

Anodic oxidation of iron(II) and copper(I) on various sulfide minerals in chloride solutions



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ABSTRACT

A comparative study of the electrochemical oxidation of iron(II) and copper(I) ions on selected sulfide minerals in concentrated chloride solutions has been carried out as part of a broader study of the kinetics of the leaching of chalcopyrite, covellite, enargite and pyrite under chloride heap leaching conditions. Mixed potential, cyclic voltammetric and potentiostatic measurements have been made using rotating disk electrodes of massive mineral samples. For comparative purposes, arsenopyrite and platinum electrodes have also been used under the same conditions. The mixed potentials of the various minerals in solutions containing 4 mol/L sodium chloride, 0.1 mol/L hydrochloric acid and 0.05 mol/L iron(II) or 0.05 mol/L copper(II) ions at 25 °C are all governed by the potentials of the redox couples with the exception of chalcopyrite in solutions of iron(II) for which the mixed potential is lower than the equilibrium potential of the iron(III)/iron(II) couple.

Cyclic voltammetry conducted at potentials positive to the mixed potentials at slow sweep rates has shown variable reactivity of the minerals for oxidation of both iron(II) and copper(I) ions. Oxidation of copper(I) occurs readily on all minerals with the limiting current density observed on all with the exception of chalcopyrite for which the limiting current is not reached even at relatively large overpotentials. Partial passivation of the oxidation of copper(I) is observed at potentials above about 0.7 V on covellite. Oxidation of iron(II) is slower than that of copper(I) on all minerals and the limiting current density is only observed on pyrite. Partial passivation of the oxidation of iron(II) is observed with all other minerals at potentials above 0.65 to 0.75 V.

Quantitative measurements of the rates of oxidation at the mixed potentials have been obtained from linear polarization measurements and the results compared with previously published data on the cathodic reduction of iron(III) and copper(II) on these mineral surfaces. The rate constant varies by about an order of magnitude within the mineral group for both iron(II) and copper(I) oxidation and the rates of oxidation on platinum are higher for both couples than for the mineral electrodes. The ratio of the rate of copper(II) reduction to iron(III) reduction is significantly greater for the minerals containing copper than for those without copper.

The effect of illumination with light of wavelength 405 nm on the rate of anodic oxidation of iron(II) on chalcopyrite has been evaluated and no positive effects that can be attributed to semi-conducting effects have been observed.

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1. Introduction

The heap leaching of copper ores has become a well-established and important process option for oxide materials and, in recent years, attention has been focused on the leaching of low grade sulfide ores. While this has been largely successful for secondary copper sulfides such as chalcocite and, to some extent, covellite, the slow leaching rates of the primary sulfides such as chalcopyrite and enargite remains an outstanding problem. Recent developments in the application of chloride processes to the heap leaching of chalcopyrite have proved to be promising (Nicol et al., 2011) and this paper is the second of three that will deal with fundamental aspects of the dissolution of

chalcopyrite and associated sulfide minerals in relatively concentrated chloride solutions.

It is now generally accepted that the oxidative dissolution of sulfide minerals is electrochemical in nature and can be described by the mixed potential model in which anodic dissolution of the metal sulfide is coupled to cathodic reduction of an oxidant such as iron(III). The problem with chalcopyrite and enargite and, to a lesser extent other sulfide minerals such as covellite and pyrite is the formation of passive or partially passive metal sulfide layers that are formed under anodic oxidation particularly at the low temperatures typical of heap leaching.

More recent unpublished but patented research and development has demonstrated that direct oxidative dissolution of chalcopyrite can be successfully used in column and crib leaching of ores containing primarily chalcopyrite by increasing the chloride concentration in conjunction with other operating modifications (Patino et al., 2014).

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Fundamental studies have demonstrated that the mixed potential model applies under these conditions.

A fundamental description of the dissolution of chalcopyrite under these conditions requires knowledge of the mixed potentials, the characteristics of anodic dissolution of the mineral and the cathodic reduction of the oxidants which are both iron(III) and copper(II) in chloride solutions. The anodic oxidation of the reduced forms of the oxidants is also of indirect importance as this information is required for a full description of the mixed-potential model (Nicol, 1993). In addition, the anodic reactions can be used as possible probes for the formation of “passive” layers on the sulfide minerals. A previous paper (Nicol et al., 2016) has dealt with the cathodic reactions of these oxidants and a later paper will deal with the anodic characteristics of the minerals in concentrated chloride solutions. The presence of other sulfides such as covellite, enargite and pyrite in such ores requires that the study also include, in a more superficial way, the electrochemical behaviour of these minerals under identical conditions. Arsenopyrite has been included to provide an additional sulfide that does not contain copper while platinum has also been added to the list as a comparative inert substrate for the anodic reactions.

2. Experimental

Details of the mineral samples used and the electrochemical methods and experimental procedures have been provided in a previous publication (Nicol et al., 2016). As previously described, electrochemical measurements were carried out using a standard three-electrode system with working mineral electrodes rotated at 500 rpm.

