J Appl Electrochem (2008) 38:363–369
DOI 10.1007/s10800-007-9447-5

ORIGINAL PAPER

Cathodic processes in the leaching and electrochemistry of covellite in mixed sulfate–chloride media

M. S. Lee · M. J. Nicol · P. Basson

Received: 24 July 2007 / Revised: 4 November 2007 / Accepted: 4 November 2007 / Published online: 20 November 2007

Abstract The cathodic processes that occur on a covellite (CuS) surface in mixed sulfate–chloride solutions in the absence and presence of copper(II) ions have been studied using potentiostatic transients and cyclic voltammetry at rotating disk electrodes in the potential range 0.3–0.7 V (versus SHE). This range is relevant to the oxidative leaching of this copper mineral in sulfate and chloride lixiviants. Variations in the concentrations of sulfate and chloride ions had a small effect on the cathodic reduction of covellite in the potential range of 0.5–0.3 V, although the presence of chloride ion resulted in a significant increase in the anodic current on the reverse sweep. On the other hand, addition of copper(II) ions resulted in enhanced cathodic currents and subsequent anodic currents in both sulfate and chloride solutions due to reduction of covellite to an undefined reduced copper sulfide species. Reduction of copper(II) to copper(I) ions becomes the preferred cathodic reaction as the concentration of chloride ions increases, becoming mass transport controlled at a rotating disc electrode at potentials below about 0.4 V. Potentiostatic measurements at potentials negative to the mixed potential in acidic chloride solutions have shown that reduction of copper(II) ions is reversible and have been used to estimate the rate of oxidative dissolution of the mineral which value agrees reasonably well with previously reported leaching rates under similar conditions. Reduction of dissolved oxygen has been found to be very much slower that that of copper(II) ions under ambient conditions.

Keywords Chloride · Covellite · Cupric · Dissolution · Reduction · Oxygen

1 Introduction

Covellite (CuS) is an important mineral source of copper and is also used for pigments, catalysts and as a solar radiation absorber. Synthetic covellite is produced by precipitating cupric ion with gaseous H_2S or sulfide ion [1]. The mineral covellite is generally associated with other copper sulfides such as chalcopyrite, bornite and chalcocite [2]. Covellite can be formed as an intermediate during the leaching of chalcocite, copper matte and other complex copper sulfide materials [3].

Copper sulfide mineral concentrates have been conventionally processed using pyrometallurgy but stricter environmental restrictions on the emission of sulphur dioxide and arsenic oxides has stimulated the development of alternative processes based on hydrometallurgy. Many studies have shown that chloride ion in sulfuric acid solution has a positive effect on the dissolution rate of copper sulfide minerals due possibly to the formation of non-adherent large sulfur crystals [3, 4]. Cupric chloride solution has been extensively studied as a lixiviant [5] and is especially suited to the treatment of secondary copper sulfides, such as chalcocite and covellite, because the leaching solution contains little dissolved iron [6, 7]

M. S. Lee
Department of Advanced Materials Science & Engineering,
Mokpo National University, Chonnam 534-729, Korea

M. J. Nicol (✉)
Extractive Metallurgy, Murdoch University, South Street,
Murdoch, WA 6150, Australia
e-mail: nicol@murdoch.edu.au

P. Basson
BHPBilliton, Johannesburg Technology Centre, Randburg,
South Africa

Several studies have been reported on the treatment of covellite and covellite-bearing ore [8–10] and thin layer bacterial (TLB) heap leaching is currently employed for the recovery of covellite and chalcocite [9]. Another bioleaching process (BRISA) has been developed to treat secondary copper sulfides in which ferric sulfate is used as a leaching agent and the ferrous iron produced is oxidized by oxygen catalysed by ferroxidans bacteria [9]. A disadvantage of such sulfate processes is the relatively high concentration of ferric ions in the leach solutions which requires careful solvent extraction processes to purify the electrolyte required for electrowinning. An alternative process based on cupric chloride leaching could reduce the requirement for ferric ions and also possibly increase the recovery of copper from chalcopyrite if present in significant amounts in the ores.

Many studies have been performed on the electrochemical behaviour of chalcopyrite and chalcocite [11–14]. However few studies have been focussed on the cathodic and anodic behaviour of covellite. In a paper to be submitted for publication, the anodic characteristics of covellite were described as they relate to the dissolution of this mineral in chloride/sulfate systems. In this paper, the results of an investigation into the cathodic behaviour of covellite in these systems are summarized particularly in relation to the use of copper(II) ions as the oxidant in chloride lixiviants. Linear sweep voltammetry and potentiostatic measurements have been made using a rotating disk of synthetic covellite under various conditions to investigate the effect of chloride and cupric ion on the reduction reactions occurring on the surface of covellite in mixed chloride–sulfate solutions.

