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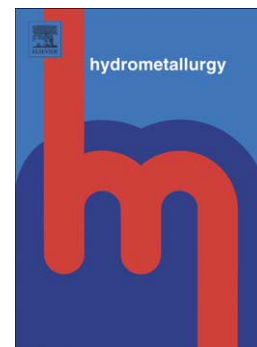
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The kinetics of dissolution of synthetic covellite, chalcocite and digenite in dilute chloride solutions at ambient temperatures.

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Abstract

An experimental study of the comparative kinetics of dissolution of various synthetic copper sulphides (covellite, chalcocite, digenite) in dilute chloride solutions has been carried out at ambient temperatures such as could be encountered in the heap leaching of secondary copper sulphide minerals.

The dissolution of sized synthetic covellite particles was carried out in dilute HCl solutions containing known concentrations of copper(II) and iron(III) at controlled potentials. The results show that the rate of dissolution is similar at potentials of 600 and 650 mV, but is predictably less at a potential of 550 mV. The rate of dissolution is remarkably similar to that of chalcopyrite under similar conditions and is largely independent of Cl⁻ and HCl concentration in the range 0.2 to 2.5 M and 0.1 to 1 M respectively. The effect of temperature is significant and an activation energy of 71.5 kJ mol⁻¹ was derived which confirms a chemical or electrochemical rate-determining reaction on the mineral surface. A mineralogical study of the residue after leaching shows that most of the sulphur is associated with unreacted covellite and occurs as isolated globules on the surface with over 90% of the unreacted covellite surface free of sulphur.

Dissolution of synthetic chalcocite and digenite is rapid compared with that of covellite under the same conditions. At a potential of 500 mV, the relatively rapid

initial dissolution of chalcocite and digenite does not proceed beyond about 50% and 45% copper dissolution, respectively, as predicted from the thermodynamics. These results confirm the formation of a covellite-like phase as an intermediate which cannot be leached at a potential of 500 mV. An increase in the potential results in rapid dissolution of this “secondary covellite”, relative to primary covellite. These results provide useful information for the conditions that should be used for the heap leaching of ores containing secondary copper sulphide minerals.

Keywords: Covellite; Chalcocite; Digenite; Kinetics; Solution potential; Chloride leaching;

1. Introduction

The recovery of copper by heap leaching of low-grade ores containing secondary copper sulphide minerals is becoming increasingly important as the easily leached oxide ores are being depleted. The present authors have recently published the results of a study of the dissolution of chalcopyrite concentrates and ores under conditions that could be appropriate to heap leaching of ores containing this refractory mineral. In dilute chloride solutions at ambient temperatures, results were obtained that have shown that the rate of leaching of chalcopyrite under these conditions is enhanced if the solution potential is controlled within a potential window (550-620 mV) (Velásquez-Yévenes et al., 2009, 2010a-b; Nicol et al., 2010). In the proposed mechanism for enhanced leaching at low potentials, it was suggested that a covellite-like phase is produced as an intermediate and a future publication will present electrochemical evidence for such an intermediate.

In the case of the secondary copper sulphide minerals, chalcocite (Cu_2S) is the most common while digenite ($\text{Cu}_{1.8}\text{S}$) and other intermediate sulphides (Cu_{2-x}S) are often associated with chalcocite. Although it is well known that the rate of leaching of the secondary copper sulphides is more rapid than that of the primary minerals of 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 sulphides and bacterially-assisted oxidation in sulphate solutions has been the generally accepted method for heap leaching of sulphide minerals.

An alternative approach using dilute chloride solutions has been applied in at least one case (Aroca, 1999) and is an attractive alternative which makes use of copper(II) as an oxidant. The rapid rate of the re-oxidation of copper(I) by dissolved oxygen in chloride solutions (Miki and Nicol, 2008, 2010) permits the use of aerated heaps without external regeneration of the oxidant.

Although there is a considerable body of published information on the dissolution of secondary copper sulphides in chloride solutions, the emphasis has been on elevated temperature processes aimed at concentrates. Research on the rates of dissolution of secondary sulphides in dilute chloride solutions at ambient temperatures is therefore desirable. In particular, the solution potentials required to effectively leach these minerals are not known with any certainty in dilute chloride solutions.

In the absence of suitable natural samples of these minerals, chalcocite, digenite and covellite were synthesized and leaching experiments have been carried out under conditions similar to those used in previous studies with chalcopyrite (Velásquez-Yévenes et al., 2010a). The effects of potential, chloride and acid concentration and temperature have been investigated.

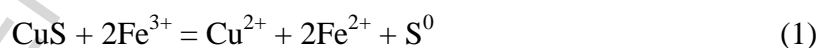
2. Copper sulphide leaching

2.1. Covellite leaching

Covellite (CuS) is a copper sulphide mineral which contains 66% copper and it is now considered as being Cu₂S₂ (Goh et al., 2006) with the copper existing as copper(I). It is widely associated with chalcopyrite and chalcocite which are the main primary and secondary copper sulphides, respectively (Dutrizac and MacDonald, 1974b).

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

The first systematic report of CuS leaching in ferric sulphate media was reported by Sullivan (1930a) who confirmed that the mineral dissolves according to following equation.



Note that this and other equations are written as published in the literature and not in terms of Cu₂S₂.

