Journal of Applied Electrochemistry (2006) 36:425–431
DOI 10.1007/s10800-005-9089-4

A rotating ring–disk study of the initial stages of the anodic dissolution of chalcopyrite in acidic solutions

I. LAZARO[1] and M.J. NICOL[2,*]
[1]*Facultad de Ingeniería-Instituto de Metalurgia, Universidad Autónoma de San Luis Potosí, Av. Sierra Leona 550, Lomas, 78210, San Luis Potosí, México*
[2]*A.J. Parker Center for Hydrometallurgy, Murdoch University, South Street, Murdoch, WA6150, WA, Australia*
*(*author for correspondence E-mail: nicol@murdoch.edu.au)*

Received 17 July 2005; accepted in revised form 24 October 2005

Key words: chalcopyrite, ferric leaching, non-oxidative dissolution, ring–disk, soluble sulfur

Abstract

The initial stages of the dissolution of chalcopyrite have been studied using rotating ring–disk electrode techniques in dilute sulfuric acid solutions at 60 °C. It has been confirmed that the mineral undergoes a dissolution process under freely dissolving conditions in the absence of an oxidant. This process involves the formation of soluble copper(II) ions and a soluble sulfur species which is presumably H_2S. By the use of an anodic stripping technique on the ring electrode, it has been possible to determine that the dissolution of chalcopyrite under oxidative conditions involves a soluble sulfur species such as thiosulfate. Collection efficiency measurements involving the detection of both iron(II) and copper(II) on the ring have been used to identify possible anodic reactions in the potential region relevant to the oxidative leaching of the mineral.

1. Introduction

The important copper mineral, chalcopyrite ($CuFeS_2$) is known to be very difficult to dissolve in acidic solutions under ambient conditions and a substantial amount of research work has been undertaken in order to understand the kinetics and mechanism of the oxidative reactions involved in the dissolution of this mineral. Most of this work has been aimed at increasing the kinetics of oxidative dissolution in the presence of ferric ions as the oxidant. There are a large number of publications on this subject and an excellent review of work in this area has recently been published [1].

It has generally been assumed that the dissolution process is electrochemical in nature and therefore much attention has been devoted to the application of electrochemical techniques to the study of the reactions involved [2–8]. Most of this work has been directed at anodic dissolution in a potential region that is now called the anodic "prewave". The study of this anodic prewave is of great significance since it represents the initial stages of oxidation of chalcopyrite. Nevertheless, the reactions involved in this potential region and the mechanism of dissolution are still not resolved. Moreover, with increasing research on leaching processes using bacteria, alternative reactions have been proposed in which an acid dissolution path (Equation (1)) combined with oxidation of dissolved hydrogen sulfide by ferric ions (Equation (2)) are now being considered [9–11].

$$\begin{aligned}&CuFeS_2(s) + 4H^+(aq)\\&\quad = Cu^{2+}(aq) + Fe^{2+}(aq) + 2H_2S(aq)\end{aligned} \tag{1}$$

$$\begin{aligned}&2H_2S(aq) + 4Fe^{3+}(aq)\\&\quad = 4Fe^{2+}(aq) + 2S(s) + 4H^+(aq)\end{aligned} \tag{2}$$

Although the use of the rotating ring–disk electrode (RRDE) technique has been suggested as a means of studying the reactions involved in the dissolution of minerals, it has not been as widely applied as could be expected [12]. The infrequent use of this technique with minerals has been attributed to the difficulty of constructing this kind of electrode [13]. In the case of minerals such as chalcopyrite ($CuFeS_2$), there have been very few applications and they have been mainly directed at the detection of the products of oxidation such as soluble copper and iron by means of collection efficiency experiments [14–15] at potentials significantly higher than those encountered during leaching.

Experimental observation of the rate of the non-oxidative reaction has been difficult and this has possibly reinforced a view that its contribution to the overall dissolution is negligible [16]. Calculations based on thermodynamic data for Equation (1) result in equilibrium concentrations for cupric ions of the order of 2.8×10^{-6} M at 60 °C in solutions of unit activity of protons. The RRDE technique provides a means of evaluating the likelihood of this reaction because its main feature is its ability to detect very low concentrations of soluble species [17].

Although thermodynamic data favors a reaction in which ferrous ions are preferentially produced by acid

$$\mathrm{CuFeS_2(s) + 2H^+(aq) = CuS(s) + Fe^{2+}(aq) + H_2S(aq)} \qquad (3)$$

the only reported evidence of formation of covellite (CuS) has been microscopic observation of a few blue spots on the chalcopyrite surface [5, 18].

