Electrochemical dissolution of fresh and passivated chalcopyrite electrodes. Effect of pyrite on the reduction of Fe^{3+} ions and transport processes within the passive film

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ABSTRACT

The effect of pyrite (FeS$_2$) on the electrochemical dissolution of fresh and passivated chalcopyrite (CuFeS$_2$) electrodes has been studied. Current density values for the dissolution of CuFeS$_2$ were calculated from EIS measurements. FeS$_2$ increased the dissolution rate of fresh and passivated CuFeS$_2$ electrodes indicating that the galvanic effect continued even after the electrode was chemically passivated. The dissolution rate of CuFeS$_2$ decreased by a factor of 3 after the passivation treatment. Due to the low diffusion rates of ions within the CuFeS$_2$ passive film and due to an increase in the resistance to the transfer of electrons at the electrode/film interface, the activity of FeS$_2$ for the reduction of Fe^{3+} ions was also reduced by a factor of 2.3 even though FeS$_2$ was not exposed to any chemical treatment. The results in this work indicate that the dissolution rate of the fresh CuFeS$_2$ electrode was controlled by the reduction of Fe^{3+} ions whereas for the passivated CuFeS$_2$ electrode the dissolution rate was controlled by diffusion within the passive film.
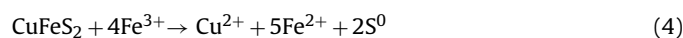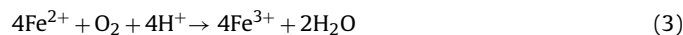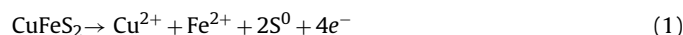
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1. Introduction

Chalcopyrite (CuFeS$_2$) is the most abundant copper sulphide mineral accounting for nearly 70% of the known reserves in the world [1]. Hydrometallurgical processes continue to attract interest since they possess the ability to treat low tonnages of complex ores containing high impurities. However, due to the slow dissolution rates of CuFeS$_2$, hydrometallurgical processes have not yet found widespread application. In spite of this, there have been a number of processes developed for the leaching of CuFeS$_2$ and other copper-bearing minerals; several of these processes have been reviewed by Baba et al. [2] and Dreisinger [3].

One of the latest developments in the chemical leaching of chalcopyrite in sulphate media under atmospheric pressure is the Galvanox^{TM} process. This process consists in the addition of pyrite (FeS$_2$) to the leach slurry in the presence of Fe^{3+} ions. FeS$_2$ and CuFeS$_2$ are thought to form a galvanic couple where FeS$_2$ acts as an extended surface for the reduction of Fe^{3+} ions, increasing in this way the rate of the anodic dissolution of CuFeS$_2$ [4,5]. Fig. 1 shows a simple schematic representation of the reactions that are thought to take place in the Galvanox^{TM} process. These reactions are represented by Eqs. 1–4; Eq. 1 represents the anodic dissolution of CuFeS$_2$ to yield cupric and ferrous ions, as well as an elemental sulfur product layer that forms on the surface of the CuFeS$_2$ particle. The second reaction (Eq. 2) comprises the reduction of Fe^{3+} ions that are further regenerated by oxidizing Fe^{2+} ions with dissolved O$_2$ (Eq. 3). The overall reaction for the process is represented by Eq. 4.

$$CuFeS_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 4e^- \tag{1}$$

$$4Fe^{3+} + 4e^- \rightarrow 4Fe^{2+} \tag{2}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{3}$$

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \tag{4}$$

The quality of FeS$_2$ as a catalyst depends on its source and its catalytic properties seem to be related to its silver content [6]. Nazari et al. [7] showed that the catalytic properties of different sources of FeS$_2$ could be enhanced by pretreating them with small amounts of silver. This effect was later suggested to be a consequence of a decrease in the electrical resistivity of the sulfur product layer covering the CuFeS$_2$ particles, thus facilitating the electrical contact between CuFeS$_2$ and FeS$_2$. A concomitant increase in the catalytic properties of FeS$_2$ for the reduction of Fe^{3+} ions was also postulated [8].

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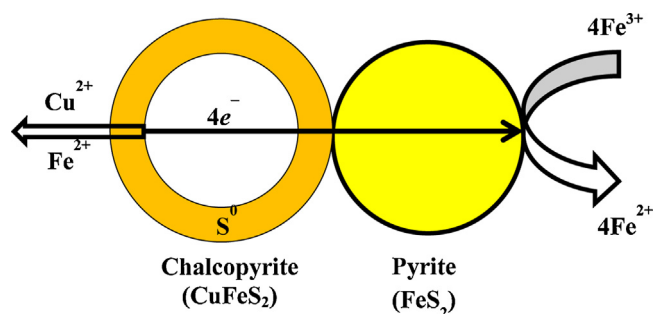
Fig. 1. Schematic representation of the reactions taking place in the Galvanox™ process.

The improvement of hydrometallurgical processes is strongly related to understanding the kinetics and mechanisms underlying the dissolution of minerals. It has been recognized that the main factors affecting the dissolution rate of $CuFeS_2$ are the concentration of the oxidizing species, the redox potential of the solution and the presence of a passivating layer [9–11].