Thomas and Ingraham (1967) leached synthetic CuS disks in ferric sulphate solutions at elevated temperatures and confirmed that synthetic CuS dissolved with the same equation and found that 4% of the leached sulphur reported as sulphate (SO₄²⁻).

Sullivan (1930a) also reported that covellite dissolution increased with increasing temperature and is insensitive to acid concentration. 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 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.

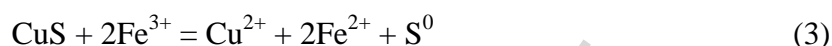
Thomas and Ingraham (1967) carried out covellite leaching experiments with ferric sulphate solutions and their dissolution curves showed that the rate increased gradually during the initial period of leaching but then became linear. Similar behaviour has been reported by Dutrizac and MacDonald (1974a) and they suggested a mechanism in which the ferric attack of covellite occurred preferentially in certain areas and the progressive development of such pits was responsible for the observed leaching behaviour.

Cheng and Lawson (1991a) investigated the leaching of synthetic covellite in sulphate-chloride solutions from 75-95°C in the presence of oxygen and they concluded that chloride concentration is important for oxygenated leaching of covellite. Under these conditions, leaching followed a shrinking core model and they suggested that the thickening surface layer of sulphur caused partial passivation.

2.2. *Chalcocite leaching*

Chalcocite, (Cu₂S) which contains 79.9% copper is the main secondary copper sulphide and has an abundance exceed only by chalcopyrite. The rate of leaching of chalcocite is high compared with other copper sulphide minerals and, for this reason, bacterially-assisted heap leaching can be used.

Sullivan (1930b) investigated the dissolution of chalcocite ores and he found that chalcocite dissolves in two steps according to the following reactions



The first step is faster than the second and is only slightly affected by temperature which suggests that it could be controlled by mass transport processes. The second, slower step is more strongly dependent on the temperature. In this and subsequent equations and discussion, the term “secondary covellite” is used to describe the product of the first stage of oxidation of chalcocite although the original description as “blaubliebender” covellite has been shown to be inaccurate in that the intermediate species is a complex mixture of sulphides within the compositional range $\text{Cu}_{1.6}\text{S}$ (geerite) to $\text{Cu}_{1.1}\text{S}$ (yarrowite) (Whiteside and Goble, 1986).

Cheng and Lawson (1991b) investigated this process in mixed chloride-sulphate solutions and suggested that for the first reaction, the rate limiting step is the diffusion of oxygen through the liquid boundary layer around the particles. In the much slower second step, dissolution can be described in terms of a model in which a shrinking core of unreacted secondary covellite is surrounded by a thickening shell of elemental sulphur. The rate of copper dissolution from the secondary covellite is initially limited by the rate of surface chemical reaction and in the latter stages by both the surface chemical reaction and pore diffusion processes. The activation energy for the first step is 33.5 kJ mol^{-1} and for the second step is 69.0 kJ mol^{-1} . Cheng and Lawson (1991b) also investigated the effect of the concentration of chloride ions on the rate of chalcocite leaching and found that it increases with addition of chloride.

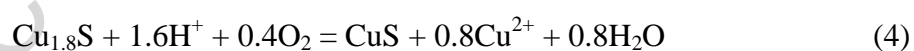
Many publications have confirmed that secondary covellite is formed as an intermediate product during the dissolution of chalcocite (McDonald and Langer, 1983; Rademan et al., 1999; Cheng and Lawson, 1991a, 1991b; Fisher et al., 1992;

Senanayake, 2007; Lee et al., 2008). According to an electrochemical study, this reaction progresses from chalcocite to djurleite, digenite and finally covellite (Arce and González, 2002; Elsherief et al., 1995).

It is generally accepted that the intermediate or secondary covellite is more reactive than the primary mineral (Cheng and Lawson, 1991b) and it has been reported that the leaching rate of the secondary species increases with increasing ferric ion concentration in the range 0.25 M and 1 M which is not the same as that of primary covellite (Dutrizac and MacDonald, 1974b).

2.3. *Digenite leaching*

Digenite can be represented as $\text{Cu}_{1.8}\text{S}$ and it normally occurs as a weathered form of chalcocite. Ruiz et al. (1998) investigated the leaching of digenite in chloride media at 50-90°C and observed that the rate depends on the chloride concentration (1-5 M) and temperature. As in the case of chalcocite, digenite leaching can be represented as the following overall reactions with the formation of a secondary “covellite” phase



Although shown as reactions involving oxygen, it was shown that copper(II) ions (produced by re-oxidation of copper(I) by dissolved oxygen) is the active oxidant. Again, the second step is much slower than the first for which the rate is controlled by boundary layer diffusion of the copper(II) ions to the particle surface. The rate of the second step reaction follows a shrinking core model and is controlled by diffusion through a porous product layer. The activation energy of the first step is 15.8 kJ mol^{-1} and that for the second step is 84.0 kJ mol^{-1} .

2.4. Thermodynamics

The thermodynamics of the oxidation of covellite by copper(II) or iron(III) ions in chloride solutions are not as favourable as that for chalcopyrite and chalcocite, as shown by the curves in Figure. 1. The formal potentials of the couples involved



are shown as a function of the concentration of chloride ions at 25 °C using published thermodynamic data at the appropriate ionic strength (Martell and Smith, 2004). Also shown for comparison is the curve for the oxidation of chalcocite to covellite,



The curves for the reduction of iron(III) and copper(II) have been calculated so that they intersect (i.e. are in equilibrium) at a potential of 580 mV at a chloride concentration of 20 g L⁻¹. At equilibrium this requires that the ratios of the concentrations are Fe(III)/Fe(II) = 0.005 and Cu(II)/Cu(I) = 50.

