy dispersive spectrometers (Thermo Noram, Quest). The analysis of the electrode surface was also made by Raman spectroscopy using a Jobin Yvon Horiba instrument (Labram HR800) equipped with a CCD detector and He–Ne laser operating at 633 nm. The power used was 20 mW focused on the sample by a BX-41 Olympus microscope comprising lenses with magnifications of 10, 50 and $100\times$. The spectral resolution was 1 cm^{-1} . An average of 10 accumulations in the acquisition time of 60 s was performed.

The scanning electron microscopy (SEM), the energy dispersive spectrometry (EDS) and Raman spectroscopy were performed immediately after sample preparation and after anodic polarization up to 1.3 V (Ag/AgCl).

3. Results and discussion

3.1. Anodic potentiodynamic polarization

The anodic polarization curves of the chalcopyrite in three types of acids are shown in Fig. 1. The polarization curves obtained with a high potential range in the three acid media are useful to give a general idea of the electrochemical behavior of the electrode in the medium studied. A tendency to concentration polarization (McCafferty, 2010) was observed in the cathodic branch of the curve of chalcopyrite in the nitric acid. On the cathodic side of the curve in HNO_3 medium, increased hydrogen evolution at large cathodic overvoltage may cause a depletion of protons near the electrode surface. In addition, the increased number of hydrogen gas molecules produced may be slow to diffuse away from the electrode surface. Either event will result in concentration polarization (McCafferty, 2010) for the cathodic reaction which was observed only in the nitric acid. In this medium, at high cathodic overvoltage, an inhibition of the cathodic reaction was identified. When electrolytes are in the sulfuric and hydrochloric acids, the reduction of protons with hydrogen evolution occurred without inhibition until 0.1 V (Ag/AgCl).

The electrochemical parameters, obtained using the potentiodynamic polarization technique, are shown in Table 1. The highest critical current density (McCafferty, 2010) to produce a protective layer was observed in the case of sulfuric acid. Another advantage of the use of sulfuric acid as a leaching agent is that the current density at the region of the protective layer is one order of magnitude higher than the current

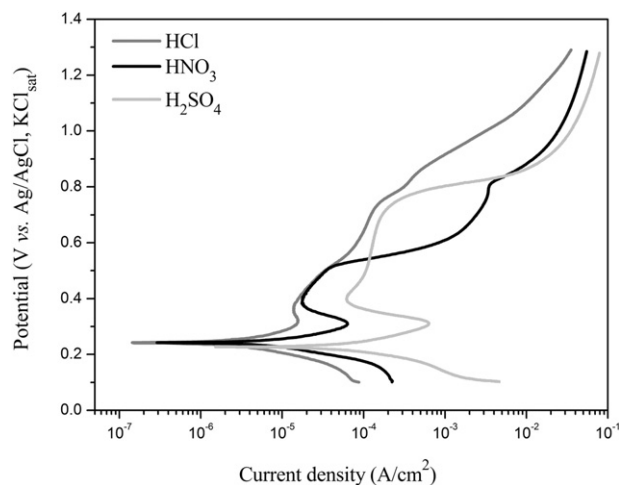


Fig. 1. Anodic polarization curves of chalcopyrite from 0.1 V (Ag/AgCl) to 1.3 V (Ag/AgCl) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ aqueous solution of HCl, HNO_3 and H_2SO_4 at room temperature and scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$.

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