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The anodic behaviour of covellite in chloride solutions

Michael Nicol[a,*], Petrus Basson[b]

[a] School of Engineering and Information Technology and Energy, Murdoch University, Perth, WA 6150, Australia
[b] Mintek, Randburg, South Africa

ABSTRACT

A detailed study of the anodic behaviour of synthetic covellite in acidic chloride solutions has been conducted as part of an overall program on the fundamental aspects of the heap leaching of copper sulfide minerals.

The anodic behaviour in chloride solutions is characterized by active (but slow) dissolution at low potentials below about 0.65 V, passivation at potentials above 0.70 V that continues to potentials greater than 1.4 V above which rapid transpassive dissolution occurs. These characteristics are also typical of chalcopyrite under similar conditions.

The anodic characteristics at potentials in the region of the measured mixed potentials in the presence of copper(II) show that there are two peaks in the voltammetric sweeps at about 0.65 V and 0.75 V, the magnitude of which increase with increasing chloride concentration. The two peaks merge into a single peak at very high chloride concentrations.

Potentiostatic current-time transients at various potentials in the region of the mixed potential show the slow passivation typical of chalcopyrite and the data can similarly be described quantitatively in terms of rate limiting solid-state diffusion. The rate of oxidative dissolution of covellite under ambient temperature conditions is slow but about an order of magnitude greater than that of chalcopyrite.

The voltammetric response of chalcopyrite after pre-treatment with a chloride solution containing a low concentration of copper(II) shows the presence of the same two peaks observed for covellite confirming the surface conversion of chalcopyrite to covellite.

A mechanism similar to that previously proposed for the dissolution of chalcopyrite has been described in terms of which the formation of polysulfides (typically CuS_2) by dissolution of a fraction of the copper in the covellite lattice is responsible for the passivation that increases slowly as the polysulfide layer increases in thickness.

Novel measurements of the mixed potential and the solution potential at a covellite surface at the bottom of a capillary have been used to simulate the situation within ore particles. The results have been simulated using a simple linear diffusion model that show that the potential at the covellite surface can be 50–100 mV lower than that in the bulk of the solution. This has important consequences for the rate of heap leaching.

1. Introduction

The recovery of copper by heap leaching of low-grade ores containing secondary copper sulfide minerals is becoming increasingly important as the easily leached oxide ores are being depleted.

In the case of the secondary copper sulfide minerals, chalcocite (Cu_2S) is the most common while digenite ($Cu_{1.8}S$) and other intermediate sulfides ($Cu_{2-x}S$) are often associated with chalcocite. Although it is well known that the rate of leaching of the secondary copper sulfides is more rapid than that of the primary minerals such as chalcopyrite and enargite under strongly oxidizing conditions, the rates are considerably slower than those for the most common oxide minerals. In addition, an oxidant is required for the sulfides and bacterially-assisted oxidation in sulfate solutions has been the generally accepted method for heap leaching of sulfide minerals. An alternative approach using dilute chloride solutions has been applied in at least one case (Aroca, 1999) and more concentrated chloride solutions are currently being used in an operation in northern Chile. Chloride is an attractive alternative which makes use of copper(II) as an oxidant. The rapid (relative to that of iron(II)) rate of the re-oxidation of copper(I) by dissolved oxygen in chloride solutions (Miki and Nicol, 2008a, 2011) permits the use of aerated heaps without external regeneration of the oxidant.

Although there is a considerable body of published information on

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* Corresponding author.
E-mail address: m.nicol@murdoch.edu.au (M. Nicol).

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the leaching of secondary copper sulfides in chloride solutions, the emphasis has been on elevated temperature processes aimed at concentrates, and research on the rates of dissolution of secondary sulfides in chloride solutions at ambient temperatures is therefore desirable. In particular, the minimum and maximum solution potentials required to effectively leach these minerals are not known with any certainty in chloride solutions.

Covellite (CuS) is a copper sulfide mineral which contains 66% copper and it is now considered as being Cu_2S_2 (Goh et al., 2006) with the copper existing as copper(I). In this paper the simpler formula CuS will be used. It is widely associated with chalcopyrite and chalcocite which are the main primary and secondary copper sulfides, respectively (Dutrizac and MacDonald, 1974b).

At elevated leach temperatures, it is generally considered that the relative rates of dissolution of the important copper sulfides are chalcocite > covellite > chalcopyrite (Cheng and Lawson, 1991).

In the first systematic report (Sullivan, 1930) of CuS leaching in ferric sulfate media it was confirmed that the mineral dissolves mainly according to following equation.

$$CuS + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} + S^{\circ} \qquad (1)$$

In a later study (Thomas and Ingraham, 1967) synthetic CuS disks were leached in ferric sulfate solutions at elevated temperatures and the above stoichiometry was confirmed although some 4% of the leached sulfur reported as sulfate. Sullivan also reported that covellite dissolution increased with increasing temperature and is insensitive to acid concentration in sulfate solutions. Dissolution increased with increasing ferric ion concentration up to about 0.005 M above which the rate was constant. This basic behaviour was confirmed in several later reports (Thomas and Ingraham, 1967; Mulak, 1971; Dutrizac and MacDonald, 1974a).