The requirement for spontaneous oxidation of covellite is that the potential for the oxidant couple be greater than that for the oxidation of covellite. Thus, at 580 mV, this is satisfied at chloride concentrations greater than 20 g L⁻¹ although this would not be true at a potential of 500 mV. However, there are no such restrictions on the oxidation of chalcocite to covellite. It is apparent, therefore that the oxidation of covellite becomes more favourable with increasing chloride concentration for both copper(II) and iron(III) as the oxidants. Thus, in solutions of low chloride concentration, complete oxidation of chalcocite to soluble copper will only be possible at relatively high potentials such as above 580 mV for a solution of 20 g L⁻¹

chloride. At lower potentials under these conditions, any secondary covellite formed would be stable. There is no reliable thermodynamic data available for the intermediate sulfides such as geerite and yarrowite and the reaction would cease after approximately 50% of the copper from chalcocite is dissolved.

Thus, using the data for the metastable species quoted by Woods et al., (1987), the standard reduction potential for the reaction $\text{Cu}_{2-x}\text{S} + x\text{Cu}^{2+} + 2xe = \text{Cu}_2\text{S}$ is 0.51 V for $x = 0.33$ (geerite) and 0.527 V for $x = 0.62$ (spionkopite) compared to the value of 0.540 V for $x = 1$. Similarly, the potential for the reaction $(2-x)\text{Cu}^{2+} + \text{S} + 2(2-x)e = \text{Cu}_{2-x}\text{S}$ is 0.571 V for $x = 0.33$ (geerite) and 0.578 V for $x = 0.62$ (spionkopite) compared to the value of 0.583 V for $x = 1$. Thus these intermediate species have stabilities that are very similar to that for covellite and therefore only that for covellite has been included in Figure 1. Similar considerations apply to digenite after about 45 % dissolution of the copper.

3. Experimental

3.1. Synthesis of copper sulphides

Copper sulphide samples were synthesised with stoichiometric quantities of acid-washed copper wire and reagent grade elemental sulphur powder which were placed in separate Vycor boats and sealed under vacuum in a Vycor tube. For covellite, copper wire (1mm diameter) was twisted into a spiral shape to maximize the surface area and the tube and contents were kept at 320 °C for 24 h to obtain the dark blue sample. For digenite, the Vycor tube containing copper wire and sulphur was kept at 450°C for 24 h to produce the grey sample. For chalcocite, the digenite sample was kept at 800°C for 48 h to obtain the dark grey sample. The products were ground in a

ring mill for 20 sec and then wet screened to obtain the +20-38 μm size fraction. XRD and chemical analysis for copper revealed that the covellite sample contained only CuS, the chalcocite sample contained mostly Cu_2S with traces of djurelite ($\text{Cu}_{1.97}\text{S}$) while the digenite sample contained only $\text{Cu}_{1.8}\text{S}$.

3.2. *Leaching experiments*

Agitated leaching experiments at controlled potential were carried out as described in a previous publication (Velásquez-Yévenes et al., 2010a) on the dissolution of chalcopyrite. The experiments were conducted using 5 g (covellite) or 3 g (chalcocite, digenite) in 900 cm^3 of solution at a fixed temperature with a stirring speed of 1200 rpm. At regular intervals, 2 ml samples of filtered solution were withdrawn and analyzed for copper using atomic absorption spectroscopy.

The solution potentials were monitored using a platinum ring electrode with a combined Ag/AgCl reference electrode (3 M KCl). All potentials are quoted with reference to the standard hydrogen electrode. The potential was controlled by injection of air or oxygen as described in a previous publication (Velásquez-Yévenes et al., 2010a).

4. **Results and discussion**

Leaching experiments were carried out at various potentials, chloride and acid concentrations and temperatures. Unless otherwise stated, the normal conditions involved the use of a solution of 0.2 M HCl containing initially 0.2 g L^{-1} Cu(II) and 2

g L^{-1} Fe(III)/Fe(II) at 35°C at a controlled potential of 600 mV. The initial solution potential was regulated by the adjustment of the ferric/ferrous ion ratio. These concentrations were chosen to simulate the composition of a typical raffinate solution in a heap leach operation.

4.1. *Leaching of synthetic covellite*

4.1.1. *Effect of potential*

The effect of the potential on covellite dissolution has been investigated in 0.2 M HCl with 0.2 g L^{-1} Cu and 2 g L^{-1} Fe at 35°C . The potential was controlled at 550 mV, 600 mV and 650 mV. Figure 2 shows the results of these leaching experiments.

The rate of copper dissolution is similar (about 80% after 1000 h) at 600 mV and 650 mV but noticeably slower at 550 mV. All subsequent experiments were therefore conducted at 600 mV.

4.1.2. *Effect of chloride concentration*

The effect of chloride ions on the rate of dissolution of covellite has been investigated at a controlled potential of 600 mV. The chloride concentration was adjusted by adding NaCl. The results are shown in Figure 3 from it is appears that the rate of dissolution is largely independent of the chloride concentration in the range investigated with marginally increased rates in a solution containing 90 g L^{-1} chloride. This agrees with the observations of Cheng and Lawson (1991a) who reported that the rate increased with increasing chloride concentration up to 0.25 M, above which concentration it became independent of the chloride concentration.

