



# Atmospheric ferric sulfate leaching of chalcopyrite: Thermodynamics, kinetics and electrochemistry



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## ABSTRACT

The dissolution of chalcopyrite has been studied from an integrated point of view where the thermodynamics, dissolution kinetics and electrochemical behavior have been considered together.

The variations in mixed potential and dissolution current density were interpreted considering the aqueous speciation of the electrolyte and the semiconductor properties of the chalcopyrite. This leads to the conclusion that CuFeS<sub>2</sub> dissolution rates are not a simple function of the nominal ferric concentration or of the nominal ratio of ferric to ferrous.

The differences observed in the anodic charge transfer coefficient for the dissolution of chalcopyrite and the limiting current densities observed in potentiodynamic experiments at different temperatures have been explained in terms of the semiconductor properties of chalcopyrite (and/or its reaction product surface film).

The differences between studying the electrochemistry of chalcopyrite by imposing an electrode potential using a potentiostat and by using a solution of known redox potential, as well as the differences in the interpretation of experimental results when redox potential is used instead of mixed potential are also discussed. It is shown that extrapolation of electrochemically-obtained results to leaching operations should be done with care.

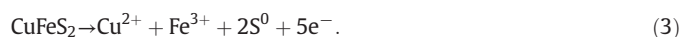
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## 1. Introduction

Chalcopyrite accounts for nearly 70% of known copper reserves (Wang, 2005). The increasing demand for copper and the continuous exploitation of high grade ores have resulted in a decrease in the quality of the remaining natural sources, with an additional increase in ore complexity as well as higher impurity concentrations. The processing of such complex materials with hydrometallurgical methods can be advantageous when compared to conventional smelting operations. This is particularly evident when impurities such as As, Sb, and others are present in the material to be processed.

The main drawback of atmospheric pressure hydrometallurgical operations, however, is the low observed rates of copper extraction, which are normally attributed to the presence of a passive film. The nature of this passive film has been the subject of a number of research papers and, although to date it remains controversial, it will not be discussed in this work. The reader is directed to the work by Klauber (2008) where a detailed discussion on the topic can be found. Previous and recent work by Crundwell (1988) and others (McMillan et al., 1982) have linked this observed passivation of chalcopyrite to either its intrinsic semiconducting nature (i.e. that of the bulk mineral) or a combination of the effects of the semiconducting bulk and the semiconducting surface film (Ghahremaninezhad et al., 2010).

In any case, the oxidative dissolution of chalcopyrite is an electrochemical process that can be described by the following half-cell reactions (Eqs. (1)–(3)):



Thus, the use of electrochemical techniques offers a means to study the oxidative dissolution of chalcopyrite and other metal sulfides. Since the early seventies the use of electrochemical techniques such as cyclic and linear voltammetry, electrochemical impedance spectroscopy (EIS), open circuit potential measurements, and chronoamperometry, to mention only some, have gained increasing importance in the study of the dissolution of different minerals (Nava and Gonzalez, 2006; Ghahremaninezhad et al., 2010). The use of electrochemical techniques presents several advantages over other techniques including leaching tests and surface characterization studies. These are: low cost, short experiment times and the use of small solution volumes.

In this paper we analyze the electrochemistry of chalcopyrite in ferric sulfate acidic solutions using an integrated approach: the thermodynamics, electrochemistry and kinetics of this leaching system are discussed together. Part of the discussion is based on new results but it also heavily relies on results presented in previous research. The first section will

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summarize the thermodynamic aspects of the ferric–ferrous sulfate system and its implications from a hydrometallurgical point of view. Then the electrochemical and kinetic aspects of chalcopyrite in this system are addressed from a fundamental point of view. The difference between establishing an interfacial potential using a potentiostat versus the use of a redox couple are also presented and the role of the semiconductor properties on the kinetics of chalcopyrite dissolution at low and high temperature are discussed.

## 2. Experimental methods

Electrochemical experiments were conducted in a typical 3-electrode cell with a glass jacket to control the electrolyte temperature using a thermostatic water bath. Chalcopyrite (99.6%) was used as a working electrode, a saturated calomel electrode (SCE) was used as reference and a graphite bar was employed as an auxiliary electrode; all the potentials in this work refer to the SCE potential scale at 25 °C (+0.24 V vs SHE), no temperature corrections were made to the reported electrode potentials for experiments conducted at different temperatures.

All the solutions used in this work were prepared using D.I. water; 0.5 M sulfuric acid solutions (Fisher Scientific, 95–98%) were prepared with different  $\text{Fe}^{3+}:\text{Fe}^{2+}$  nominal ratios in the 0.01:1–100:1 range. Total iron concentration was kept at 0.2 M for all the solutions.  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  (Sigma Aldrich, 97%) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Fisher Scientific, 100%) were used as iron salts. The electrolytes were always prepared immediately prior to starting the electrochemical experiments and nitrogen was bubbled 30 min before and during the measurements to remove oxygen from solution and prevent oxidation of  $\text{Fe}^{2+}$  ions.

A Parstat 2273 potentiostat was used to perform the electrochemical measurements. Open circuit potential (OCP) was always measured until the electrode potential stabilized to a change in the electrode potential of no more than  $0.1 \text{ mV min}^{-1}$ . After a steady OCP was observed electrochemical impedance spectroscopy (EIS) experiments were performed at OCP using an AC perturbation of  $\pm 5 \text{ mV}$  in the frequency range of 10 kHz–10 mHz; the ZSimpWin v3.30 software was used to fit the impedance data.