A particular characteristic of Equations (1) and (3) is the formation of a soluble sulfur species (H_2S) which can be oxidized by ferric ions to produce the commonly observed elemental sulfur product [9–11]. The potential region in which this non-oxidative process occurs has not been established. However there are reports which suggest that the non-oxidative dissolution of sulfides is potential dependent with reduced rates at potentials positive to the freely dissolving potential [19].

The versatility of the RRDE technique allows for independent control of potential and current of the ring and disk and this permits the detection on the ring of the soluble species generated during the dissolution of the mineral disk. In the case of intermediate species, detection is possible before further reaction in the bulk solution. The aim of this study is to demonstrate the utility of combining RRDE experiments with techniques such as anodic stripping and potential measurements to establish the stoichiometry of the initial stages of dissolution of chalcopyrite under oxidative and non-oxidative conditions.

2. Experimental

A platinum rotating disk electrode (RDE) and a chalcopyrite disk/platinum ring electrode (RRDE) were fabricated as described in a previous publication [20]. The calculated theoretical collection efficiency for the RRDE electrode was 0.39. Before making any electrochemical measurements, the surfaces of the ring and disk were prepared by being ground on fine silicon carbide paper (grade 2400). In some instances, the electrodes were also polished with 0.05 μm alumina paste followed by ultrasonic cleaning. Unless otherwise stated the RRDE was rotated at a speed of 200 rpm. A platinum wire was used as counter-electrode and a mercurous sulfate electrode with a potential of 0.64 V vs the standard hydrogen electrode (SHE) was used as reference. All potentials reported have been converted to the SHE scale.

The electrochemical experiments were performed in a typical three electrode glass jacketed cell. The potential of the electrodes was controlled with a PINE RDE3 bipotentiostat. Both the potentials and currents of the ring and the disk were monitored and recorded using a LabView™ data acquisition system. All solutions were made up with analytical grade reagents and Millipore quality water. Unless otherwise stated, most solutions were deoxygenated by bubbling with high purity nitrogen

3. Results and discussion

3.1. *Potential measurements*

To establish the relevant potential region for non-oxidative (freely dissolving) and oxidative dissolution of chalcopyrite, potential measurements were carried out by recording the potential of both the disk (E_d) and ring (E_r) of a rotating platinum ring-chalcopyrite disk electrode (RRDE) and an additional platinum wire (E_h) in 0.1 M H_2SO_4 solutions with or without added ferric ions at 60 °C. The potentials were recorded for 1 h and the effects on the potential of the acid concentration (0.01–1 M), iron(III) concentration (0.01–1 M) and rotation speed (100–1000 rpm) were investigated. Some of these results are shown in Figures 1 and 2.

While the potential on the platinum wire was not affected by changes in the iron(III) concentration, the potential of both the disk and ring increased with

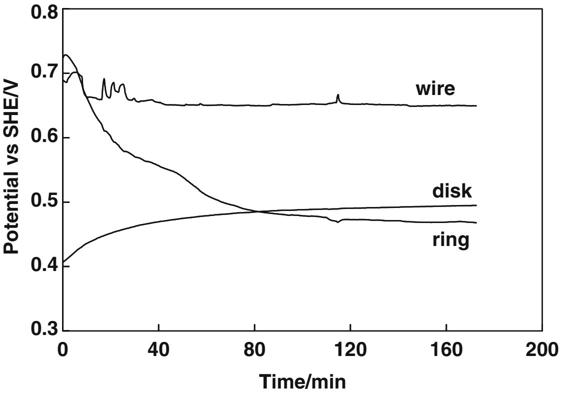

Fig. 1. Open circuit potentials for a platinum wire, platinum ring and chalcopyrite disk in 0.1 M H_2SO_4 solution at 60 °C.

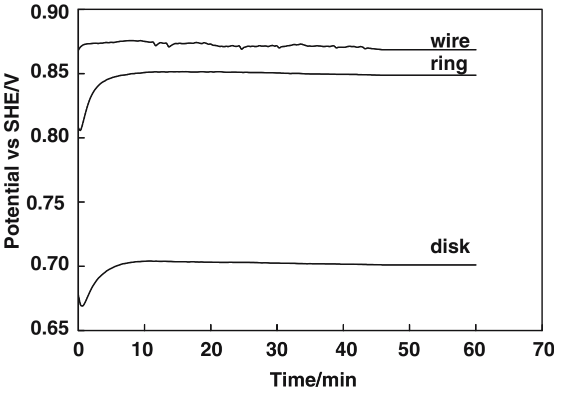

Fig. 2. Open circuit potentials for a platinum wire, platinum ring and chalcopyrite disk in solutions containing 0.1 M H_2SO_4 + 0.01 M Fe(III) at 60 °C.

increasing Fe(III) concentration. This effect was observed only at concentrations lower than 0.5 M (Figure 2). It is apparent that the maximum potential achievable on chalcopyrite in the presence of iron(III) under these conditions is around 0.7 V. This potential is within the so-called prewave region. A more detailed interpretation of these results has been recently published [20].