4.1.3. *Effect of acid concentration*

Leaching experiments were carried out in 0.1 M, 0.2 M and 0.5 M HCl solutions with 0.2 g L⁻¹ Cu and 2 g L⁻¹ Fe at 600 mV at 35 °C. Figure 4 shows the results which confirm that the rate is essentially independent of acidity in this range which is appropriate to heap leaching.

Cheng and Lawson (1991a) showed that the rate of covellite dissolution increased with increasing sulphuric acid concentration up to 0.02 M above which concentration the effect became negligible. In contrast, Ghali and Dandapani (1982) reported that a high concentration of HCl accelerated the anodic dissolution of covellite because of the formation of a CuCl₂⁻ complex ion.

4.1.4. *Effect of temperature*

Again, the effect of temperature on the rate of dissolution of covellite was investigated in 0.2 M HCl with 0.2 g L⁻¹ Cu and 2 g L⁻¹ Fe at 600 mV. Figure 5 shows, as expected, that the rate increased rapidly with increasing temperature.

The slopes of the approximately linear sections of the plots were used in the Arrhenius plot in Figure 6 from which, an activation energy of 72 kJ mol⁻¹ can be calculated. This value is similar to that obtained by Cheng and Lawson (1991a) and Dutrizac et al. (1974a). It is also similar to the value of 73 kJ mol⁻¹ for the dissolution of chalcopyrite obtained by Velásquez-Yévenes (2009, 2010b) under similar conditions. This high value of the activation energy suggests that the rate of covellite dissolution is limited by the rate of chemical and/or electrochemical reactions on surface of the covellite.

4.1.5. *Effect of dissolved oxygen*

The effect of dissolved oxygen on the rate of covellite leaching was investigated because the rate of dissolution of chalcopyrite was found to be enhanced in the presence of dissolved oxygen (Velásquez-Yévenes et al., 2009, 2010a). Leaching experiments were carried out, with or without dissolved oxygen, at the same potential (600 mV). In order to control the potential in the absence of dissolved oxygen, permanganate was added using a Metrohm titrator controlled by Labview software. During an experiment, the potential was monitored and a solution of potassium permanganate was added to restore the potential to the set point. Nitrogen was bubbled through the slurry throughout the experiments. As shown in Figure 7, the rate of copper dissolution is not significantly higher in the presence of oxygen. After 700 h, nitrogen bubbling was stopped in the reactor controlled by permanganate addition and air allowed to enter the reactor. The rate did not show any noticeable change in the presence of dissolved oxygen. Thus, unlike chalcopyrite, the effect of dissolved oxygen on the rate of covellite leaching is negligible.

4.1.6. *Effect of pyrite*

Addition of fine pyrite has been shown to catalyse the leaching of chalcopyrite under similar conditions and Figure 8 shows the result of an experiment in which fine (-25 μm) pyrite at a mass ratio of 4:1 to the covellite was added to the reactor. These experiments used a different sample of covellite and the potential was controlled at 580 mV which explains the slightly lower rates. It is apparent that the rate does show an increase initially but that the slope of the leach curve appears to decline to that observed in the absence of pyrite after about 500 h. Addition of coarse (-38+25 μm) pyrite had no effect on the rate.

Also shown in Figure 8 is the result of a similar experiment carried out with a chalcopyrite concentrate of the same particle size range in the absence of pyrite. The remarkably similar rates of dissolution of covellite and chalcopyrite and the similar activation energies could be an indication of similar mechanisms of dissolution of these two mineral sulphides, or that covellite may be an intermediate in the dissolution of chalcopyrite.

4.1.7. Mineralogy of the residue

The mineralogy of the residue from the dissolution of covellite under normal conditions after 1500 h (580 mV, 80% dissolution) was investigated by mineral liberation analysis (MLA) which showed that the deportment of elemental sulphur in the residue occurs as isolated particles presumably from completely leached covellite particles or as “globules” on the surface of incompletely leached particles (see Fig.9). There is no evidence of sulphur covering the surface of the mineral and the MLA analysis shows that more than 90% of the remaining covellite surface is free of sulphur. Thus, it appears that sulphur is not formed by direct oxidation of the mineral but, as in the case of chalcopyrite, it crystallizes in a secondary form or is produced by a reaction involving a soluble intermediate such as hydrogen sulphide.

\ The mineral map obtained on the residue after dissolution for 1500 h in the presence of pyrite showed little evidence of significant amounts of sulphur associated with fine pyrite particles, unlike chalcopyrite..

A detailed discussion of the mechanism involved in the deportment of elemental sulphur in the case of chalcopyrite dissolution has recently been presented (Nicol et al., 2010) and this mechanism possibly also applies in the case of covellite.

4.2. *Leaching of synthetic chalcocite*

Leaching experiments were carried out with synthetic chalcocite at various potentials, 500 mV, 550 mV and 600 mV. The results in terms of copper dissolution at the three potentials are shown in Fig. 10.

It is apparent that the rate of copper dissolution from chalcocite is rapid compared with that of covellite and that the rate of copper dissolution increased with increasing potential up to 600 mV. At a potential of 500 mV, copper dissolution ceased after about 50% of the copper had been dissolved but then increased at a slower rate when the potential was increased to 550 mV after about 400 h.