Linear voltammetry tests were also conducted to study the kinetics of the reduction of  $\text{Fe}^{3+}$  ions and the anodic dissolution of chalcopyrite at 25 and 70 °C. A 0.5 M  $\text{H}_2\text{SO}_4$  and 0.2 M total Fe electrolyte with a  $\text{Fe}^{3+}:\text{Fe}^{2+}$  nominal ratio of 1.26:1 was used to study the reduction of  $\text{Fe}^{3+}$  ions. Three different scan rates were tested for these experiments: 0.05, 0.5 and  $5 \text{ mV s}^{-1}$ , all potential scans started at OCP. The anodic dissolution of chalcopyrite was studied using a 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte in the absence of iron salts to prevent the interference of other oxidation reactions; the scan rate for these tests was  $0.1 \text{ mV s}^{-1}$ . As with the previous tests, potential sweeps started from OCP.

Finally, to evaluate the semiconductor properties of the  $\text{CuFeS}_2$  electrode, Mott–Schottky experiments were also conducted. A 1 kHz frequency was used with a 5 mV a.c. amplitude in the 0.25–0.90 V potential range.

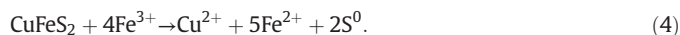
## 3. Aqueous speciation of the ferric–ferrous sulfate system

The thermodynamics of the iron sulfate system in acidic aqueous solutions have been recently studied by Yue et al. (2014). The relevance of this work comes from the fact that not all Fe(III) species in solution are electrochemically active and therefore not all species can act as oxidizers for chalcopyrite and other sulfides (Ashurst and Hancock, 1977). In this work we have considered the same species and thermodynamic data considered in Yue et al. (2014) to perform the necessary calculations. The nonlinear algebraic system of equations was solved using the *fsolve* routine of the Matlab software.

Fig. 1 shows the Fe(III) and Fe(II) species distribution at different Fe(III):Fe(II) ratios at 25 (left) and 70 °C (right); the temperatures and concentrations used for these calculations correspond to the conditions used in the electrochemical evaluations. The reason why

these temperatures were selected was that while most electrochemical studies are conducted at room temperature, it is of interest to study the effect of higher temperatures as these are often seen in proposed hydrometallurgical processes for chalcopyrite leaching.

When ferric sulfate acts as an oxidant, the dissolution of chalcopyrite proceeds according to Eq. (4):



According to Crundwell (1988) only the  $\text{Fe}^{3+}$  and  $\text{FeHSO}_4^+$  species, being the only Fe(III) outer-sphere complexes, are electroactive for the oxidation. Fig. 2 shows the effect of temperature on the sum of the concentrations of these species. An increase in temperature results in decreased concentrations of  $\text{Fe}^{3+}$  and  $\text{FeHSO}_4^+$ . Therefore, in the presence of ferric sulfate an increase in temperature will result in increased heterogeneous rate constants but this is mitigated by the decrease in concentration of electroactive Fe(III) species by factors ranging from 2.25–3.93, depending on the Fe(III):Fe(II) ratio.

## 4. Kinetics and electrochemistry of the dissolution of chalcopyrite in acidic ferric sulfate media

### 4.1. Literature review on the dissolution of chalcopyrite from an electrochemical point of view

The dissolution of chalcopyrite has been studied by several investigators from an electrochemical point of view. Early studies started around the beginning of the seventies when the oxidative dissolution of chalcopyrite and other minerals was recognized as an electrochemical process. Thereafter, the dissolution of metal sulfides has been interpreted using mixed potential theory, Wagner's theory of oxidation and semiconductor electrochemistry concepts. The works by Crundwell (1988), Osseo-Asare (1992) and Crundwell (2015) are excellent references to understand the relationship between semiconductor electrochemistry and the dissolution reactions of different metal sulfides.

Despite this, the interpretation of electrochemical results in terms of the semiconductor properties of the electrode being studied does not occur as often as perhaps it should. This is very interesting since, as explained in the references mentioned in the previous paragraph, both the electrochemical and semiconducting properties of metal sulfides, chalcopyrite included, are very important factors affecting the dissolution rate of such materials. An example of this can be observed in the work by McMillan et al. (1982) where two chalcopyrite samples with different impurities and presenting different types of semiconductor behavior (*n*-type and *p*-type) were compared; the *n*-type samples yielded dissolution currents that were 3.3 times higher than those observed with the *p*-type sample, when the samples were immersed in 0.3 M HCl or  $\text{H}_2\text{SO}_4$  solutions. The same two samples were also compared in the presence of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple in a 0.3 M HCl electrolyte, while the *n*-type sample showed reversible kinetics, very similar to those observed with a Pt electrode, the *p*-type electrode showed current densities that were lower by an order of magnitude.

More examples can be cited where a clear link between semiconductor and electrochemical properties have been shown with the rate of dissolution. The recent work by Crundwell (2015) made emphasis on the subject, claiming that what has been described as a passive dissolution behavior is only a consequence of the semiconducting nature of the bulk chalcopyrite; nonetheless, it is still debatable whether the current (or dissolution)-potential behavior of chalcopyrite is due to the semiconducting properties of chalcopyrite itself or to the presence of a surface film with different stoichiometry and semiconductor properties. Moreover, the experimental evidence for the presence of this film, regardless of its composition and effect on chalcopyrite dissolution, is too strong to neglect it (Klauber, 2008). The role of the semiconductor properties of chalcopyrite was also discussed by Parker et al. (1981) who suggested that a semiconductor surface film was formed during chalcopyrite oxidation

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