The base electrolyte contained 4 M sodium chloride and 0.1 M hydrochloric acid. Solutions were prepared using ferrous chloride and cuprous chloride (Ajax Chemical), analysed by potentiometric titration with standard chromium(VI) solution and kept under nitrogen. Due to the presence of small amounts of iron(III) and copper(II) in the reagents and unavoidable oxidation during preparation and measurement (conducted using solutions sparged with high-purity nitrogen), the solutions contained variable amounts of the oxidised ions. The potential of a platinum electrode was used to establish that the concentrations of the oxidised metal ions was <5% of the reduced forms.

A silver/silver chloride (3 mol/L potassium chloride) reference electrode (0.207 V versus SHE) was used and the potentials were measured and controlled relative to this electrode at room temperature (25 ± 0.5 °C). All potentials are shown relative to the standard hydrogen electrode (SHE).

In the case of the cyclic voltammetry (at a low sweep rate of 0.2 mV/s), the potentials were manually corrected for the voltage drop in each sample electrode using the resistance values as measured in the determination of the mineral resistivity. These corrections were made automatically during the potentiostatic experiments.

Photocurrent measurements on chalcopyrite in solutions containing iron(II) were made as previously described (Nicol, 2016).

3. Results and discussion

3.1. Mixed potential measurements

With the exception of chalcopyrite in solutions containing iron(III), the measured mixed potentials after immersion for 5 min were all within 5 mV of the potential as measured by a platinum electrode. This confirms that the mixed potential is determined by the equilibrium potential of the relevant redox couple and that the rate of anodic oxidation of the minerals is negligible at these potentials in comparison to the rates of oxidation/reduction of the iron(II)/(III) and copper(I)/(II) couples i.e. a so-called Type III system (Nicol, 1993). In the case of chalcopyrite in iron(II) solutions, the rate of oxidation of iron(II) is very slow (see below) and, in this case, the rate of oxidation of the mineral is comparable with a resulting negative shift in the mixed potential.

3.2. Linear sweep voltammetric measurements

The results of the anodic oxidation of iron(II) and copper(I) on each of the minerals are shown for comparison in Figs. 1 and 2 as linear sweep voltammograms (plotted on a log scale to accommodate the wide variation) obtained in a positive sweep direction from the mixed potentials. For all minerals with the exception of chalcopyrite, anodic currents at potentials in the region of interest in the absence of iron(III) or copper(II) were found to be small as will be shown below. Thus, the currents shown in Figs. 1 and 2 can be attributed to the oxidation of iron(II) and copper(I) respectively.

Examination of the curves shows that there are significant differences in reactivity for the oxidation of iron(II) with only the rate on pyrite exhibiting relatively reversible behaviour similar to platinum. In the case of the other minerals, the maximum current densities are lower and most curves pass through a maximum at potentials between about 0.65 and 0.75 V. The differences are not so marked in the case of the oxidation of copper(I) ions and only covellite provides evidence of partial passivation at potentials above about 0.75 V. In this context, the term “passivation” will be used to describe a reduction in the rate of an anodic process that occurs as the potential increases. Depending on the rate at which the process responsible for passivation occurs, this reduction in rate can appear as a relatively small peak or shoulder on a voltammogram but can be observed as significant decays in current in potentiostatic measurements over longer times.

The limiting current density for mass transport controlled oxidation of 0.05 M iron(II) can be calculated from the Levich equation to be 119 A/m² and 150 A/m² for the oxidation of copper(I) at 500 rpm. These estimates were made using data for the diffusion coefficients obtained previously (Nicol et al., 2016). Thus, the limiting current density is only approached at high potentials for the oxidation of iron(III) in the case of pyrite (and platinum) while limiting current oxidation of copper(I) is achieved on all minerals. The slightly lower limiting current in the case of pyrite is due to a lower copper(I) concentration in this case while the limiting current is approached more slowly in the case of chalcopyrite.

Details of the behaviour of each mineral will be discussed in the following section.

Comparative results for the oxidation of iron(III) and copper(I) are shown in Fig. 3 for pyrite which also includes the voltammogram obtained in the base electrolyte in the absence of iron(II) or copper(I) ions.

The reverse sweeps have been omitted from the voltammograms obtained in the presence of iron(II) or copper(I) as the hysteresis between the forward and return sweeps is small. In the case of pyrite, the greater reactivity for oxidation of copper(I) than iron(II) is apparent from the slopes of the curves although, at high potentials, both processes become mass transport controlled. There is no evidence of

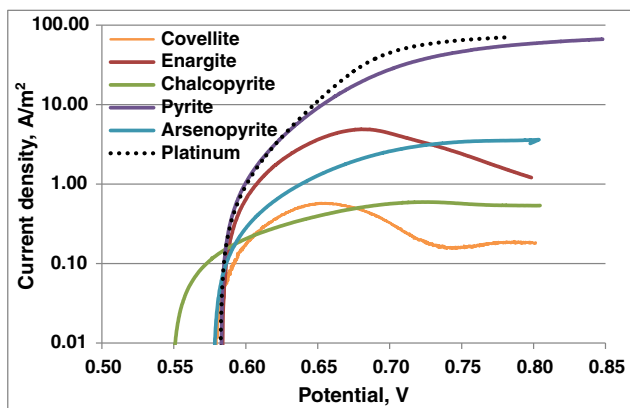


Fig. 1. Linear sweep voltammograms for the minerals in base electrolyte containing 0.05 M iron(II).

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