



The anodic behaviour of chalcopyrite in chloride solutions: Overall features and comparison with sulfate solutions



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ABSTRACT

The anodic behaviour of chalcopyrite at high potentials (transpassive region) in both sulfate and chloride solutions has been compared. It has been shown that the apparent plateau in the current/potential curve for the oxidation of chalcopyrite in dilute sulfuric solution at high potentials as observed in a recently published study has not been confirmed by several similar studies including the present one.

Anodic oxidation at high potentials occurs at lower potentials in sulfate than in chloride solutions. Anodic oxidation in concentrated chloride solutions is more rapid at low potentials but severely inhibited relative to dilute chloride or sulfate solutions at high potentials. The behaviour in sulfate and chloride solutions has been confirmed by the results obtained from the oxidation of fine chalcopyrite particles that showed current peaks in the same potential regions as found using the bulk electrodes.

The stoichiometry of anodic dissolution in both sulfate and chloride solutions at high potentials has confirmed published data of a consistent value of 6.5–6.7 F/mol copper dissolved that is independent of the source of the mineral, potential and solution composition. An alternative mechanism involving initial oxidation to $\text{H}_2\text{S}_2\text{O}_2$ and subsequent disproportionation to elemental sulfur and sulfate ions has been proposed that is consistent with the above stoichiometry and the yield of elemental sulfur.

A possible explanation for slow oxidation in concentrated chloride solutions has been proposed that involves the formation of an inhibiting layer of S_2Cl_2 on the surface.

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1. Introduction

As part of a detailed study of the electrochemistry of chalcopyrite in chloride solutions under conditions appropriate to the heap leaching of the mineral under ambient conditions, the anodic behaviour has been investigated in three stages. The first, reported in a previous paper (Nicol and Zhang, 2017) summarized the results of potentiostatic measurements in concentrated chloride solutions in the potential region relevant to heap leaching. This paper deals with the overall characteristics of the mineral in both chloride and sulfate solutions using voltammetry, potentiostatic measurements, coulometry and capacitance measurements. A subsequent paper will deal with a voltammetric study of the anodic characteristics at potentials relevant to oxidative dissolution in chloride solutions.

As a result of the slow kinetics of leaching of chalcopyrite (CuFeS_2), a substantial amount of research work has been undertaken in order to understand the oxidative dissolution processes of this mineral. Most of this work has been aimed at increasing the oxidative dissolution

kinetics in the presence of ferric ions as the oxidant in the sulfate system with the overall reaction being mainly.



There are a large number of publications on this subject and excellent reviews of these publications have been published (Burkin, 2001; Debernardi and Carlesi, 2013).

The parabolic kinetics observed in the ferric sulfate system are believed to be due to passivation or inhibition of the rate of dissolution (Dutrizac et al., 1969; Dutrizac, 1978, 1989). Although many studies have been performed in order to establish the nature of this passivating layer and the conditions under which it is formed, this is still the most serious point of controversy and recent electrochemical studies (Viramontes-Gamboa et al., 2006, 2007, 2010) have avoided discussion of the mechanistic details of passivation. It is now widely accepted that the passivation is not due to coating of the mineral surface with elemental sulfur.

Linear dissolution kinetics are observed in chloride systems and the difference with sulfate systems has been ascribed (Majima et al., 1985) to the different morphology of the sulfur layer in that leaching with

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ferric chloride produces a porous elemental sulfur layer whereas ferric sulfate results in the formation and peeling-off of an aggregate of plate-like crystals of elemental sulfur.

Several authors (Ammou-Chokroum et al., 1977; Parker et al., 1981; Warren et al., 1982; Hackl et al., 1995; Barriga Mateos et al., 1987) proposed that the retardation in the dissolution is the result of formation of a sulfide layer that is less reactive than chalcopyrite. This layer was proposed to be a metal-deficient copper rich polysulfide, thought to result from a solid-state transformation of the chalcopyrite surface during the reaction. A similar hypothesis had in fact been first introduced in 1969 (Burkin, 1969). The characteristic rapid decay in the anodic current for oxidation of chalcopyrite at potentials in the region of the mixed potential i.e. below the so-called critical potential has been investigated (Lazaro and Nicol, 2003) and interpreted in terms of a model which is very similar to that found for the dealloying process in many binary alloys. In terms of this, a relatively rapid initial but selective dissolution of the iron from chalcopyrite results in the formation of a copper-rich surface layer. Further dissolution is inhibited by the relatively slow solid-state diffusion of copper and iron through this layer which has a steady-state thickness of only several nanometers even at 60 °C.

An alternative explanation has been advanced in several papers (Crundwell et al., 2015 and references therein) in terms of which the passivation is due to limitations imposed by the semiconducting properties of chalcopyrite and not to the formation of the metal-deficient layer described above. This theory has recently been subject to criticism in that a) apparent photoeffects at chalcopyrite (Crundwell et al., 2015) have been shown to be thermal in origin (Nicol, 2016) and b) capacitance measurements suggesting Mott-Schotky behaviour are probably unreliable due to lack of steady-state conditions and incorrect choice of the measurement frequency (Nicol, 2017).

It has become apparent that there still remains much uncertainty in respect of the formation of this passivating layer and its composition and effect on the kinetics of dissolution of chalcopyrite.