Although the potential of a platinum electrode in acid media is not determined by a well-defined redox couple, it is interesting to note that the platinum wire potential (E_h) differed from that of the ring in that while the potential on the platinum wire remained constant during the measurement period, the potential on the platinum ring slowly decreased with time eventually approaching that of the chalcopyrite disk (Figure 1). This change in E_r was not expected in the absence of iron(III) since there were no species in solution that could induce this change in potential. The proximity of the ring to the chalcopyrite disk implies that non-oxidative dissolution of chalcopyrite in acid solution results in soluble species which are sufficiently reducing to be detected as a decrease in the potential of the ring.

3.2. *Overall voltammetric behavior*

Cyclic voltammograms were obtained using the chalcopyrite disk in 0.1 M H_2SO_4 solutions at 60 °C. The potential sweep was initiated from the open-circuit potential (OCP) to positive potentials within the relevant oxidative potential region (previously established through potential measurements). It was noticed that in order to achieve a reproducible response, the chalcopyrite disk had to be immersed in the solution for at least 3 min before sweeping.

A typical cyclic voltammogram is shown in Figure 3 and it shows the characteristic anodic prewave region that is within the potential range measured during non-oxidative and oxidative dissolution. It is obvious that the mixed potential of 0.65 V in 0.04 M iron(III) at 60 °C is located close to the potential of maximum current in this region.

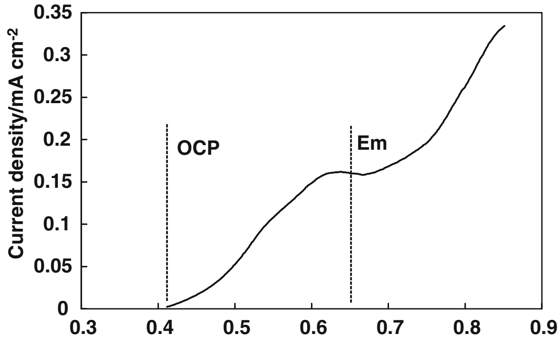

Fig. 3. Typical linear sweep (5 mV s^{-1}) voltammogram for a chalcopyrite rotating (200 rpm) disk electrode in 0.1 M H_2SO_4 at 60 °C.

3.3. *RRDE experiments*

In order to characterize dissolution in the presence of acid and ferric ions, various RRDE experiments were conducted. Under both oxidative and non-oxidative conditions, copper ions could be expected as one of the products in accordance with Equations (1) and (4).

$$CuFeS_2(s) + 4Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 5Fe^{2+}(aq) + 2S(s) \quad (4)$$

In these experiments the dissolution of copper from the chalcopyrite disk was monitored at the platinum ring and for this purpose the ring was held at a potential of −0.06 V which was found to be suitable for the reduction of copper(II) ions to copper metal. The amount of accumulated copper on the ring could then be measured by anodic stripping following a period of dissolution.

3.3.1. *RRDE measurements under non-oxidative conditions*

An investigation of the sensitivity of the analysis for copper ions by anodic stripping measurements on a rotating platinum disk electrode were performed and showed that adequate results could be obtained for concentrations of copper as low as 1×10^{-6} M.

In order to detect the presence of a non-oxidative reaction involving the dissolution of copper, the rotating disk was left at the OCP in solutions containing only acid for 1 h during which period the ring was potentiostatted at −0.06 V. Figure 4 shows the curve for the anodic stripping of copper accumulated on the ring during this period. A broad anodic peak at around 0.35 V is obtained which differs from the sharp peak at 0.25 V (see Figure 5) expected for the oxidation of copper metal. As will be discussed at a later stage, the potential and shape of this peak appears to correspond to oxidation of a product formed by reduction of both copper(II) and H_2S.

3.3.2. *RRDE measurements under oxidative conditions*

Similar experiments to those described above were performed in sulfuric acid solutions containing 0.04 M iron(III). Ascorbic acid was added to the solution to reduce ferric ions before anodic stripping of the ring thereby preventing chemical re-dissolution of the copper deposit. The same procedure was followed in a solution containing only sulfuric acid during which time the chalcopyrite disk was potentiostatted for 1 h at the mixed potential observed in the solution containing the ferric ions (0.65 V). The anodic stripping curves obtained in each experiment are shown in Figure 5.