The thermodynamics of the reactions that are possible at a covellite surface under reducing conditions in the presence of copper ions in solutions of increasing chloride concentration are summarized in Fig. 1. These lines have been calculated using published thermodynamic data for the sulfides and the stability constants of the copper(II) and copper(I) chloride complexes [15]. In particular the equilibrium potentials for the following reactions are shown as a function of the chloride concentration.

$$\mathrm{Cu^{2+} + e = Cu^{+}}$$

$$\mathrm{Cu^{2+} + S + 2e = CuS}$$

$$\mathrm{CuS + Cu^{2+} + 2e = Cu_2S}$$

$$\mathrm{Cu^{+} + S + e = CuS}$$

$$\mathrm{2CuS + 2H^{+} + 2e = Cu_2S + H_2S(aq)}$$

It has been reported that not only covellite and chalcocite but also djurleite ($Cu_{1.96}S$) and anilite ($Cu_{1.75}S$) exist as stable copper sulfide phases in the copper–sulfur–water system [16]. Moreover, metastable copper sulfides, such as $Cu_{1.93}S$, $Cu_{1.83}S$, $Cu_{1.67}S$, and $Cu_{1.38}S$, can be formed during the oxidation/reduction of the stable copper sulfide minerals [17]. For the ease of interpretation the reactions of these intermediate copper-sulfide species have not been included in the figure.

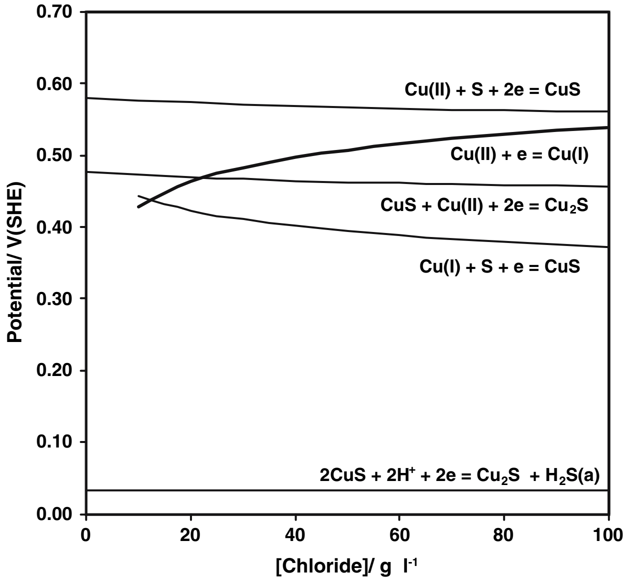

Fig. 1 Thermodynamics of various reactions in the system CuS/Cu_2S/Cu(I)/Cu(II) at 25 °C. Concentrations are Cu(II) = Cu(I) = 1 g L^{-1}, $H^+ = 0.1$ M and $H_2S(aq) = 1$ mM

Table 1 summarizes the standard reduction potentials for the formation of these metastable species calculated from published free energy of formation data [16]. It is apparent that the differences in stability of these species is small and therefore would not materially alter the conclusions that can be drawn from Fig. 1.

2 Experimental

The covellite used in this study was synthesized by high temperature reaction of the elements using a published technique [1]. Mineralogical analysis showed that, unlike most natural samples, the material was 98.5% covellite with undetectable amounts of chalcocite. Solutions were prepared using analytical grade reagents and Milli-Q distilled water.

Electrochemical measurements were performed using a three-electrode system at ambient temperature. A modified Metrohm glass cell covered with a detachable lid was used as the reaction vessel. The rotating disk electrode was fabricated from a 1 mm diameter extruded sintered pellet of the synthetic mineral imbedded in a cylindrical resin holder. The reference electrode was a KCl saturated calomel electrode which was joined to the main cell by a

Table 1 Standard potentials for reduction of covellite in acid solutions at 25 °C [16]

Reaction	Standard potential/V
$1.38CuS + 0.76H^+ + 0.76e = Cu_{1.38}S + 0.38H_2S$	−0.010
$1.67CuS + 1.34H^+ + 1.34e = Cu_{1.67}S + 0.67H_2S$	0.024
$1.83CuS + 1.66H^+ + 1.66e = Cu_{1.83}S + 0.83H_2S$	0.030
$1.93CuS + 1.86H^+ + 1.86e = Cu_{1.93}S + 0.93H_2S$	0.031
$1.96CuS + 1.92H^+ + 1.92e = Cu_{1.96}S + 0.96H_2S$	0.031
$1.75CuS + 1.5 H^+ + 1.5e = Cu_{1.75}S + 0.75H_2S$	0.035

Luggin capillary passing through a screw fitting in the base of the cell. The Luggin capillary was placed below the surface of the working electrode. The counter electrode was a platinum wire electrode housed in a glass tube which was separated from the bulk solution by a glass frit.