This paper presents the results of a study of the voltammetric characteristics of chalcopyrite under various conditions appropriate to low temperature leaching with acidic chloride solutions. In addition, several comparative experiments have been conducted in sulfate solutions. It follows previous papers on the potentiostatic behaviour (Nicol and Zhang, 2017), the reduction of copper(II) and iron(III) on chalcopyrite (Nicol et al., 2016) and the oxidation of copper(I) and iron(II) (Nicol and Zhang, 2016) in chloride solutions.

2. Experimental

The chalcopyrite samples used in this study were natural crystals of high purity (XRD analysis failed to detect any impurity phases) from Messina and China. The samples were fabricated into roughly rectangular electrodes using silver epoxy as the contact between the mineral and a stainless steel stud both of which were encased in epoxy resin. The base electrolyte contained 3 M NaCl and 0.05 M HCl. Other solutions containing various concentrations of HCl and H₂SO₄ were also studied. For the preparation of the electrolytes, analytical grade reagents of HCl, NaCl and H₂SO₄ were used with deionized water from a Millipore system.

Electrochemical measurements were performed using a three electrode system with double jacketed glass cell maintained at either 25 °C or 35 °C. The reference electrode was either a calomel electrode (saturated KCl) or a silver/silver chloride electrode (3 M KCl) and platinum wire was used as the counter electrode.

Voltammetric experiments were carried out using an EG&G Princeton Applied Research (PAR) Model 173 Potentiostat together with an EG&G PAR Model 175 Universal Programmer or a Solartron 1285 Potentiostat. Capacitance measurements were made using an EG&G 5210 Lock-in Amplifier with sine wave excitation (4 mV pp) at 300 Hz. Analogue data from the potentiostats and lock-in amplifier

were collected using National Instrument data acquisition boards controlled by Labview software.

Before all experiments, the solutions were maintained at the required temperature for 15 min. During this period, nitrogen gas was bubbled through the solution. A fresh chalcopyrite electrode surface was prepared by wet-grinding using #1200 followed by #3000 emery paper and rinsing with deionized water before placing in the cell. The electrode was maintained at the open circuit or a predetermined potential for the desired time before a positive potential sweep was carried out at a rate of 0.1 or 1 mV s⁻¹. All potentials shown are quoted with respect to the standard hydrogen electrode (SHE).

In some experiments, the solutions were analysed by ICP for dissolved copper and iron after completion of each experiment and the results compared with the total charge passed during the oxidation either by voltammetric or potentiostatic methods.

3. Results

3.1. Anodic polarization of chalcopyrite—overall features

Although not directly relevant to the potentials at which leaching of chalcopyrite occurs under ambient conditions, the anodic characteristics of the mineral over an extended potential range are important in terms of a comparison of sulfate and chloride systems. Furthermore, recent claims (Crundwell et al., 2015) that apparent saturation (limiting) currents at high potentials are due to semiconductor limitations in n-type chalcopyrite are unexpected and require re-evaluation including a comparison with the results of previous investigations. Thus, data from a number of previous studies are compared in Fig. 1 that summarizes the anodic behaviour of chalcopyrite in dilute sulfuric acid solutions at low temperatures in the high potential region (above about 0.9 V).

Allowing for the differences in origin of the samples, temperature and uncompensated resistances in both solution and the solid electrodes that can be significant at the higher currents, the results show that the anodic behaviour is relatively similar and can be divided into two main potential regions. At potentials below about 0.9 V (designated as “low potentials” in this paper), the anodic currents are small and generally decrease with time at constant potential. This is the region appropriate to the leaching of chalcopyrite that will be dealt with in detail in a subsequent paper. At potentials above 1.0 V (designated as “high potentials” in this paper), the current increases rapidly with increasing

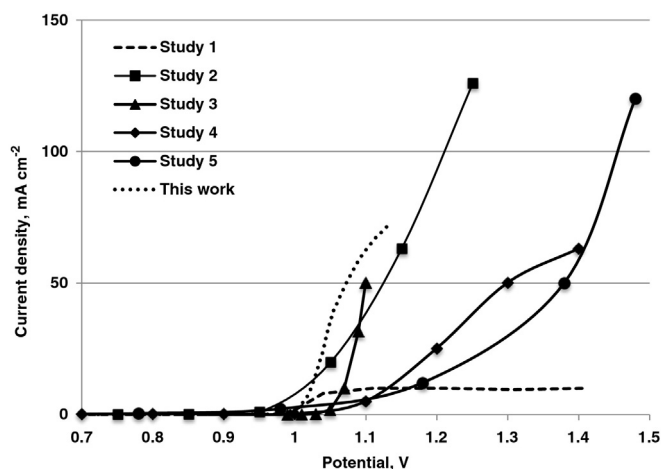


Fig. 1. Comparison of the overall anodic characteristics of chalcopyrite in dilute sulfuric acid solutions. Study 1: Crundwell et al., 2015, 0.3 M H₂SO₄, 30 °C. Study 2: Ghahremaninezhad et al., 2010, 0.2 M H₂SO₄, 25 °C. Study 3: Biegler and Swift, 1979, 1 M H₂SO₄, 25 °C. Study 4: Jones and Peters, 1976, 1 M H₂SO₄, 6 °C. Study 5: McMillan et al., 1982, 1 M H₂SO₄, 25 °C. This work: Messina, 0.3 M H₂SO₄, 25 °C. Not plotted is a value of 40 mA cm⁻² at a potential of 1.09 V (Warren et al., 1982).

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