Reduction of chalcopyrite with copper (I)

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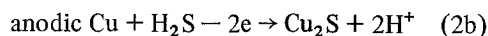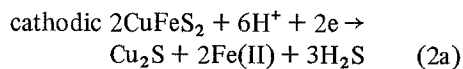*Mineral Chemistry Research Unit, Murdoch University, Murdoch, Western Australia, 6150, Australia*

In the presence of Cu(I), chalocopyrite is reduced to Cu_2S and Cu_5FeS_4. Electrochemical studies on polished chalcopyrite crystals establish that this reaction is electrochemical in nature and dependent on the redox potential of the copper(II)/copper(I) couple. A sharp decrease in the initial rate of reduction is observed which is attributed to the rapid formation of bornite and diffusion of Cu(I) through a thickening film. Subsequent reaction of bornite to chalcocite is a slow electrochemical reaction with a Tafel slope of $-162 \pm 5\,mV$.

1. Introduction

In the presence of certain water-soluble ligands such as chloride ion or acetonitrile (AN), copper(I) is stabilised in solution as $CuCl_2^-$ or as $Cu(AN)_3^+$ which are useful reductants in hydrometallurgical processes [1]. In certain solutions containing AN or Cl^-, copper(I) quantitatively reduces sulphur and covellite to chalococite [2]. However, the reduction of chalcopyrite by Cu(I) to chalcocite and other copper enriched sulphides (Equation 1) rapidly ceases unless copper metal is added [3].

$$CuFeS_2 + 4Cu(I) \rightleftharpoons 2Cu_2S + Fe(II) + Cu(II) \tag{1}$$
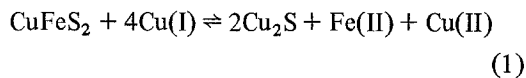
Nicol [4] has shown that the reduction of chalcopyrite with copper metal in acid solution is probably electrochemical in nature (Equation 2)

$$\text{cathodic } 2CuFeS_2 + 6H^+ + 2e \rightarrow Cu_2S + 2Fe(II) + 3H_2S \tag{2a}$$

$$\text{anodic } Cu + H_2S - 2e \rightarrow Cu_2S + 2H^+ \tag{2b}$$

but it is not possible to determine the precise stoichiometry of the cathodic and anodic processes which occur or whether Cu(I) is involved as an intermediate.

The reaction of Cu(I) with chalcopyrite is fundamental to the understanding of the formation and transformation of copper sulphide minerals. The reaction of Cu(II) with these minerals is quite different [2]. In a hydrometallurgical process the reaction of Cu(I) with chalcopyrite, allows iron to be leached selectively leaving a more reactive copper sulphide [3]. Such work established that the initial reaction was fast at 25° C but rapidly decreased as the product layer was formed.

This paper reports an electrochemical study of the reduction of pure polished chalcopyrite crystals with Cu(I) to establish whether the reaction is electrochemically controlled or whether the reaction is limited by the formation of a surface passivating film. For an electrochemically controlled process, the rate of reaction should vary according to the Butler–Volmer equation as the potential of the reductant in solution is changed. However, rather than use a series of different reductants, the rate of reaction of chalcopyrite with Cu(I) was studied at different redox potentials simply by changing the ligand concentration and hence the potential of the Cu(II)/Cu(I) couple due to the equilibrium

$$Cu^{2+}(aq) + 3AN + e \rightleftharpoons Cu(AN)_3^+.$$

We chose to use mainly AN/H_2O solutions but the same chemical principles apply with Cl^-/H_2O sol-

utions. The potential of the Cu(II)/Cu(I) couple in AN/H_2O and Cl^-/H_2O shows a similar dependence on the concentration of AN or Cl^- [5].

