



Research Paper

The effect of chloride ions on the electrochemical dissolution of chalcopyrite in sulfuric acid solutions

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ABSTRACT

The dissolution of chalcopyrite in 0.2 M sulfuric acid solutions with different sodium chloride concentrations was investigated. Different anodic potentials were applied, and the behavior of the electrode was observed using potentiodynamic, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) techniques. The results showed that the chalcopyrite open circuit potential (OCP, approximately 245 mV vs. SCE) decreased as the NaCl concentration increased. Four different surface conditions emerged on the chalcopyrite surface as the anodic potentials increased: (1) a $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2$ passive layer formed at OCP–500 mV; (2) a second passive layer ($\text{Cu}_{1-x-z}\text{S}_2$) formed at 500–700 mV (electrolyte without NaCl) or 500–800 mV (electrolyte with NaCl); and (3) chalcopyrite was in an active area at 700–800 mV (electrolyte without NaCl) or 800–900 mV (electrolyte with NaCl), and all the previous passive layers disappeared. In this case, SO_4^{2-} or $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_4\text{O}_6^{2-}$ for the electrolyte without NaCl or with NaCl, respectively, are the oxidized forms of sulfide sulfur; (4) when the potential is above 800 mV (for the electrolyte without NaCl) or 900 mV (for the electrolyte with NaCl), pseudo-passive CuS is formed. Subsequently, the sulfur of CuS was oxidized to SO_4^{2-} , and Cu^{2+} changed into CuCl^+ with a NaCl concentration of 0 mol/L and 0.5 mol/L, respectively. However, a new passive layer(s) of $\text{Cu}_2(\text{OH})_3\text{Cl}$ formed with NaCl concentrations above 0.5 mol/L. Overall, the results revealed that Cl^- ions are advantageous for chalcopyrite dissolution. However, the oxidation of chalcopyrite generated chloride and cupric ions that can form the cuprous complexes CuCl^0 , CuCl_2^- or CuCl_3^{2-} , which dramatically inhibit the on-going dissolution of chalcopyrite. EIS data confirmed that a high concentration of Cl^- ions was not essential for chalcopyrite dissolution under the present conditions. Moreover, the critical Cl^- ion concentrations were different for the four distinct potential areas outlined above, namely, 1.0 mol/L, 1.25 mol/L, 1.25 mol/L and 0.5 mol/L, respectively.

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1. Introduction

Chalcopyrite (CuFeS_2), one of the most abundant primary copper ores, is mined extensively for its copper, with the extractive method changing from traditional thermometallurgy to hydrometallurgy. Nicol [1] indicated that the interest in the electrochemistry of sulfide minerals stems largely from the fact that their dissolution in oxidizing solutions occurs via an electrochemical mechanism. This mechanism is important in hydrometallurgical processes and in the surface activation of sulfide minerals prior to flotation [2]. Therefore, many reports have emerged to clarify the

dissolution kinetics of chalcopyrite in different media using various electrochemical techniques [3–7].

Because of its strong oxidation-reduction quality and complex power, chloride ions have always been employed in electrochemical studies of sulfide minerals. For example, Ammou-Chokroum et al. [8,9] investigated the anodic behavior of chalcopyrite in chloride media, with a particular emphasis on the dissolution of chalcopyrite in acidic solutions. They postulated that the initial stage of dissolution involves the formation of hydrogen sulfide, ferrous ions and covellite. Furthermore, they postulated that the ohmic potential drop across the precipitated chalcocite plays an important role in establishing the electrochemical behavior of chalcopyrite. McMillan et al. [10] studied the anodic dissolution of chalcopyrite in both acidic sulfate and acidic chloride media and suggested that the slow the rate of electron transfer is caused by the formation of a surface layer. In the hydrometallurgical field,

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chlorides have always been used for the hydrometallurgical treatment of sulfide ores, particularly complex sulfides, because of their high degree of leaching power efficiency [11–14]. Researchers have reported that the cause of this fast leaching rate in chloride is morphological, whereby a porous coating layer is formed on the chalcopyrite particles during the leaching process in the chloride medium [15,16]. The role of chloride ions is believed to limit the extent of passivation by elemental sulfur [17,18]. Note that increases in the chloride concentration had little effect on the leaching rate of chalcopyrite with chloride concentrations above 0.5 mol/L [15,19].

In this work, the electrochemical dissolution of chalcopyrite in sulfuric acid solutions with different chloride ion concentrations was studied. First, the potentiodynamic curve was used to understand the chalcopyrite electrode passivation, trans-passivation and activation potential intervals. Cyclic voltammetry (CV) was then used to acquire qualitative information on the electrochemical reactions. Finally, electrochemical impedance spectroscopy (EIS) experiments were performed to study the electrode characteristics and the electrochemical reactions at different potential intervals. The aim of this work was to determine how the chloride ions affect the surface properties and growth sequence of chalcopyrite surface layers in a sulfuric acid solution at different anodic potentials. This work also seeks to provide an experimental basis for the highly effective electrochemical leaching of chalcopyrite in the presence of chloride ions conditions.