Fe^{3+} ions are the most commonly applied oxidizing agent used in $CuFeS_2$ leaching [11 and references within]. It has been reported that the leaching rate of $CuFeS_2$ depends on Fe^{3+} ions when concentration is below $0.1\,mol\,L^{-1}$ whereas at higher concentrations no further increase in the dissolution rate is observed [12–14]. An explanation for this effect was given by Hirato et al. [15] who calculated that the concentration of Fe^{3+} and $FeHSO_4^{2+}$ increased when total Fe concentration increased up to $0.1\,mol\,L^{-1}$ whereas for higher concentrations the predominant species was $FeSO_4^{+}$. This explanation flows from the fact that, according to Ashurst and Hancock [16], the Fe^{3+} and $FeHSO_4^{2+}$ species are outer-sphere complexes while $FeSO_4^{+}$ is an inner-sphere complex where charge transfer is retarded since it involves the breaking of the Fe^{3+} and SO_4^{2-} bond to form the $FeSO_4$ outer-sphere complex. Thus only $FeHSO_4^{2+}$ and Fe^{3+} would act as the electroactive species [17].

With regards to the rate determining step in the dissolution of $CuFeS_2$, Linge [18] demonstrated that pore diffusion through the sulphur film did not limit the dissolution rate; instead it was proposed that a solid diffusion process was the rate controlling step. Similarly, Dutrizac [19] studied the dissolution of $CuFeS_2$ in ferric sulphate and ferric chloride media and found that leaching rates were independent of acid concentration (for acid concentrations lower than $1\,mol\,L^{-1}$) and degree of agitation. More recently Ghahremaninezhad et al. [20] showed that any contribution of the Fe^{3+} reduction limiting current density could be neglected and that the major contribution to the dissolution current of a $CuFeS_2$ electrode came from charge transfer reactions; these authors also suggested that the passive film was a better electronic conductor than an ionic conductor and that the diffusion of atoms within the passive film was the reason for the slow reduction of Fe^{3+} on the surface of the electrode. There have also been several works reporting that the kinetics of $CuFeS_2$ leaching with Fe^{3+} occur under linear or parabolic kinetic chemical control regimes, with activation energies ranging from 40 to $130\,kJ\,mol^{-1}$ between 35 to $100\,°C$ both in sulphate and chloride media [10,12,15,21–23].

As mentioned before, the presence of a passivating layer is one of the main factors affecting the leaching rate of chalcopyrite. This passivating layer causes the mineral to leach at very low rates, which is one of the main drawbacks of hydrometallurgical processes. In addition to this, the presence of a passivating layer complicates the analysis of the kinetics and mechanisms involved in the leaching of $CuFeS_2$. To date there are different theories regarding the nature of the passive layer formed during the leaching of the mineral and the nature and mechanisms of formation have been the subject of several articles and

reviews [9,12,24–26]. The following passivating films have been suggested: elemental sulfur in both porous and compact layers; metal-deficient sulphides; polysulphides and, iron precipitates such as jarosite, $KFe_3(SO_4)_2(OH)_6$, and ferrihydrite, $Fe_5O_3(OH)_9$. Interestingly, regardless of the nature of this passive film, in a recent work Rivera [27] observed that adding FeS_2 to a $CuFeS_2$ concentrate that was showing signs of passivation increased the leaching rate and overcame the passivation effects observed prior to its addition. Similar results were observed when activated carbon was added to an enargite (Cu_3AsS_4) concentrate after having observed its passivation [28].

In the present work we have studied the effect of FeS_2 on the electrochemical dissolution of fresh and passivated $CuFeS_2$ electrodes. The dissolution current density values were determined using electrochemical impedance spectroscopy (EIS). The effect of the passive film on the dissolution rate of $CuFeS_2$ was also quantified. An experimental rate expression for the electrochemical dissolution of fresh $CuFeS_2$ electrodes was obtained and compared against a theoretical model based on mixed potential theory. A simple kinetic analysis was conducted to determine the rate controlling step on the dissolution of fresh and passivated $CuFeS_2$ electrodes.

2. Experimental

2.1. Mineral characterization

The $CuFeS_2$ sample used in this study was from the La Ranita mine in Chihuahua, Mexico. The mineral sample was analyzed by X-ray powder-diffraction (XRD) for quantitative phase analysis using the Rietveld method and the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. The sample was reduced to the optimum grain-size range for quantitative X-ray analysis ($<10\,\mu m$) by grinding under ethanol in a vibratory McCrone Micronising Mill for 7 minutes. Step-scan XRD data were collected over a range 3-80° 2θ with CoKα radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

2.2. Electrochemical techniques

The dissolution of a $CuFeS_2$ electrode was studied in a conventional three electrode cell. A $CuFeS_2$ electrode was used as working electrode, a graphite rod as counter electrode and a saturated calomel electrode (SCE, +0.24 V/SHE) as reference electrode. Most experiments were performed at $25\,°C$ except for those performed during the passivation of the electrode at $50\,°C$. The working electrode consisted of cubic-shaped $CuFeS_2$ with an exposed surface of $1.9\,cm^2$. The $CuFeS_2$ electrode was fixed to a copper wire using silver-containing epoxy resin. The whole assembly was further embedded in a high temperature non-conductive epoxy resin. Prior to each electrochemical experiment the electrode was polished with 1200 grit carbide paper. Electrodes were rinsed with deionized water and acetone and left to dry. The polishing and acetone rinsing steps were omitted for the experiments with the passivated $CuFeS_2$ electrode to avoid changes in the formed product layer.

The electrolyte used in the experiments was a $0.5\,mol\,L^{-1}$ H_2SO_4 (Fisher Scientific, 95 to 98%) aqueous solution prepared with deionized water; $FeSO_4\cdot7H_2O$ (Fisher Scientific, 100%) and $Fe_2(SO_4)_3\cdot5H_2O$ (Sigma Aldrich, 97%) were added in the desired concentrations. Nitrogen gas was sparged 30 minutes before and during the electrochemical experiments to remove dissolved oxygen from the electrolyte. The measured pH of the solutions used in this study was always in the range of 0.77–0.80.