2. Experimental procedure

Rotating disc electrodes of chalcopyrite were prepared from single crystals of high quality mounted in epoxy resin and a teflon sleeve. Working surfaces (area $\approx 8\,mm^2$) were polished to a mirror finish just prior to measurement and showed no evidence of twinning or inclusions of gangue material when examined under a microscope. Passivation was observed on chalcopyrite after exposure to air for periods longer than 10 minutes. Similar behaviour has been reported by Peters [6]. The resistance of the electrode was ≈ 20 ohms.
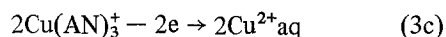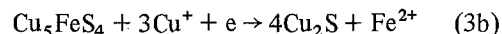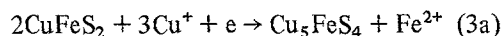
All solutions were purged of oxygen with a slow stream of high purity nitrogen pre-saturated with the same solution. Solutions were prepared from Analar sulphuric acid, distilled water and acetonitrile which had been distilled over potassium permanganate and which was free of ammonia and electroactive species such as acrylonitrile. A stock solution of copper(I) and copper(II) sulphate was prepared by stirring a solution of copper(II) sulphate containing 0.3 $mol\,dm^{-3}$ H_2SO_4 and 3.8 $mol\,dm^{-3}$ AN with copper metal and was analysed by permanganate and iodometric titrations.

The electrode potential was controlled by a PAR 170 electrochemistry system and current–time curves were recorded on an x–y recorder in the y–t mode with time base of 20 or 50 seconds per inch. Potentials of the Cu(II)/Cu(I) couple in the test solutions were measured with an electrolytically cleaned Pt electrode and found to remain constant within $\pm 2\,mV$ throughout the experiment. All measurements were made at $25 \pm 0.1°C$ and potentials were measured using saturated calomel or silver/silver chloride electrodes. Potentials were converted to the normal hydrogen electrode (NHE) after correction for a liquid junction potential of about $25\,mV$ for calomel versus 4 $mol\,dm^{-3}$ AN/H_2O [7].

3. Results and discussion

In pure water, chalcopyrite is reduced by acid (Equation 2a) with a standard potential of

$-0.14\,V$ (NHE) [8] and it was found that there is virtually no reaction at 0.00 V even in the presence of 4 $mol\,dm^{-3}$ AN or Cl^-. However, in the presence of 0.1 $mol\,dm^{-3}$ Cu(I), chalcopyrite rapidly tarnishes to form a purple and then black layer at 0.00 V associated with the consecutive formation of copper enriched chalcopyrite, bornite and chalcocite [3] (Equations 3(a) and 3(b)).

$$2CuFeS_2 + 3Cu^+ + e \rightarrow Cu_5FeS_4 + Fe^{2+} \quad (3a)$$

$$Cu_5FeS_4 + 3Cu^+ + e \rightarrow 4Cu_2S + Fe^{2+} \quad (3b)$$

$$2Cu(AN)_3^+ - 2e \rightarrow 2Cu^{2+}aq \quad (3c)$$

After refluxing chalcopyrite crystals in a 1 mol dm^{-3} Cu(I) solution containing 4 $mol\,dm^{-3}$ AN, a polished section revealed distinct layers or reaction zones (Fig. 1). Microprobe analysis confirmed that the outer layer consisted of mainly Cu_2S followed by an inner layer of Cu_5FeS_4 and copper enriched $CuFeS_2$ and a core of unreacted $CuFeS_2$.

We calculate from standard free energies of formation that the standard potential for reactions
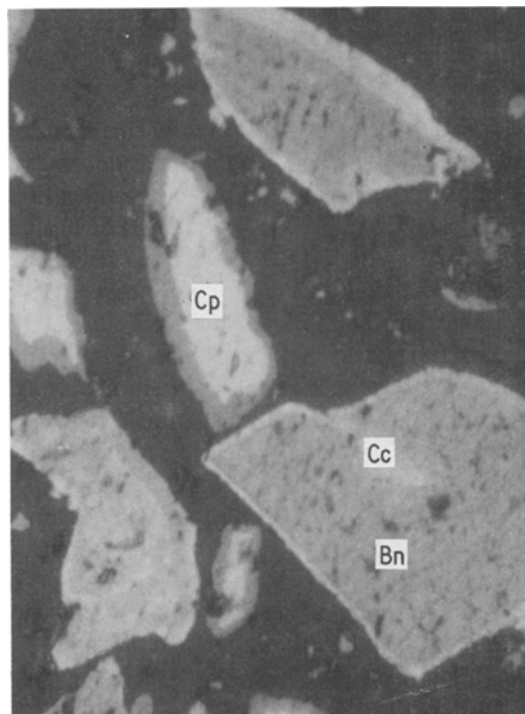