After either open-circuit in the presence of iron(III) or potentiostatic dissolution at the mixed potential in the absence of iron(III) for 1 h, similar results are obtained in which a sharp peak (A1) characteristic of copper oxidation can be observed at around 0.25 V. However,

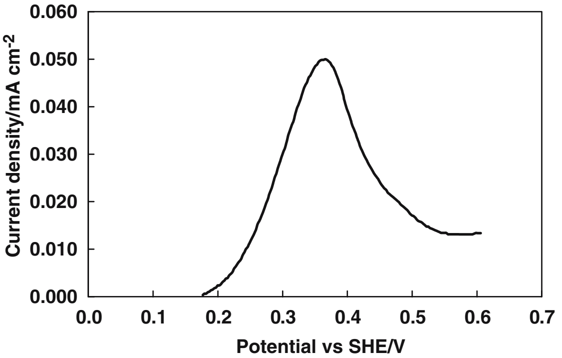

Fig. 4. Anodic stripping of copper from the platinum ring after dissolution of $CuFeS_2$ at open circuit in sulfuric acid at 60 °C.

in the potentiostatic experiment two additional anodic peaks A2 and A3 in the potential range of 0.35–0.5 V were observed. These peaks are masked in the experiment carried out under OCP conditions due to the presence of iron(II) ions in solution (which were produced by the reduction of iron(III) by ascorbic acid) which are oxidized to iron(III) in this potential region. The charge involved in the stripping of the copper (as metal) from the ring is similar in both experiments. The charge under the peak is directly proportional to the amount of copper deposited on the ring and therefore also to the amount of copper ions dissolved from the chalcopyrite disk surface during the open circuit period. These results show that in the initial stages, the rate of dissolution of copper is similar under open circuit oxidative and potentiostatic conditions. This suggests that the mixed potential model [21] for oxidative dissolution is operative under these conditions.

3.4. *Effect of potential on dissolution*

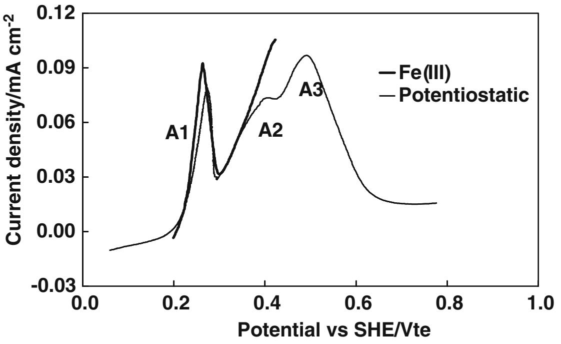

Fig. 5. Comparative results of the response of the platinum ring when oxidative dissolution of $CuFeS_2$ is carried out with ferric ions or by potentiostatting at the mixed potential (0.65 V) at 60 °C.

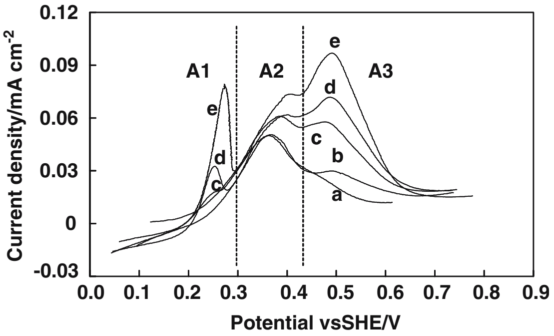

Fig. 6. Anodic stripping curves for a platinum ring held at −0.06 V after dissolution of a $CuFeS_2$ disk which was held at potentials of (a) 0.45, (b) 0.49, (c) 0.54, (d) 0.59 and (e) 0.65 V for 1 h at 60 °C and 200 rpm.

To investigate the effect of potential on the dissolution process, RRDE experiments similar to the above were carried out in which the potential of the chalcopyrite disk was held at different values within the non-oxidative and oxidative region (0.45–0.65 V) in acid solutions for 1 h. The anodic stripping curves obtained at each applied potential are shown in Figure 6. A remarkable feature of the stripping curves is the apparent evolution of the anodic peaks labeled as A1, A2 and A3. Although these experiments were carried out with the objective of obtaining an indirect analysis of the rate of dissolution of copper by way of the stripping technique, the appearance of peaks (A2 and A3) in addition to that for the stripping of copper metal (A1) led to a more detailed study of the species responsible for these peaks. Some interesting features of these peaks are that A2 appears at all potentials and the magnitude of A2 does not seem to be dependent on potential during the prior potentiostatic period while the magnitude of peaks A1 and A3 do vary with this potential. These additional peaks are observed in a potential region similar to those which are known to be associated with the oxidation of the copper sulfides. Unfortunately it is difficult to assign these peaks to a particular copper sulfide, since different copper sulfides can be oxidized in this potential region. For example, it is reported in the literature [22] that Cu_2S can be oxidized at potentials between 0.44 and 0.505 V, according to the following reaction:

$$Cu_2S(s) = Cu^{2+}(aq) + CuS(s) + 2e \qquad (5)$$

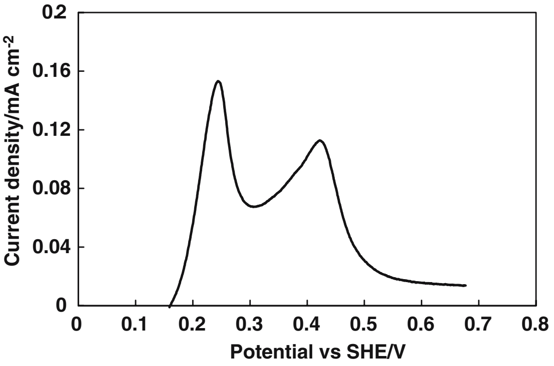

Fig. 7. Voltammograms for the stripping of copper species produced by the reduction for 1 h on a platinum disk at −0.06 V at 60 °C, of solutions containing 2×10^{-6} M $Cu(II)/S_2O_3^{2-}$.

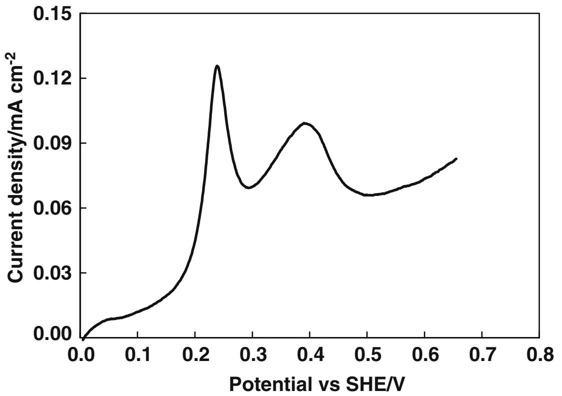

Fig. 8. Voltammograms for the stripping of copper species produced by the reduction for 1 h on a platinum disk at −0.06 V at 60 °C, of solutions containing 2×10^{-6} M Cu(II)/H_2S.

however, CuS can also be oxidized at potentials within this region [23] according to

$$\mathrm{CuS(s)} = \mathrm{Cu^{2+}(aq)} + \mathrm{S(s)} + 2\mathrm{e} \qquad (6)$$

For simplicity, only the species CuS and Cu_2S are suggested, although one or more of the well-known non-stoichiometric copper sulfides (Cu_xS) could also be involved [24]. Thus, if these peaks are due to the oxidation of copper sulfides, these results suggest that, in addition to copper ions, soluble sulfur species such as thiosulfate ($S_2O_3^{2-}$) and/or hydrogen sulfide (H_2S) could be formed in the dissolution reaction at the disk. Reduction of copper ions in the presence of these species at −0.06 V on the ring could produce copper sulfides which would then be responsible for the peaks A2 and A3 during anodic stripping. Independent experiments showed that the reduction of these sulfur species in the presence of copper ions on a platinum surface produces similar anodic stripping peaks. The results of these experiments are shown in Figure 7 ($S_2O_3^{2-}$) and Figure 8 (H_2S). The similarity of the anodic stripping peaks with those in Figure 6 is obvious. The presence of two peaks A2 and A3 was also observed under certain conditions in the latter experiments. However, the reasons for the appearance of one or two peaks have not yet been established.

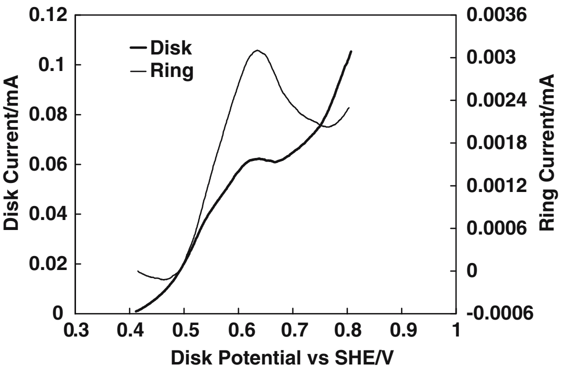

Fig. 9. Currents at the RRDE with $E_r = 1$ V. The $CuFeS_2$-disk was swept in the positive direction from the open circuit potential in a 0.1 M H_2SO_4 solution at 60 °C, 200 rpm and 5 mV s^{-1}.