This result confirms the thermodynamic prediction that oxidation of chalcocite to covellite is possible under these conditions but that 500 mV is too low for the subsequent oxidation of the secondary covellite which can be at least partially dissolved by an increase to 550 mV. Comparison of the rates of dissolution of chalcocite from 50 to 100% dissolution in Figure 10 with that for synthetic (primary) covellite in Figure 2, shows that the secondary material dissolves very much more rapidly (at least an order of magnitude) than the primary covellite. This supports the results of authors such as Cheng and Lawson (1991b) who indicated that the intermediate secondary covellite is more amenable to leaching than primary covellite. This effect has been ascribed to the significantly increased surface area of the secondary covellite formed by dissolution of approximately 50% of the copper from chalcocite.

4.3. *Leaching of synthetic digenite*

Leaching experiments were also carried out with synthetic digenite at various potentials, 500 mV, 550 mV and 600 mV and the results are shown in Fig. 11. It is

apparent that the rate of copper dissolution appears to be slightly lower than that from chalcocite. The rate increases with increasing potential and, as in the case of chalcocite, it ceases after about 45% dissolution at 500 mV. An increase of the potential to 550 mV results in resumption of leaching at about the same rate observed in the experiment at 550 mV. Again, this result is predicted from the thermodynamics of the oxidation of covellite.

5. Implications for the heap leaching of secondary copper sulphide minerals

The results of this study have provided some useful pointers to the optimization of the heap leaching of secondary copper sulphide minerals.

1. The slow rate of leaching of primary covellite relative to that of secondary material produced by oxidation of chalcocite or digenite indicates that recovery of at least 50% copper from chalcocite is likely to be rapid while copper recovery from covellite in the ore will be slow.
2. Although low potentials (below 550 mV) are suitable for first stage leaching of chalcocite, oxidation of either primary or secondary covellite will require potentials close to the mineral surface of at least 600 mV. This requires that the rate of regeneration of copper(II) ions by oxidation with dissolved oxygen in the heap must be such that the solution potential is maintained above 600 mV.
3. The absence of any strong dependence of the rate of covellite dissolution on the chloride concentration suggests that it is not necessary to increase the chloride concentration in the raffinate solutions to concentrations above 20 g L^{-1} provided that the rate of oxidation of copper(I) is adequate.

4. Similarly, the lack of dependence of the rate of covellite dissolution on pH shows that acid consumption could be reduced by operation of the heaps at pH values above about 1.5 or even 2.

5. The high activation energy for the dissolution of covellite indicates that, as in the case of chalcopyrite, even small increases in heap temperatures could provide significant benefits in terms of increased rates of copper recovery.

6. Conclusions

The results of an experimental program to study the comparative kinetics of dissolution of sized synthetic covellite, chalcocite and digenite particles in dilute acidic chloride solutions at controlled potentials has shown that:

- The rate of covellite dissolution is similar at potentials of 600 and 650 mV while the rate is noticeably less at a lower potential of 550 mV as predicted from the thermodynamics of this system. This is remarkably similar to that of chalcopyrite under similar conditions. However, it does not appear to be significantly influenced by the presence of dissolved oxygen or fine pyrite.
- The rate of covellite dissolution is largely independent of the chloride and HCl concentration in the range of 0.2 to 2.5 M and 0.1 to 1 M respectively. An activation energy of 71.5 kJ mol^{-1} was derived which is similar to literature values and confirms a chemical and/or electrochemical rate-determining reaction on the mineral surface.
- The rates of leaching of chalcocite and digenite are rapid compared with that of covellite. At low potentials, chalcocite and digenite convert to secondary covellite which can only be dissolved at potentials of about 550 mV and above as predicted.

The intermediate, secondary covellite dissolves at a rate which is significantly greater than that of primary covellite.

- A mineralogical study of the residue after leaching of covellite has shown that most of the sulphur is associated with unreacted covellite as isolated globules on the surface with over 90% of the unreacted covellite surface free of sulphur.

7. Acknowledgements

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8. References

- Arce, E., González, I., 2002. A comparative study of electrochemical behaviour of chalcopyrite, chalcocite and bornite in sulfuric acid solution. *International Journal of Mineral Processing*, 67, 17-28.
- Aroca, F., 1999. Plant description and operation of heap leaching, solvent extraction, and electrowinning of copper at Minera Michilla. In: Jergensen, G. V. (Ed.), *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, Society for Mining, Metallurgy and Exploration, Littleton, Co., pp. 279-294.
- Cheng, C.Y., Lawson, F., 1991a. The kinetics of leaching covellite in acidic oxygenated sulphate-chloride solutions. *Hydrometallurgy* 27, 269-284.
- Cheng, C.Y., Lawson, F., 1991b. The kinetics of leaching chalcocite in acidic oxygenated sulphate-chloride solutions. *Hydrometallurgy* 27, 249-268