Fig. 1. Polished section of chalcopyrite crystals ($\times$ 600) after refluxing in 4 $mol\,dm^{-3}$ AN/H_2O containing 1 mol dm^{-3} Cu(I) for three hours. Bn = bornite; Cp = chalcopyrite; Cc = chalcocite.

3(a) and 3(b) are -0.27 V and -0.30 V respectively, assuming $\Delta G^0_{298} Cu(I) = 20$ kJ g ion^{-1}. Parker *et al.* [1] report that in practical solutions the free energy of Cu(I) in about 4 mol dm^{-3} AN/H$_2$O varies between 10–30 kJ g ion^{-1} according to the concentration of Cu(I) and free AN.

Cyclic voltammograms of rotating discs of pure chalcopyrite crystals proved to be very similar in acidified sulphate solutions containing 0.1 mol dm^{-3} Cu(I) and 4 mol dm^{-3} AN, and in chloride solutions containing 0.1 mol dm^{-3} Cu(I) and 4 mol dm^{-3} NaCl (Figs. 2a, 2b). Between 0.5–0.1 V there was no evidence of any reaction with CuFeS$_2$ but below 0.1 V there was a significant current, particularly below -0.1 V, which was dependent upon rotation speed. This current is associated with the formation of first bornite, then chalcocite, and finally copper by reduction of Cu(I). There was no evidence of H$_2$S evolution or precipitation of Cu$_2$S in the bulk solution. On a rotating platinum disc, copper metal deposited at -0.05 V (NHe) from the same Cu$_2$SO$_4$/AN/H$_2$O solution. The oxidation of Cu(I) to Cu(II) on CuFeS$_2$, reaction 3(c), occurred above 0.5 V in AN/H$_2$O mixtures, but much higher currents were observed in chloride than in sulphate solutions at similar voltages. Likewise, the oxidative leaching of CuFeS$_2$ with Cu(II) or Fe(II) is faster in chloride than in sulphate media [9, 10].

In order to study the reduction of CuFeS$_2$ with Cu(I) in acidified AN/H$_2$O solution the electrode was potentiostatted at 0.00 V (NHE) and solutions were kept under N$_2$ to avoid Cu(II) formation. The background current associated with reduction of any Cu(II) to Cu(I) was found to be negligible.

When the chalcopyrite electrode was dipped into dilute solutions of Cu(I) containing 4 mol dm^{-3} AN, a large cathodic current was observed initially but this rapidly decayed. Plots of ln i versus time at 0.00 V show a sharp decrease in current over the initial 30 s and apparently plateau after 2 minutes (Fig. 3). After 1 minute the surface was visibly black due to the surface layers of the chalcocite.

The rapid decrease in current is believed to be associated with the build-up of a Cu$_5$FeS$_4$ layer which effectively covers the electrode surface in the first few seconds. Subsequent reaction requires the Cu(I) to diffuse through this dense layer to the

fresh chalcopyrite surface. If the current is determined by cationic diffusion through a thickening film the current will progressively decrease with time. The initial current–time response in solutions of high redox potential ($+0.509$ V) is similar to that observed by Gueshi *et al.* from chronoamperometric measurements at partially covered electrodes [11]. In solutions of low redox potential the conversion of chalcopyrite to bornite is relatively slow and the current–time curve is indicative of a partially covered electrode for the first three seconds. Once the bornite film has formed the i–t relationship is essentially given by the Cottrell equation : Equation (4).