The rotating disk electrode was rotated using a drive consisting of an optically controlled unit coupled to a dc motor. 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. Analogue data from the potentiostat were collected using a National Instrument data acquisition board controlled by Labview software.

In all experiments, purified nitrogen gas was bubbled through the electrolyte solution for 30 min before the start of the experiments and an inert atmosphere was maintained within the cell during the tests. Prior to every experiment, the exposed surface of working electrode was wet-ground with Milli-Q water on 1200 silicon carbide paper. The electrode was transferred to the cell immediately after washing with Milli-Q water. Prior to the start of experiment, the working electrode was maintained at open-circuit in the electrolyte solution for 3 min. The solution volume used for all the experiments was 100 cm^3. In each experiment, cyclic voltammetry was initiated from the open circuit potential (OCP) with a sweep rate of 10 mV s^{-1} and at a rotation speed of 500 rpm unless otherwise stated. The positive and negative potential sweep limits were restricted to the range that the mineral would experience under typical leaching conditions. All potentials are quoted with respect to the standard hydrogen electrode (SHE).

3 Results and discussion

3.1 Solutions without added copper ions

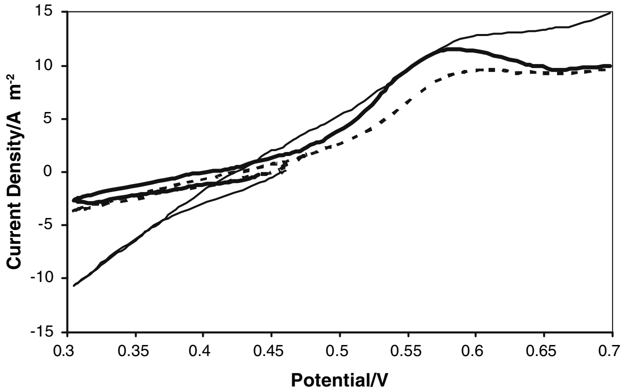

Fig. 2 Linear sweep voltammograms for a covellite electrode in sulfuric acid solutions of various concentrations (— 2.0 M, - - - 0.2 M, ▬ 0.02 M)

The effect of sulfuric acid concentration in the range 0.02–2.0 M on the cathodic behaviour of covellite is shown in Fig. 2 for scans in a negative direction from the open-circuit potential (OCP). Small increasing cathodic currents are observed as the potential is swept in a negative direction and these increase with increasing acid concentration. Current/time transients (not shown) obtained on potentiostatting the electrode at potentials below 0.45 V show that the reactions responsible for these cathodic currents are transient in that the current rapidly decays to very small values. In the absence of copper ions in solution, the following general reaction would be expected to be the only cathodic process that could take place in acidic solutions

$$(2-x)CuS + 2(1-x)H^+ + 2(1-x)e = Cu_{2-x}S + (1-x)H_2S \qquad (1)$$

However, as shown in Fig. 1 and Table 1, this reaction is not possible thermodynamically at potentials as positive as 0.3 to 0.4 V even in the initial absence of low (less than 1 μM) concentrations of H_2S.

The anodic peak in the region 0.5 to 0.6 V on the reverse sweep is associated (unpublished work) with the partial oxidation of covellite, as shown in the following equation,

$$2CuS = Cu_{2-x}S + xCu^{2+} + S + 2xe \qquad (2)$$

As in the case of sulfuric acid solutions, relatively small cathodic currents are observed in hydrochloric acid solutions at potentials lower than the OCP as shown in Fig. 3. These currents increase in magnitude with increasing HCl concentration but are somewhat lower than in the equivalent concentration of sulfuric acid. There are two anodic peaks in the potential range of 0.55–0.7 V, when the potential sweep is reversed at 0.3 V. The charge involved in these anodic reactions increases with increasing acidity.

The effect of chloride ion on the cathodic behaviour of covellite in 0.2 M sulfuric acid solution was investigated by varying the concentration of NaCl and the results are shown in Fig. 4.