- Dutrizac, J.E., MacDonald, R.J.C., 1974a. The kinetics of dissolution of covellite in acidified ferric sulphate solutions. *Canadian Metallurgical Quarterly* 13, 423-433.
- Dutrizac, J.E., MacDonald, R.J.C., 1974b. Ferric ion as a leaching medium. *Minerals Science and Engineering*, 6, 59-100.
- Elsherief, E.E., Saba, A.E., Afifi, S.E., 1995. Anodic leaching of chalcocite with periodic cathodic reduction. *Minerals Engineering*, 8, 967-978.
- Fisher, W.W., Flores, F.A., Henderson, J.A., 1992. Comparison of chalcocite dissolution in the oxygenated, aqueous sulfate and chloride systems. *Minerals Engineering* 5, 817-834.
- Ghali, E., Dandapani, B., 1982. Electrodissolution of synthetic covellite in hydrochloric acid. *Journal of Applied Electrochemistry*, 12, 369-376.
- Goh, S.W., Buckley, A.N., Lamb, R.N., 2006. Copper(II) sulfide?. *Minerals Engineering* 19, 204-208
- Lee, M.S., Nicol, M.J., Basson, P., 2008. Cathodic processes in the leaching and electrochemistry of covellite in mixed sulfate-chloride media. *Journal of Applied Electrochemistry*, 38, 363-369.
- Martell, A.E. and Smith, R.M., 2004. NIST Standard Reference Database 46, Ver 8. National Institute of Standards and Technology, Gaithersburg, MD, USA.
- McDonald, G.W., Langer, S.H., 1983. Cupric chloride leaching of model sulfur compounds for simple copper ore concentrates. *Metallurgical Transactions* 14B, 559-570.
- Miki, H., Nicol, M.J., 2008. The kinetics of the copper-catalysed oxidation of iron(II) in chloride solutions. In: Young, C., Anderson, C., Taylor, P., Choi, Y. (Eds.),

- Hydrometallurgy 2008, The Minerals, Metals and Materials Society, Warrendale, PA, USA, pp. 971-979.
- Miki, H., Nicol, M.J., 2010. The dissolution of chalcopyrite in chloride solutions. Part 4. The kinetics of the auto-oxidation of copper(I). *Hydrometallurgy* (in press).
- Mulak, W., 1971. Kinetics of dissolving polydispersed covellite in acidic solutions of ferric sulphate. *Roczn. Chem.* 45, 1417-1424.
- Nicol, M.J., Miki, H., Velásquez-Yévenes, L., 2010. The dissolution of chalcopyrite in chloride solutions: Part 3. Mechanism. *Hydrometallurgy* 103, 86-95.
- Rademan, J.A.M., Lorenzen, L., Van Deventer, J.S.J., 1999. The leaching characteristics of Ni-Cu matte in the acid-oxygen pressure leach process at Impala Platinum. *Hydrometallurgy* 52, 231-252.
- Ruiz, M.C., Honores, S., Padilla, R., 1998. Leaching kinetics of digenite concentrate in oxygenated chloride media at ambient pressure. *Metallurgical and Materials Transactions B* 29, 961-969.
- Senanayake, G., 2007. Chloride assisted leaching of chalcocite by oxygenated sulphuric acid via Cu(II)-OH-Cl. *Minerals Engineering* 20, 1075-1088.
- Sullivan, J.D., 1930a. Chemistry of leaching covellite. Washington, DC, USA, U.S. Bureau of Mines, TP 487.
- Sullivan, J.D., 1930b. Chemistry of leaching chalcocite. Washington, DC, USA, U.S. Bureau of Mines, TP 473.
- Thomas, G., Ingrahan, T.R., 1967. Kinetics of dissolution of synthetic covellite in aqueous acidic ferric sulphate solutions. *Canadian Metallurgical Quarterly* 6, 153-165.
- Velásquez-Yévenes, L., 2009. The kinetics of the dissolution of chalcopyrite in chloride media. Ph.D. thesis, Murdoch University, Perth Australia.

Velásquez-Yévenes, L., Nicol, M.J., Miki, H., 2010a. The dissolution of chalcopyrite in chloride solutions: Part 1. The effect of solution potential. *Hydrometallurgy* 103, 108-113.

Velásquez-Yévenes, L., Miki, H., Nicol, M.J., 2010b. The dissolution of chalcopyrite in chloride solutions: Part 2. The effect of various parameters on the rate. *Hydrometallurgy* 103, 80-85.

Whiteside, L.S., Goble, R.J., 1986. Structural and compositional changes in copper sulfides during leaching and dissolution. *Canadian Mineralogist* 24(2), 247-58.

Woods, R., Yoon, R.H. and Young, C.A., 1987. E_h -pH diagrams for stable and metastable phases in the copper-sulfur-water system. *International Journal of Mineral Processing* 20, 109-120.

Figures

Figure 1 Potentials of various redox couples as a function of chloride concentration at 25 °C. Fe(III)/Fe(II) = 0.005, Cu(II)/Cu(I) = 50. (▲) Cu(II)/Cu(I), (◆) Fe(III)/Fe(II), (■) Cu(I),S/CuS, (●) CuS,Cu(I)/Cu₂S.

Figure 2 The effect of solution potential on the dissolution of copper from synthetic covellite in 0.2 M HCl with 0.2 g L⁻¹ copper(II) and 2 g L⁻¹ iron at 35 °C. (■) 550 mV, (●) 600 mV, (▲) 650 mV.