2. Experimental

2.1. Electrode preparation

High quality natural polycrystalline chalcopyrite was obtained from Mt Lyell, Australia. X-ray diffraction analysis confirmed that the Fe, Cu and S contents (wt %) of chalcopyrite were 30.8%, 33.7% and 34.2%, respectively. Chalcopyrite electrodes were prepared by cutting the chalcopyrite samples into approximately cube-like shapes with working areas of 0.25 cm², and as much as possible, with no visible imperfections. The specimens were placed on an epoxy resin and connected to a copper wire by silver paint on the back face, leaving only one face of the electrode exposed to the solution. Prior to each test, the chalcopyrite electrode was polished with no. 1200 carbide paper to obtain fresh surfaces, and then degreased by alcohol. The electrode was then rinsed with deionized water and dried in a stream of air.

2.2. Electrochemical measurements

Electrochemical measurements were performed using a computer-controlled electrochemical measurement system (PAR-STAT 2273, Princeton Applied Research) on a conventional three-electrode electrolytic cell with platinum as an auxiliary electrode (AE) and chalcopyrite as the working electrode (WE). A saturated calomel electrode (SCE) was used as the reference electrode for all of the electrochemical tests; unless otherwise mentioned, all further potentials reported in this study are relative to the SCE (0.242 V vs. standard hydrogen electrode). The reference electrode was connected to a Luggin capillary to minimize the resistance of the solution between the working and reference electrodes. The electrolyte was composed of 0.2 mol/L H₂SO₄ with different NaCl concentrations: (1) 0 mol/L, (2) 0.5 mol/L, (3) 1.0 mol/L, (4) 1.25 mol/L and (5) 1.5 mol/L. The working, auxiliary and reference electrodes were each situated in the same position to ensure identical spatial relationships for each experiment. All of the experiments were conducted at 25 ± 1 °C.

Potentiodynamic curves, CV and EIS were utilized to study the behaviors of the chalcopyrite electrode. First, the chalcopyrite

electrodes open circuit potential (OCP) was measured, and the electrochemical experiments started only when the OCP reached a quasi-steady state. In this study, potentiodynamic cycles were performed with a positive-going potential sweep from OCP to +0.8 V/1.0 V (0.8 V is the electrolyte without NaCl and 1.0 V is the electrolyte with NaCl) and back with a negative-going potential sweep from +0.8 V/1.0 V to – 0.60 V, and then a positive-going potential sweep back to +0.8 V/1.0 V at a scan rate of 5 mV s⁻¹. Potentiodynamic polarization curves were obtained by automatically changing the electrode potential from –100 mV to 1000 mV at a scan rate of 0.5 mV s⁻¹. EIS tests were conducted at different potentials in the frequency range of 0.01 ~ 10000 Hz with a peak-to-peak amplitude of 10 mV. The electrode potential was allowed to stabilize for 400 s before commencement of the measurements. ZSimpWin 3.20 (2004) software was used to fit the impedance data.

3. Results and discussion

3.1. Open circuit potential study

The open circuit potential curves of the chalcopyrite electrode in 0.2 mol/L sulfuric acid solutions with different NaCl concentrations (0, 0.5, 1.0, 1.25 and 1.5 mol/L) as a function of time are shown in Fig. 1. As seen, sodium chloride causes a decrease in the chalcopyrite OCP as the NaCl concentration increases. Furthermore, the electrode potential increases for 10 min before reaching a quasi-steady state in all of the curves, which indicates the spontaneous growth of a passive film on the electrode surface. The steady state OC potentials were found to be approximately 245 ± 10 mV, 122 ± 10 mV, 108 ± 10 mV, 95 ± 10 mV and 84 ± 10 mV, respectively, where the steady-state was defined here as a change of less than 2 mV/min.

Antonijević et al. [20] indicated that the chalcopyrite potential in redox solutions could be defined as: $E_{\text{CuFeS}_2} = E_{\text{const}} + n \log[\text{Ox}]/[\text{Red}]$, where E_{CuFeS_2} is the chalcopyrite potential, V; E_{const} is the chalcopyrite potential when [Ox] = [Red], V; n is the slope of line in the system $E_{\text{CuFeS}_2} = f(\log [\text{Ox}]/[\text{Red}])$; [Ox] is the concentration of oxidized species, M; and [Red] is the concentration of reduced species, mol/L.

As mentioned above, sodium chloride causes the chalcopyrite OCP to decrease as the NaCl concentration increases. One reason for this phenomenon is related to the amount of oxygen present in the solution. The presence of chloride ions in solution reduces the

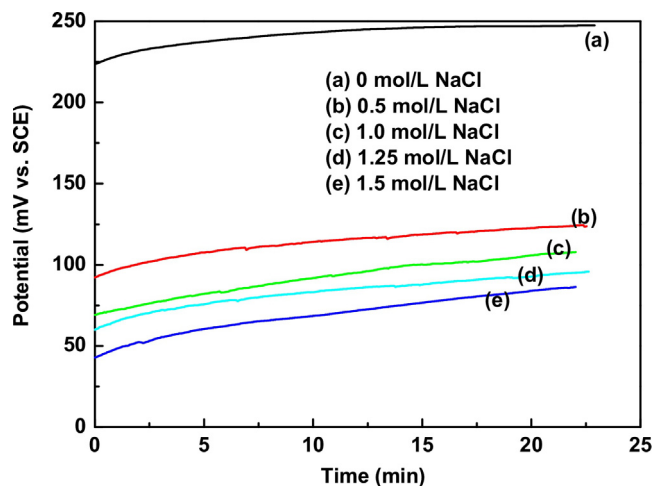


Fig. 1. Time-potential relationships of chalcopyrite in 0.2 mol/L sulfuric acid with different NaCl concentrations.

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