$$I_d = nFA(D)^{1/2}c^0/(\pi t)^{1/2} \qquad (4)$$

A plot of the observed cathodic current against $t^{-1/2}$, after correction for the residual background current at 0.00 V in the absence of Cu(I), gives an excellent straight line (rho value $\geqslant 0.997$) for solutions of moderate reducing strength (Fig. 4). We conclude that the rapid decrease in current and rate of reaction is consistent with the diffusion of Cu(I) through a thickening product layer of dense Cu$_5$FeS$_4$ and with the direct formation of Cu$_5$FeS$_4$ from CuFeS$_2$ at the lattice site.

Similar current–time relationships were observed by Etienne [12, 13] for the oxidation of copper metal in H$_2$S saturated solutions where the growth of Cu$_2$S is determined by ionic diffusion of Cu(I) from the copper through the film of Cu$_2$S to the surface.

It is notable that although the initial reaction of chalcopyrite with copper(I) seems to be diffusion controlled, measurements of ln i versus time in solutions of increasing AN concentration and Cu(II)/Cu(I) potential, show a corresponding decrease in the rate of change of current and in the limiting steady state current (i_{lim}) after 10 minutes (Fig. 3). Thus it seems that the subsequent rate of reaction of bornite to chalcocite (Equation 3b) is proportional to the chemical potential of the reductant. In this case diffusion of Cu(I) through a thickening film of chalcocite is fast relative to electron transfer.