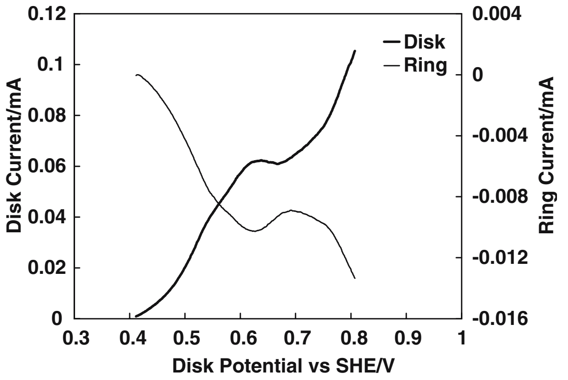

Fig. 10. Currents at the RRDE with $E_r = -0.06$ V. The $CuFeS_2$-disk was swept in the positive direction from the open circuit potential in a 0.1 M H_2SO_4 solution at 60 °C, 200 rpm and 5 mV s^{-1}.

3.5. *Products of dissolution*

The complex nature of the initial stage of dissolution of chalcopyrite has been illustrated in Figure 6. From these results it is apparent that a soluble sulfur species is involved in the dissolution of chalcopyrite. It has also been found that both H_2S and $S_2O_3^{2-}$ are capable of forming copper sulfides during reduction in the presence of copper ions. At the positive potentials involved, $S_2O_3^{2-}$ would seem to be the more likely soluble species formed on oxidation of chalcopyrite (Equation (7)). Thiosulfate as product of oxidation of chalcopyrite has not previously been proposed in the literature despite the fact that formation of this species has been proposed for the oxidation of other sulfide minerals [9]. In order to substantiate formation of thiosulfate, collection efficiency (N_{exp}) measurements were made which would enable comparisons to be made with the oxidation reactions more frequently proposed in the literature [2–8] (Equations (8) and (9)).

$$\begin{aligned}\mathrm{CuFeS_2(s)} + 3\mathrm{H_2O(l)} &= \mathrm{Cu^{2+}(aq)} + \mathrm{Fe^{2+}(aq)}\\ &\quad + \mathrm{S_2O_3^{2-}(aq)} + 6\mathrm{H^+(aq)} + 8\mathrm{e}\end{aligned} \qquad (7)$$

$$\begin{aligned}\mathrm{CuFeS_2(s)} &= 0.75\mathrm{CuS(s)} + 0.25\mathrm{Cu^{2+}(aq)}\\ &\quad + \mathrm{Fe^{2+}(aq)} + 1.25\mathrm{S(s)} + 2.5\mathrm{e}\end{aligned} \qquad (8)$$

$$\mathrm{CuFeS_2(s)} = \mathrm{Cu^{2+}(aq)} + \mathrm{Fe^{2+}(aq)} + 2\mathrm{S(s)} + 4\mathrm{e} \qquad (9)$$

For the purpose of explaining how these collection efficiency measurements were achieved it is necessary to point out that the experimental values were obtained by means of the relationship

Table 1. Experimental collection values

Equations	E_r/V	N_{calc}	N_{exp}, potential/mV					
			450	500	550	600	650	700
7	1.0	0.049	0	0.008	0.04	0.052	0.056	0.04
	−0.06	0.146	0.179	0.207	0.19	0.171	0.158	0.137
8	1.0	0.156	0	0.008	0.04	0.052	0.056	0.04
	−0.06	0.078	0.179	0.207	0.19	0.171	0.158	0.137
9	1.0	0.098	0	0.008	0.04	0.052	0.056	0.04
	−0.06	0.195	0.179	0.207	0.19	0.171	0.158	0.137

$$N_{exp} = \frac{|-I_r|}{I_d} \quad (10)$$

in which N_{exp} is the ratio of the measured ring current (I_r) to disk current (I_d), and represents the fraction of species generated at the disk, which is detected on the ring. N_{exp} is then compared to a predicted value (N_{calc}) for each possible species detected on the ring which is related to the theoretical collection efficiency (N_o) of the RRDE by

$$N_{calc} = \frac{n_r}{n_d} N_o \quad (11)$$

in which n_r is the number of electrons involved in the oxidation or reduction of 1 mole of product at the ring which is produced in a disk reaction involving n_d electrons. The value of N_o (=0.39) was calculated from the dimensions of the electrode using the method described by Albery and Hitchman [17].