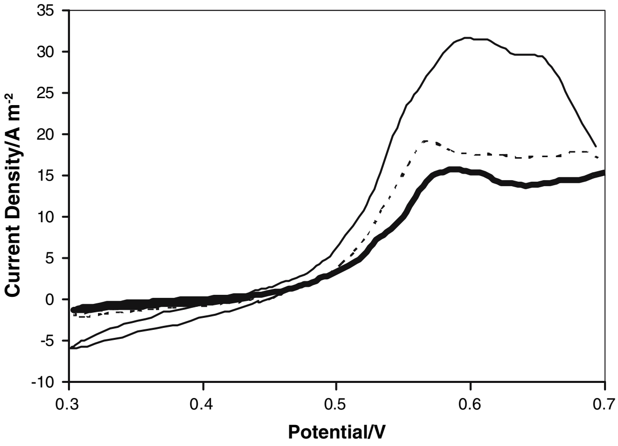

Fig. 3 Effect of concentration of hydrochloric acid on the response of a covellite electrode. Sweeps initiated in a negative direction from the OCP (— 2.0 M, - - - 0.2 M, ▬ 0.02 M)

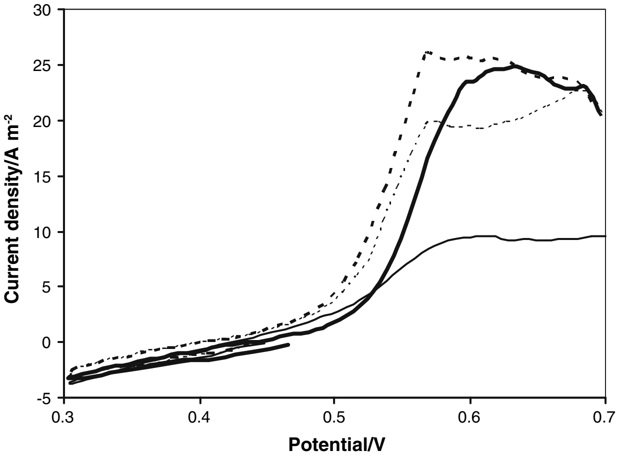

Fig. 4 The effect of the chloride concentration on the response of a covellite electrode in 0.2 M sulfuric acid solution (— 0 M, - - - 0.3 M, - - - 0.8 M, ▬ 1.8 M)

There is obviously little difference in the cathodic behaviour with increasing concentration of chloride ion under these conditions. However the addition of chloride greatly affects the anodic behaviour of covellite on the reverse sweep (unpublished work). In a similar result, it was found that addition of increasing concentrations of sulfuric acid to a solution of 0.2 M NaCl produced a cathodic response very similar to that in the absence of chloride and a negligible effect on the anodic currents when the sweep potential is reversed. The addition of sodium sulfate to a solution of 0.2 M HCl also revealed little difference from the characteristics observed in the absence of added sulfate.

3.2 Solutions containing copper ions

In the presence of copper ions, the voltammetric characteristics are substantially different as shown by the curves in Fig. 5 for solutions having increasing amounts of cupric ions in a solution containing 0.2 M H_2SO_4 and 0.2 M NaCl.

The addition of cupric ion greatly increases the cathodic current density and a small cathodic shoulder appears at about 0.38 V, a larger anodic peak in the reverse sweep at 0.43–0.44 V. The cathodic current at a fixed potential increases with increasing copper ion concentration.

As shown by the similarity with the potentials summarized in Table 2 and shown in Fig. 1, it is likely that the following general reduction reaction occurs in which a reduced copper sulfide phase is initially formed,

$$\mathrm{CuS} + (1 - \mathrm{x})\mathrm{Cu}^{2+} + 2(1 - \mathrm{x})\mathrm{e} = \mathrm{Cu}_{2-\mathrm{x}}\mathrm{S} \tag{3}$$

Thus, the potential of the broad anodic peak at 0.44 V is consistent with reversible re-oxidation of species $\mathrm{Cu}_{2-\mathrm{x}}\mathrm{S}$ to CuS.

The cathodic charge under the curve obtained in the solution containing 1 g L^{-1} cupric ions of 1,220 C m^{-2} exceeds that under the anodic branch of the curve of 950 C m^{-2} and this can be explained in terms of a parallel cathodic reduction of cupric to cuprous ions in the chloride solution. As shown in Fig. 1, this reaction is possible at potentials below about 0.42 V.