Figure 3 The effect of chloride concentration(added as NaCl) on the dissolution of copper from synthetic covellite in 0.2 M HCl with 0.2 g L⁻¹ copper(II) and 2 g L⁻¹ iron at 35 °C and 600 mV. (●) 7 g L⁻¹, (▲) 20 g L⁻¹, (◆) 50 g L⁻¹, (■) 90 g L⁻¹.

Figure 4 The effect of hydrochloric acid concentration on the dissolution of copper from synthetic covellite in dilute HCl solutions with 0.2 g L⁻¹ copper(II) and 2 g L⁻¹ iron at 35 °C and 600 mV. (■) 0.1 M HCl, (●) 0.2 M HCl, (▲) 0.5 M HCl.

Figure 5 The effect of temperature on the dissolution of copper from synthetic covellite in 0.2 M HCl with 0.2 g L⁻¹ copper(II) and 2 g L⁻¹ iron at 600 mV. (■) 25 °C, (●) 35 °C, (▲) 45 °C.

Figure 6 Arrhenius plot for the dissolution of covellite using linear slopes of the curves in Fig. 5.

Figure 7 Dissolution of copper from synthetic covellite in 0.2 M HCl with 0.2 g L⁻¹ copper(II) and 2 g L⁻¹ iron at 35 °C at a controlled potential of 600 mV using (●) air-nitrogen and (▲) permanganate.

Figure 8. Effect of fine pyrite on the rate of dissolution of copper from synthetic covellite in 0.2 M HCl with 0.2 g L⁻¹ copper(II) and 2 g L⁻¹ iron at 35 °C at 580 mV. Also shown are the data for the dissolution of copper from a chalcopyrite concentrate under similar conditions. (●) covellite without pyrite addition, (▲) covellite with fine pyrite addition, (■) chalcopyrite.

Figure 9. Partial mineral map of the residue from the dissolution of covellite in 0.2 M HCl at 35 °C for 1500 h. Covellite particles are shown as red(on-line) or dark grey and sulphur as light grey.

Figure 10. Copper dissolution from synthetic chalcocite in 0.2 M HCl with 0.2 g L⁻¹ copper(II) and 2 g L⁻¹ iron at 35 °C. (▲) 550 mV, (■) 600 mV, (●) 500 mV with potential increased to 550 mV after 400 h.

Figure 11. Copper dissolution from synthetic digenite in 0.2 M HCl with 0.2 g L⁻¹ copper(II) and 2g L⁻¹ iron at 35 °C. (▲) 550 mV, (■) 600 mV, (●) 500 mV with potential increased to 550 mV after 800 h.