RRDE experiments were carried out to analyze the products of oxidation in the relevant potential region (0.45–0.75 V). Assuming that ferrous and cupric ions are the products of oxidation in this region, experiments were performed in which the ring was held at suitable potentials to detect these species (1 and −0.06 V respectively).

Thus, at a ring potential of 1.0 V, iron(II) is detected by oxidation to iron(III) (Equation (12)).

$$Fe^{2+}(aq) = Fe^{3+}(aq) + e \quad (12)$$

For a ring potential of −0.06 V reaction (13) is proposed for disk reaction (7) and reaction (14) for disk reactions (8) and (9).

$$4Cu^{2+}(aq) + S_2O_3^{2-}(aq) + 6H^+(aq) + 12e = 2Cu_2S(s) + 3H_2O(l) \quad (13)$$

$$Cu^{2+}(aq) + 2e = Cu(s) \quad (14)$$

A typical example of the response of the disk and ring currents when the chalcopyrite disk is swept in a positive direction from 0.41 V are shown in Figures 9 and 10.

To establish possible reaction products, experimental collection values (N_{exp}) were calculated from the ratio of the currents measured on the ring (I_r) and disk (I_d). The results (Table 1) show that the experimental values measured at 1 V are more consistent with the expected values for reaction (7) than for reactions (8) and (9). However, the collection values obtained with $E_r = -0.06$ V were more consistent with reaction (9) at disk potentials below 0.6 V and with reaction (7) at potentials above 0.6 V.

3.6. *Soluble sulfur species*

RRDE experiments revealed that a soluble sulfur species is produced under both oxidative and non-oxidative conditions. Under non-oxidative conditions there is thermodynamic support for the formation of H_2S while $S_2O_3^{2-}$ would not be a product of non-oxidative dissolution. However, under oxidative conditions, formation of $S_2O_3^{2-}$ is possible but has only been suggested for the minerals "known as non-soluble in acid" [9–10]. Nevertheless, collection efficiency measurements have shown that Equation (7) could occur since the collection value measured at a potential of 1 V on the ring is consistent with that calculated for this reaction. It is also consistent with experiments at a ring potential of −0.06 V in which copper(II) and $S_2O_3^{2-}$ were considered to be the species which are co-reduced on the ring.

$$4Cu^{2+}(aq) + S_2O_3^{2-}(aq) + 6H^+(aq) + 12e = 2Cu_2S(s) + 3H_2O(l) \quad (15)$$

The collection efficiency measurements have also ruled out reaction (8), since the measured collection values (Table 1) were always higher or lower than the theoretical values for this reaction (Table 2).

The partial oxidation of the mineral sulfide to $S_2O_3^{2-}$ would depend of course on the potential and this would explain the effect of potential on the collection values which seem to be in better agreement with the theoretical values for Equation (7) at potentials close to the potential of maximum current on the disk.

Table 2. Theoretical collection values (N_{calc})

E_R/V	Reactions		
	(7)	(8)	(9)
1	0.049	0.156	0.098
−0.06	0.146	0.078	0.195

The fact that at a ring potential of −0.06 V the collection efficiencies were higher for disk potentials below 0.6 V could be attributed to the contribution from a parallel reaction, such as the non-oxidative dissolution, occurring at these potentials.

The occurrence of two or more reactions is also supported by the stripping curves shown in Figure 6. In these curves it can be observed that the ratio of copper metal to sulfides produced during the anodic dissolution of the products on the ring apparently changes within the potential region studied. For instance, the copper peak (A1) can only be observed at disk potentials above 0.54 V and it becomes larger as the potential increases. The charge associated with peak A3 also appears to increase with increasing disk potential while this is not as obvious for peak A2 (Figure 6). The fact that the copper metal peak appears only at potentials higher than 0.54 V could mean than the ratio of copper ions to $S_2O_3^{2-}$ formed at the disk becomes higher in this region and that there is insufficient $S_2O_3^{2-}$ to convert all the copper ions to a Cu_xS species on the ring.

The well known instability of thiosulfate in acidic solutions would, of course, result in eventual formation of elemental sulfur. However, this reaction is slow enough [25] at the low concentrations of thiosulfate produced at the disk under the conditions of these experiments that it is detectable at the ring. In addition, thiosulfate is relatively rapidly oxidized by copper(II) ions [26] and this could also contribute to the instability of thiosulfate in these experiments.