Figure 6 shows the effect of cupric ion concentration on the cyclic voltammograms of covellite in 0.2 M sufuric acid solutions containing a higher concentration of chloride i.e. 2.0 M NaCl. It is obvious that the cathodic processes are significantly affected by the higher concentration of chloride ion in that (a) reduction commences at more positive potentials, (b) two processes are apparent, one of which appears to result in a poorly defined current plateau at about 0.4 V the magnitude of which is approximately proportional to the concentration of copper ions, (c) the

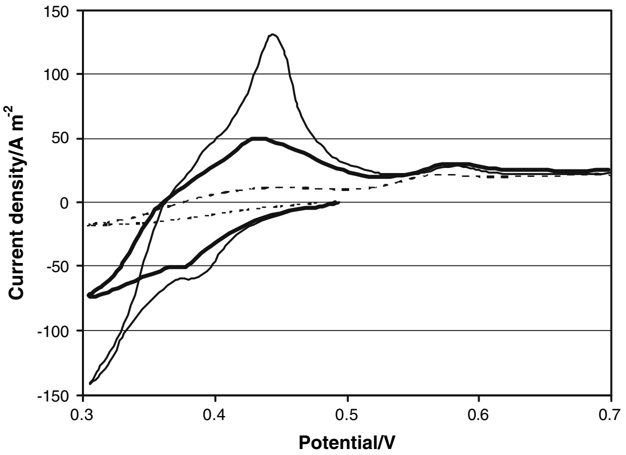

Fig. 5 Voltammograms for a covellite electrode in a solution of 0.2 M H_2SO_4 and 0.2 M NaCl containing increasing concentrations of cupric ions (— 1 g L^{-1}, ▬ 0.5 g L^{-1}, - - - 0.1 g L^{-1})

Table 2 Reduction potentials for covellite in solutions containing cupric ion (1 g L^{-1}) at 25 °C [16]

Reaction	Formal potential/V
$CuS + 0.38Cu^{2+} + 0.76e = Cu_{1.38}S$	0.414
$CuS + 0.67Cu^{2+} + 1.34e = Cu_{1.67}S$	0.447
$CuS + 0.83Cu^{2+} + 1.66e = Cu_{1.83}S$	0.453
$CuS + 0.93Cu^{2+} + 1.86e = Cu_{1.93}S$	0.454
$CuS + 0.96Cu^{2+} + 1.92e = Cu_{1.96}S$	0.455
$CuS + 0.75Cu^{2+} + 1.5\ e = Cu_{1.75}S$	0.459

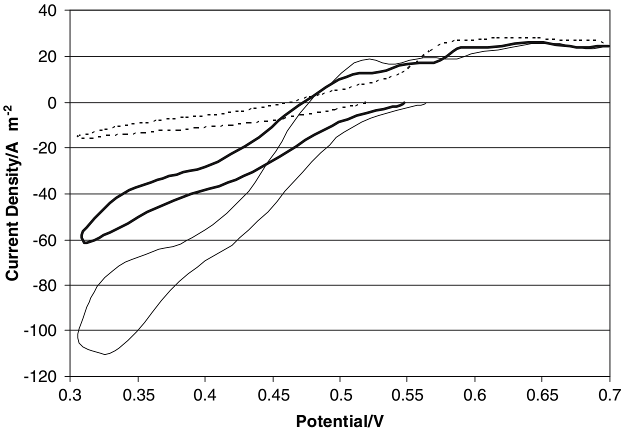

Fig. 6 Voltammograms for a covellite electrode in a solution of 0.2 M H_2SO_4 + 2 M NaCl containing increasing concentrations of cupric ions (— 1 g L^{-1}, ▬ 0.5 g L^{-1}, - - - 0.1 g L^{-1})

anodic peak at about 0.44 V is no longer present and (d) a cathodic peak at about 0.33 V appears to be related to a corresponding anodic peak at 0.5–0.53 V. Use of the Levich equation reveals that mass transport controlled reduction of copper(II) to copper(I) ions will require about 70 A m^{-2} for a solution of 1 g L^{-1} copper ions at 500 rpm, assuming a reasonable value of the diffusion coefficient of 10^{-5} cm^2 s^{-1}. This value is similar in magnitude to that of the current plateau at 0.4 V. Thus, at high chloride concentrations, reduction of copper(II) ions to copper(II) ions is favoured over reduction of covellite and this is consistent with the data in Fig. 1 which shows that the potential for the former reaction increases while that for the latter decreases as the chloride concentration increases.

In order to further investigate the effect of chloride ion, the concentration of NaCl was varied in 0.2 M sulfuric acid solution containing 1.0 g L^{-1} Cu and the results are shown in Fig. 7. It is apparent that the potential at which reduction of copper(II) to copper(I) ions commences increases while the small cathodic peak in the potential range of 0.35–0.4 V shifts in a negative direction with increasing chloride concentration as predicted by Fig. 1 for the two parallel cathodic reactions described above.