Tafel plots of log i_∞ (obtained by extrapolation of i–$t^{-1/2}$ plots) versus E Cu(II)/Cu(I) gave a slope of -162 ± 5 mV. A Tafel slope of 180 mV was observed by Nicol [5] for the cathodic reduction of chalcopyrite in 1 mol dm^{-3} H$_2$SO$_4$ (Equation
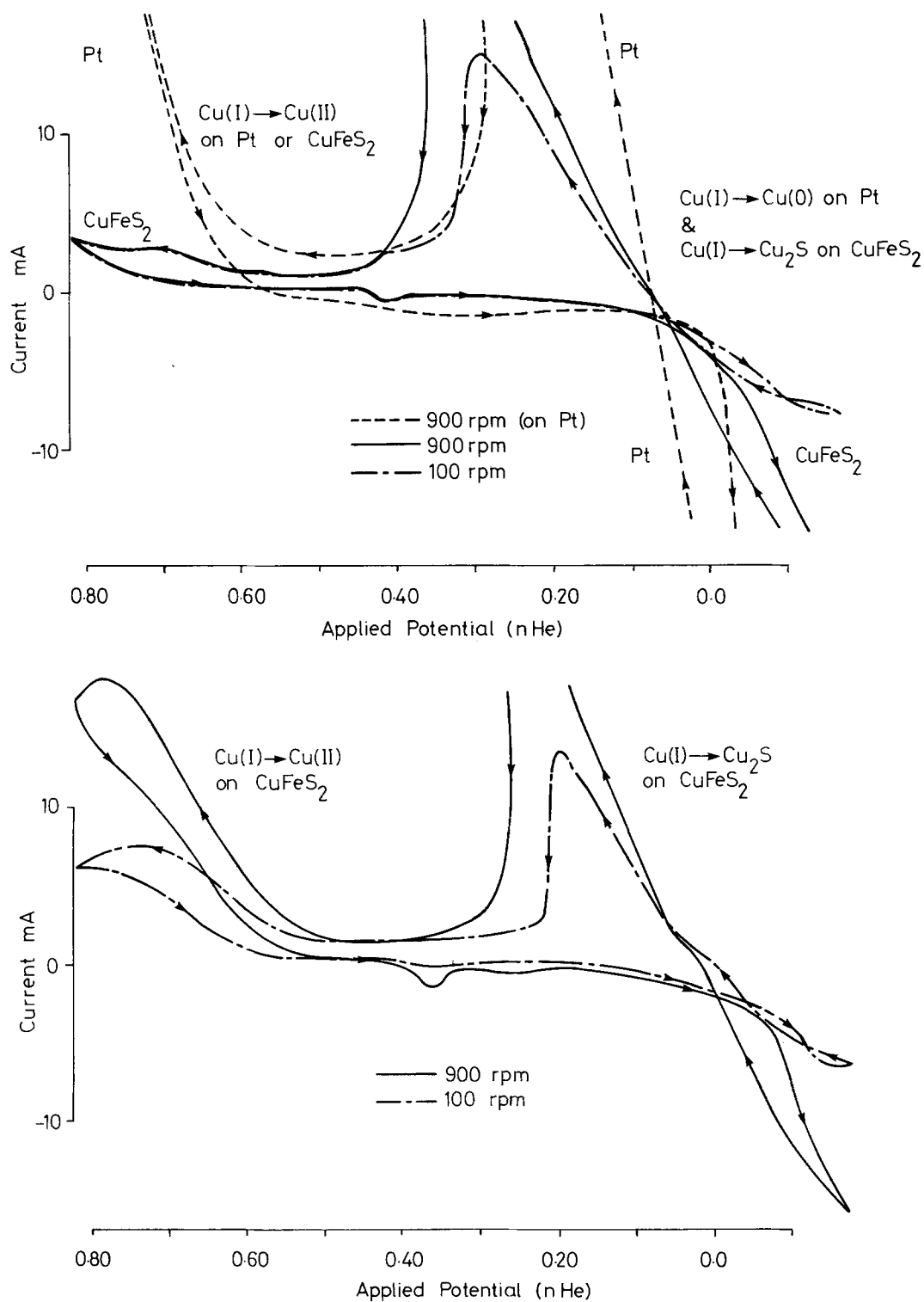
Fig. 2. Cyclic voltammogram of $CuFeS_2$ and Pt in the presence of $0.1 \, mol \, dm^{-3} \, Cu(I)$, first sweeps. A. as sulphate in $4 \, mol \, dm^{-3}$ AN and $1 \, mol \, dm^{-3} \, H_2SO_4$; B. as chloride in $4 \, mol \, dm^{-3}$ NaCl and $1 \, mol \, dm^{-3}$ HCl. Sweep rate $= 20 \, mV$ s^{-1}. Area $CuFeS_2 = 8 \, mm^2$; Pt $= 28 \, mm^2$. Starting potential $+ 0.3$ volt versus NHE.
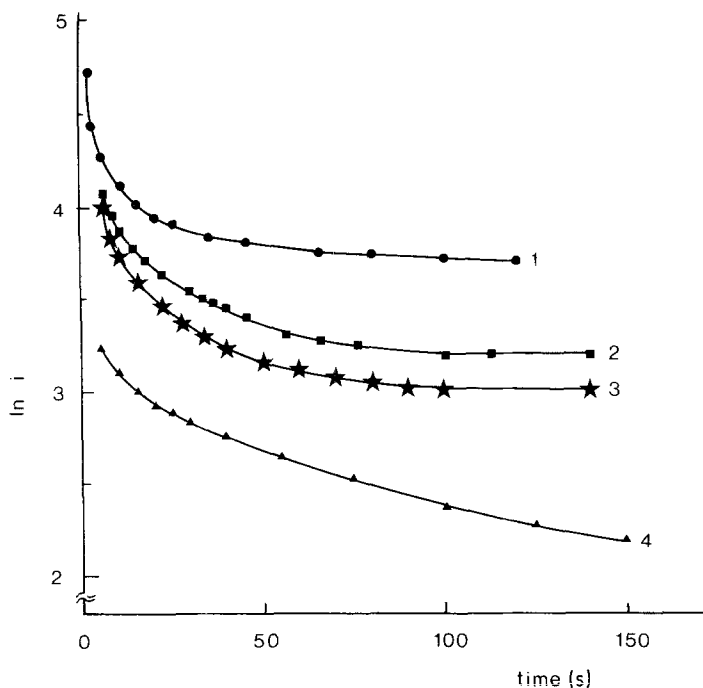
Fig. 3. Reaction of Cu(I) with chalcopyrite. Variation of current flow (ln i) with time and effect of E(Cu(II)/Cu(I)). Key, 1, $E = 0.340$ V in 0.38 mol dm^{-3} AN; 2, $E = 0.400$ V in 0.95 mol dm^{-3} AN; 3, $E = 0.439$ V in 1.9 mol dm^{-3} AN; 4, $E = 0.509$ V in 3.8 mol dm^{-3} AN.