Various papers (Thomas and Ingraham, 1967; Mulak, 1971; Dutrizac and MacDonald, 1974a) reported on the effect of temperature and this resulted in activation energies in the range from 77 to 92 kJ mol^{-1} which suggests that the rate of covellite leaching is controlled by slow chemical and/or electrochemical steps.

In the study using synthetic covellite (Thomas and Ingraham, 1967) the dissolution curves showed that the rate increased gradually during the initial period of leaching but then became linear. Similar behaviour has been reported (Dutrizac and MacDonald, 1974a) and a mechanism was suggested in which ferric attack of covellite occurred preferentially in certain areas and the progressive development of such pits was responsible for the observed leaching behaviour.

In a later study (Cheng and Lawson, 1991) the leaching of synthetic covellite in mixed sulfate-chloride solutions from 75 to 95 °C in the presence of oxygen was studied and the importance of chloride for oxygenated leaching of covellite was established. Under these conditions, leaching followed a shrinking core model and it was suggested that the thickening surface layer of sulfur caused partial passivation. It appears that there has been no published comparison of the rates of leaching of various copper sulfide minerals under similar conditions.

In the most recent study (Miki et al., 2011), the effect of controlled solution potential on the rate of dissolution of synthetic covellite, chalcocite and digenite was studied in chloride solutions containing copper(II) and iron(III) ions under ambient conditions. The results showed that the rate of dissolution of covellite is similar at solution potentials of 0.60 and 0.65 V while the rate is noticeably less at a lower potential of 0.55 V as the system approaches equilibrium as predicted from the thermodynamics of this system. The rate of dissolution appeared to be largely independent of the chloride concentration in the range 0.2 to 2.5 M and the HCl concentration in the range 0.1 to 1 M. The rate of dissolution of secondary covellite produced by the leaching of chalcocite at 0.5 V was found to be at least an order of magnitude greater than that of primary covellite.

There is little published information on the electrochemical characteristics of the dissolution of covellite with most of the studies focussed on sulfate solutions (Hillrichs and Bertram, 1983; MacKinnon, 1976; Peters, 1977; Kato and Oki, 1972) in which it was found that, at low current densities (less than 0.5 to 1 mA/cm^2) dissolution occurred according to the reaction.

$$CuS = Cu^{2+} + S^{\circ} + 2e \qquad (2)$$

At higher current densities, the surface of the mineral passivated and the potential increased to very high values greater than 1.5 V accompanied by oxygen evolution. In chloride solutions, the only published data (Ghali et al., 1982) revealed similar passivation in dilute hydrochloric acid/sodium chloride solutions with a characteristic peak in the voltammograms at about 0.7 V above which the curves consisted of a wide plateau region of low current to potentials above 1.75 V. The height of the peak was found to increase with increasing chloride concentration and, as expected, with increasing temperature. The passivation process was attributed to the formation of elemental sulfur on the covellite surface. These previous studies have not made use of the mixed potential model to describe the kinetics of dissolution.

In previous studies (Miki and Nicol, 2008b; Lee et al., 2008; Nicol et al., 2016) of the cathodic reactions on various sulfide minerals in chloride solutions, it was found that the rate of reduction of copper(II) ions on covellite was significantly greater than the reduction of iron(III) and that the presence of both metal ions resulted in synergistic reduction.

This paper presents the results of a study of the anodic behaviour of covellite over a wide range of chloride concentrations at potentials relevant to the dissolution of the mineral under ambient conditions appropriate to heap leaching.

Unlike the leaching of fine-milled concentrates and ores in which the target copper sulfide mineral is usually well-liberated, this is not the case in heap leaching of whole ores, where a substantial portion of the target mineral is often locked in the gangue matrix. Depending on the mineralogy, significant proportions of the valuable mineral may occur in capillaries or pores in the gangue material, into which the leach lixiviant has to penetrate in order to establish solid/liquid contact for leaching. Therefore, in order to investigate whether the physical dimensions of such a capillary or pore would have any effect on the solution potential at the covellite surface and thereby also on the rate of dissolution of the mineral, experiments were conducted with a specially designed cell.

2. Experimental

2.1. Electrodes

Covellite was synthesized by high temperature reaction of the elements using a published technique (Dutrizac and MacDonald, 1974a) and consisted of an extruded 1 mm cylindrical sintered pellet about 10 mm long. Mineralogical analysis showed that the material was 98.5% covellite with undetectable amounts of chalcocite. It was fabricated into a disk electrode using silver epoxy as the contact to a stainless steel stud that was encased in epoxy resin. The calculated surface area of the mineral electrode exposed to the solution was 0.8 mm^2.

The counter electrode was a thin, coiled platinum (Pt) wire of about 10 cm in length. The reference electrode was a saturated potassium sulfate, mercury-mercurous sulfate (sat. K_2SO_4, Hg/Hg_2SO_4) electrode with a potential of 0.651 V against the standard hydrogen electrode (SHE) at 25 °C. All potentials in this study have been reported against SHE.

2.2. Cell

A schematic diagram of the apparatus used is presented in Fig. 1. It consisted of an aluminium holder in which the resin disk, containing the mineral electrode, was inserted for support. The holder was open at