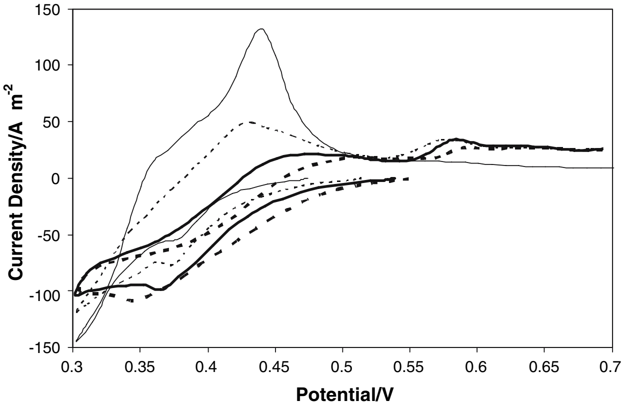

Fig. 7 Voltammograms for a covellite electrode in a solution of 0.2 M H_2SO_4, 1 g L^{-1} copper(II) ions and increasing concentrations of chloride ions (— 0 M, - - - 0.5 M, ▬ 1.0 M, - - - 1.5 M)

A well-defined anodic peak appears at 0.42 V during the anodic scan when the concentration of chloride ion is lower than 0.5 M and the negative potential sweep is extended below 0.35 V. The charge associated with this anodic peak decreases with increasing chloride ion concentration. The nature of this peak has been discussed in connection with the results shown in Fig. 5 and is due to re-oxidation of a reduced copper sulfide, $Cu_{2-x}S$, formed at potentials below about 0.35 V in the presence of copper(II) ions. The reduced amount of this species in the presence of increasing concentration of chloride ions can be attributed to the fact that the concentration of copper(II) ions available for reaction (2) is reduced at the surface of the covellite due to reduction to copper(I) ions at the mass-transport controlled rate. The potential required for reaction (2) is thereby reduced to more negative potentials.

3.3 Rotation speed

The effect of rotation speed on the cyclic voltammograms of covellite in 0.2 M sulfuric acid solution containing 2.0 M NaCl and 0.5 g L^{-1} copper ions is shown in Fig. 8. As expected, the cathodic current density increases with increase in rotation speed confirming that reduction of copper(II) ions is at least partially controlled by mass transport at potentials below about 0.45 V. The small anodic current peaks on the reverse sweep suggest that a degree of reduction of covellite is also occurring at potentials below about 0.45 V.

3.4 Sweep rate

In order to investigate the effect of sweep rate, the cyclic voltammograms of covellite were obtained at different

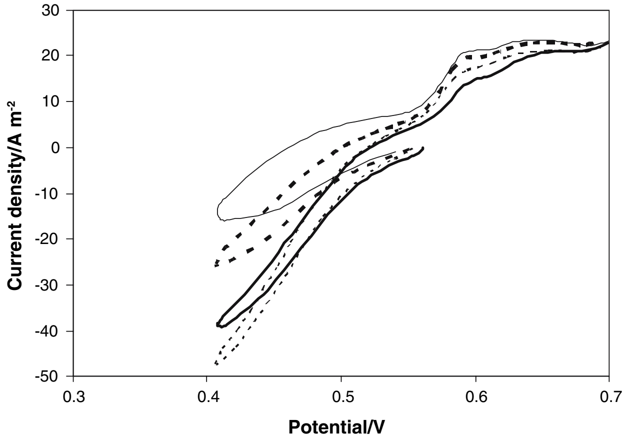

Fig. 8 The effect of rotation speed of the electrode on the reduction of covellite in a solution containing 0.2 M H_2SO_4, 2 M NaCl and 0.5 g L^{-1} copper ions (— 0 rev min^{-1}, - - - 200 rev min^{-1} ▬ 500 rev min^{-1}, - - - 1,000 rev min^{-1})

sweep rates. In these experiments, the rotation speed was 500 rpm and sweep rate was varied from 2 to 20 mV s^{-1} and the results are shown in Fig. 9. It is apparent that the sweep rate has a negligible effect on the cathodic behaviour of covellite under these conditions. The relatively large effect of sweep rate on the subsequent anodic processes will be discussed in a parallel paper [17].