2a) whilst Biegler and Swift [7] found a Tafel slope of 144 mV for the same reduction in 1 mol dm^{-3} HClO$_4$. We would not expect a slope of 120 mV per decade as for a simple one electron process since the reaction involves a collapse of the chalcopyrite crystal lattice and formation of a semiconductive thickening film.
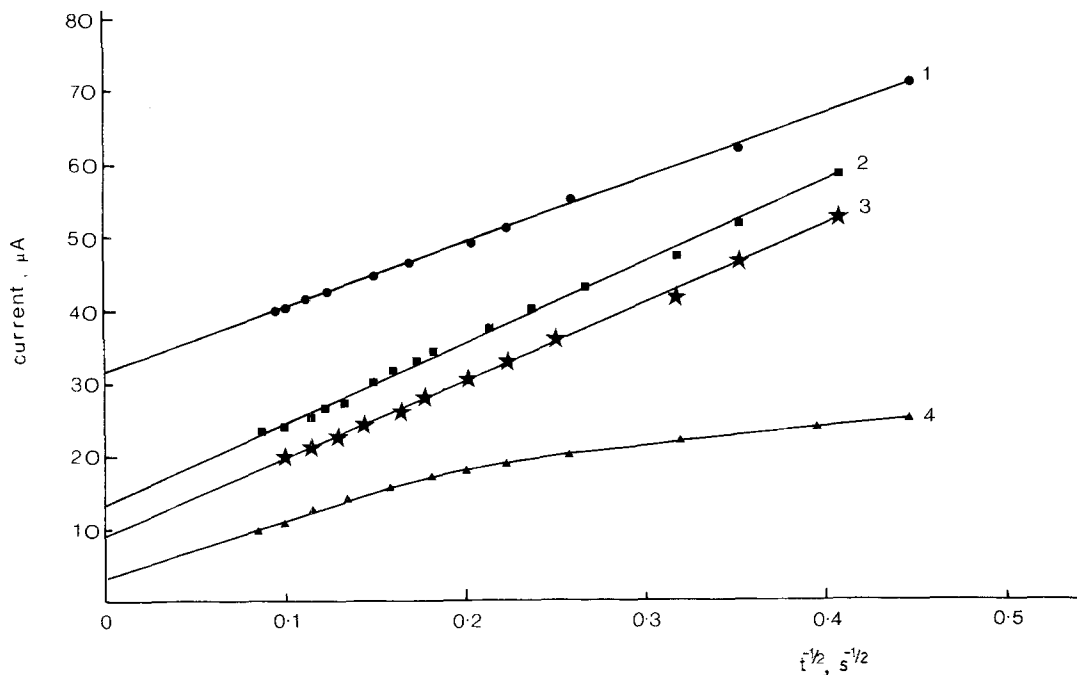
We conclude that the reaction of chalcopyrite

Fig. 4. Diffusion of Cu(I) through Cu$_2$S. Variation of current with time$^{-1/2}$ for solutions of varying acetonitrile concentration. Key; 1, $E = 0.340$ V in 0.38 mol dm^{-3} AN; 2, $E = 0.400$ V in 0.95 mol dm^{-3} AN; 3, $E = 0.439$ V in 1.9 mol dm^{-3} AN; 4, $E = 0.509$ V in 3.8 mol dm^{-3} AN.

with Cu(I) is a two step process involving a fast diffusion controlled formation of bornite followed by a slower electrochemically controlled formation of chalcocite.

Acknowledgements

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