4. Conclusions

An investigation of the products formed during the initial stages of the dissolution of chalcopyrite using rotating ring–disk electrode techniques have produced evidence of a non-oxidative dissolution process for chalcopyrite under freely dissolving conditions in dilute sulfuric acid solutions at elevated temperatures. This process involves the formation of soluble copper(II) ions and a soluble sulfur species which is presumably H_2S. By the use of an anodic stripping technique on the ring electrode, it has been possible to determine the nature of the products formed on the chalcopyrite disk electrode under various conditions. Collection efficiency measurements involving the detection of both iron(II) and copper(II) on the ring have been used to identify possible anodic reactions in the potential region relevant to the oxidative leaching of the mineral.

The results are consistent with the formation of copper(II) and iron(II) ions together with detectable amounts of a soluble sulfur species. The ring–disk data suggests that this species is thiosulfate. These results have implications in regard to the accepted mechanisms of the oxidative dissolution of this mineral.

Acknowledgement

The authors acknowledge research funding provided by the A.J. Parker CRC for Hydrometallurgy.

References

1. A.R. Burkin, *Chemical Hydrometallurgy: Theory and Principles* (Imperial College Press, London, 2001), pp. 327(chapter 5).
2. P.B. Munoz, J.D. Miller and M.E. Wadsworth, *Metall. Trans. B* **10** (1979) 149.
3. T. Biegler and D.A. Swift, *J. Appl. Electrochem.* **9** (1979) 545.
4. A.J. Parker, R.L. Paul and G.P. Power, *Aust. J. Chem.* **34** (1981) 13.
5. A.J. Parker, R.L. Paul and G.P. Power, *J. Electroanal. Chem.* **118** (1981) 305.
6. T. Biegler and M.D. Horne, *J. Electrochem. Soc.* **132** (1985) 1363.
7. G. Warren, M.E. Wadsworth and S.M. El-Raghy, *Metall. Trans. B* **13** (1982) 571.
8. T. Hirato, H. Majima and Y. Awakura, *Metall. Trans. B* **18** (1987) 489.
9. W. Sand, T. Gehrke, R. Hallmann and A. Schippers, *Hydrometallurgy* **59** (2001) 159.
10. T. Rohwerder, T. Gehrke, K. Kinzler and W. Sand, *Appl. Microbiol. Biotechnol.* **63** (2003) 239.
11. M.J. Nicol and I. Lázaro, *in* P.A. Riveros, D.G. Dixon, D.B. Dreisinger and J.H. Menacho (Eds), Proceedings of the Copper-Cobre 2003 Conference, Santiago, Chile, 2003, p. 367.
12. M.J. Nicol, *Inst. Min. Metall., Trans., Sect. C* **84** (1975) C206.
13. M. Ammou-Chokroum, D. Steinmetz and A. Malve, *Bull. Soc. Fr. Mineral. Cristallogr.* **101** (1978) 26(English translation).
14. R.I. Holliday and W.R. Richmond, *J. Electroanal. Chem.* **288** (1990) 83.
15. G.H. Kelsall and P.W. Page, *in* P.E. Richardson and R. Woods (Eds), Int. Symp. Electrochem. Miner. Met. Process (The Electrochem. Soc., 1984), p. 303.
16. M. Ichikuni, *Bull. Chem. Soc. Jpn.* **33** (1960) 1052.
17. W.J. Albery and M.L. Hitchman, *Ring–Disc Electrodes* (Oxford University Press, London, 1971)(chapter 3).
18. D.L. Jones and E. Peters, *in* Int. Symp. Extr. Metall., 1976, p. 633.
19. M.J. Nicol, *in* K. Osseo-Asare and J.D. Miller (Eds), Hydrometallurgy: Research, Development and Plant Practice (The Metallurgical Society of AIME, Warrendale, PA, 1982), p. 177.
20. M.J. Nicol and I. Lázaro, *Hydrometallurgy* **63** (2002) 15.
21. M.J. Nicol, C.R.S. Needes and N.P. Finkelstein, *in* A.R. Burkin (Ed), Leaching Reduction in Hydrometallurgy (Institution of Mining and Metallurgy, London, UK, 1975), pp. 1–11.
22. P. Brennet, S. Jafferali, J.M. Vanseveren, J. Vereecken and R. Winand, *Trans. Metall. B* **5** (1974) 127.
23. J. Gerlach and E. Küzeci, *Hydrometallurgy* **11** (1983) 345.
24. D.F.A. Koch and R.J. McIntyre, *J. Electroanal. Chem.* **71** (1976) 285.
25. T. Loucka, *Coll. Czech. Chem. Comm.* **63** (1998) 20.
26. G. Rabai and I.R. Epstein, *Inorg. Chem.* **31** (1992) 3239.