3.5 Current transient behaviour

The open circuit potential of a covellite electrode in a 0.2 M sulfuric acid solution containing 2.0 M NaCl and 0.5 g L^{-1} cupric ions was found to be 0.560 V. In order to investigate the current behaviour at constant potential, potentiostatic experiments were performed in the potential range 0.525–0.403 V. Figure 10 shows the cathodic current recorded for 30 min as a function of time at each potential. Reasonably stable currents are achieved after about 30 min.

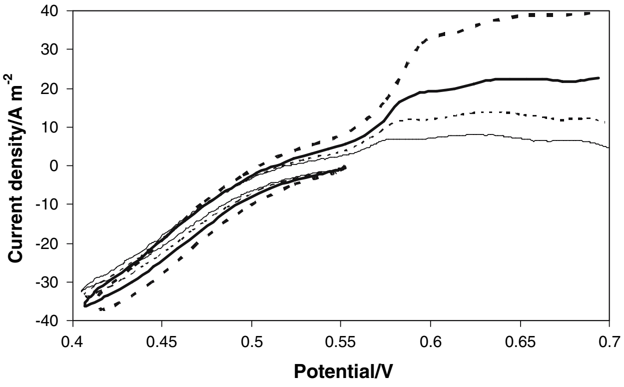

Fig. 9 Effect of sweep rate on the cyclic voltammetry of covellite in 0.2 M sulfuric acid solutions containing 2.0 M NaCl and 0.5 g L^{-1} cupric ions (— 2 mV s^{-1}, - - - 5 mV s^{-1}, ▬ 10 mV s^{-1}, - - - 20 mV s^{-1})

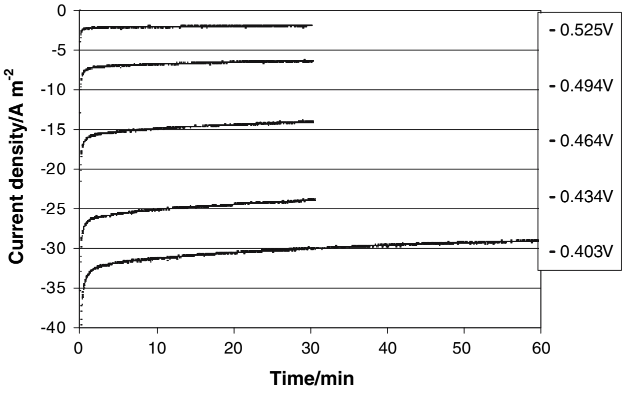

Fig. 10 Current–time transients for a covellite electrode at various potentials in a solution of 0.2 M sulfuric acid containing 2.0 M NaCl and 0.5 g L^{-1} cupric ions

The current density after 30 min at each potential is shown as a modified Tafel plot in Fig. 11. This plot allows for correction due to mass transport limitations and the limiting current density (i_L) used in this case was calculated using the Levich equation. From this plot, a Tafel slope of 64 mV/decade is obtained which suggests a reversible 1-electron reduction of copper(II) to copper(I) ions. Extrapolation of the linear section to the mixed potential of 0.56 V gives a rate of dissolution of covellite of 0.025 A m^{-2} or 2.6×10^{-11} mol cm^{-2} s^{-1} (assuming a 2-electron process) which is reasonably close to that observed for the leaching of covellite under similar conditions [17]. Interestingly, this value is also close to that estimated from the published data of Dutrizac and MacDonald [1] of 1.5×10^{-11} mol cm^{-2} s^{-1} in a solution containing 0.1 M Fe(III) and 0.1 M H_2SO_4 suggesting that the mixed potential in the iron(III)/sulfate system is close to that in the copper(II)/chloride system.

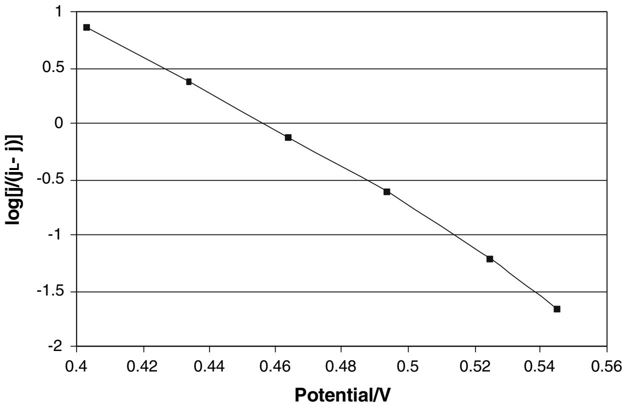

Fig. 11 Modified Tafel plot for the data in Fig. 10

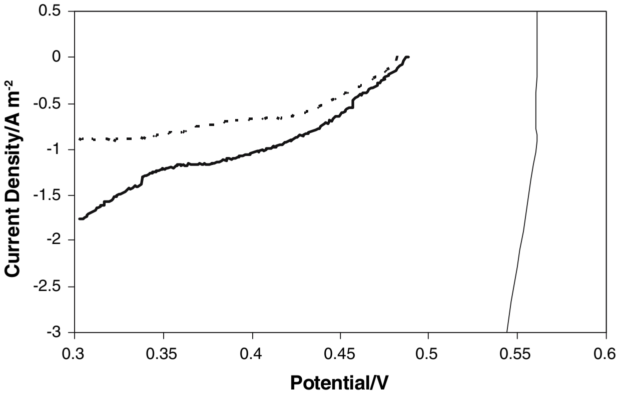

Fig. 12 Voltammograms for a covellite electrode in solutions of 0.2 M HCl and 2 M NaCl saturated with nitrogen and oxygen. Also shown is the curve for the reduction of copper(II) ions in this solution (— 0.5 g L^{-1} Cu(II), ▬ ; O_2, - - - N_2)

3.6 Reduction of Oxygen

Previous work has suggested that, at elevated temperatures, dissolved oxygen is an effective oxidant for the dissolution of covellite and it is of interest therefore to compare the rate of reduction of oxygen with that of copper(II). Figure 12 shows the cathodic response of a covellite electrode in chloride solutions in the absence of dissolved oxygen and in a solution saturated with oxygen from which it is apparent that the rate of reduction of oxygen is slow in the region of stability of the mineral. The curve for reduction of copper(II) from a solution containing 0.5 g/L copper is also shown for comparison and it is obvious that, under ambient conditions, copper(II) is orders of magnitude more effective as an oxidant for the mineral as shown by the significant positive shift in the mixed potential and the greater cathodic reactivity of copper(II) ions in this potential region.

4 Conclusions

Variations in the concentrations of sulfate and chloride ions had a small effect on the cathodic reduction of covellite in the potential range of 0.5–0.3 V, although the presence of chloride ion resulted in a significant increase in the anodic current on the reverse sweep. On the other hand, addition of copper(II) ions resulted in enhanced cathodic currents and subsequent anodic currents in both sulfate and chloride solutions due to reduction of covellite to an undefined reduced copper sulfide species. Reduction of copper(II) to copper(I) ions becomes the preferred cathodic reaction as the concentration of chloride ions increases, becoming mass transport controlled at potentials below about 0.4 V. Potentiostatic measurements at potentials negative to the mixed potential in acidic chloride solutions have shown that reduction of copper(II) ions is reversible and have been used to estimate the rate of oxidative dissolution of the mineral which value agrees reasonably well with previously reported leaching rates under similar conditions. The reduction of dissolved oxygen has been shown to contribute to a very small extent to the oxidation of the mineral under ambient conditions.

Acknowledgements This research was supported in part by Mokpo National University in Korea and by the Parker Centre for Integrated Hydrometallurgy Solutions.

References

1. Dutrizac JE, MacDonald RJC (1974) Can Metall Q 13:423
2. Dunna JD, Muzenda C (2001) Thermochimica Acta 369:117
3. Cheng CY, Lawson F (1991) Hydrometallurgy 27:269
4. Lu ZY, Jeffrey MI, Lawson F (2000) Hydrometallurgy 56:145
5. Lundström M, Aromaa J, Forsén O, Hyvärinen O, Barker MH (2005) Hydrometallurgy 77:89
6. McDonald GW, Langer SH (1983) Metall Trans B 14B:559
7. McDonald GW, Udovic TJ, Dumesic JA, Langer SH (1984) Hydrometallurgy 13:125
8. Konishi Y, Katoh M, Asai S (1994) Mater Trans JIM 35:695
9. Palencia I, Romero R, Mazuelos A, Carranza F (2002) Hydrometallurgy 66:85
10. Acar S, Brierley JA, Wan RY (2005) Hydrometallurgy 77:239
11. Lázaro I, Martínez-Medina N, Rodríguez I, Arce E, González I (1995) Hydrometallurgy 38:277
12. Arce EM, González I (2002) Int J Miner Process 67:17
13. Elsherief AE (2002) Miner Eng 15:215
14. Nava D, González I (2006) Electrochim Acta 51:5295
15. Martell AE, Smith RM (2004) NIST Standard Reference Database 46, Version 8.0, Gaithersburg
16. Woods R, Yoon RH, Young CA (1987) Int J Miner Process 20:109
17. Koch DFA, McIntyre RJ (1976) J Electroanal Chem 71:285