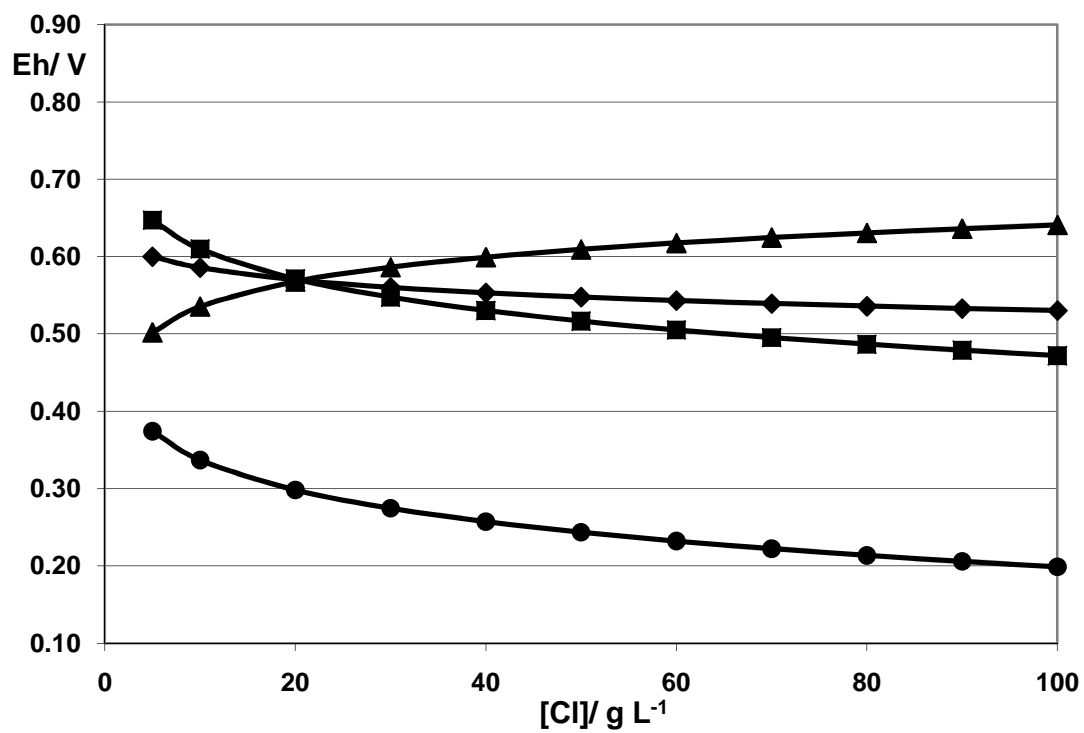


Figure 1

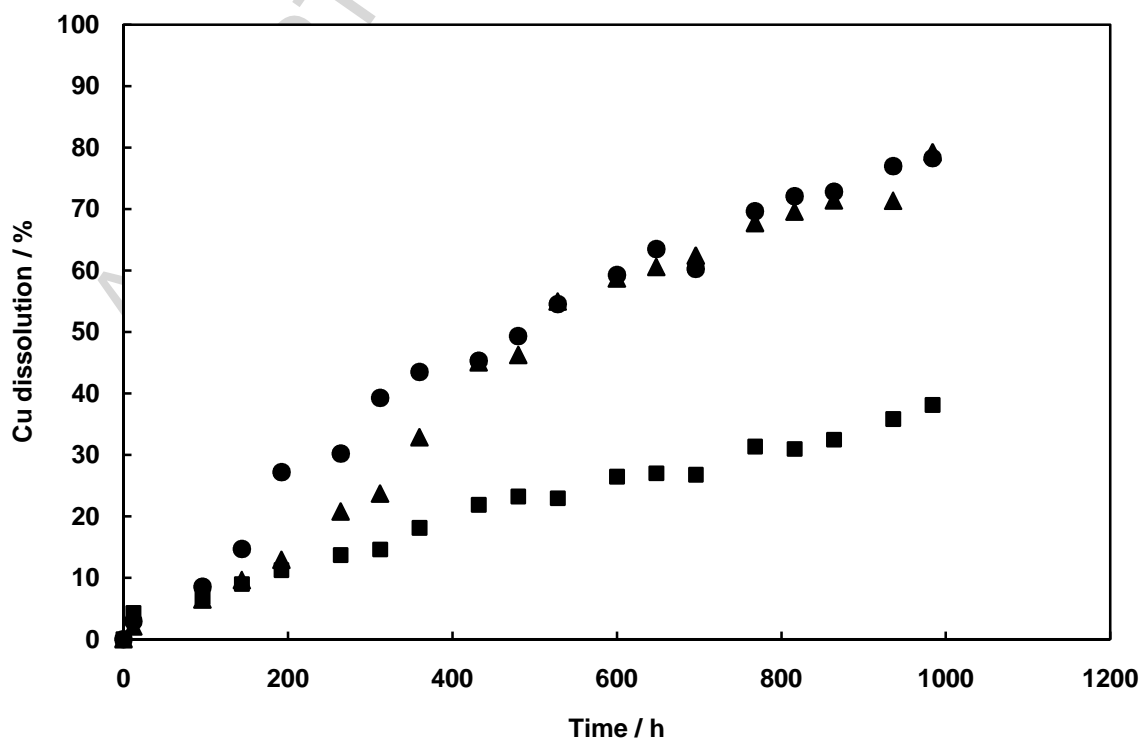


Figure 2

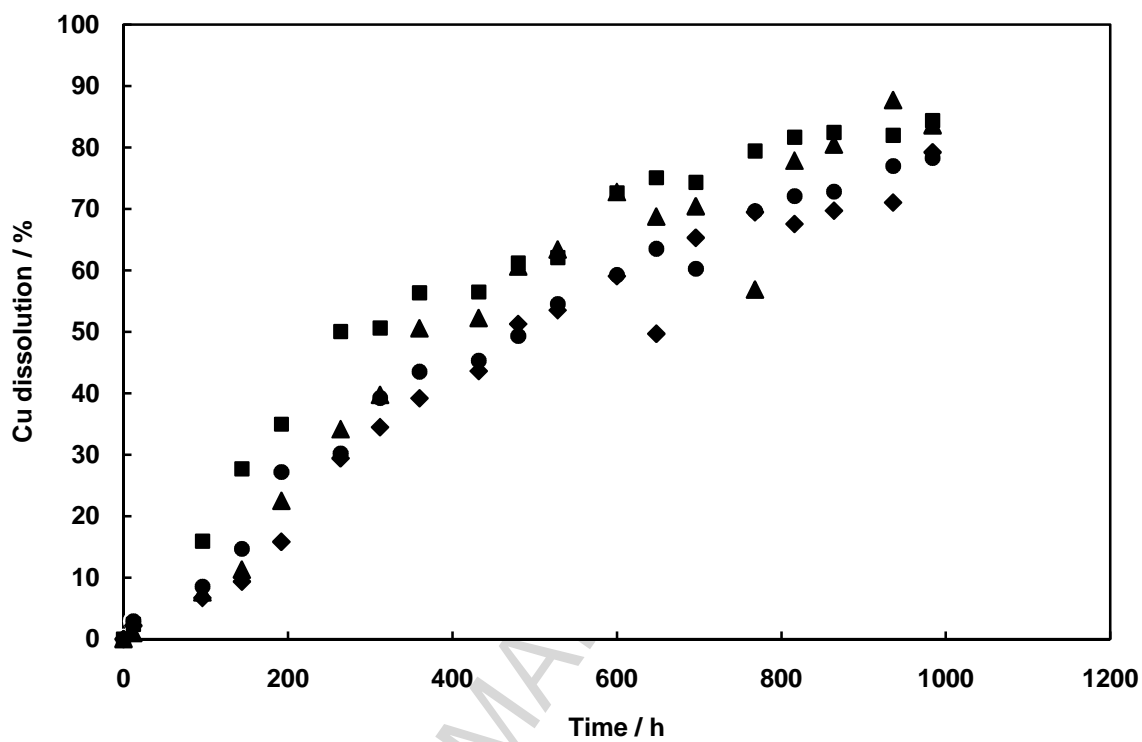


Figure 3

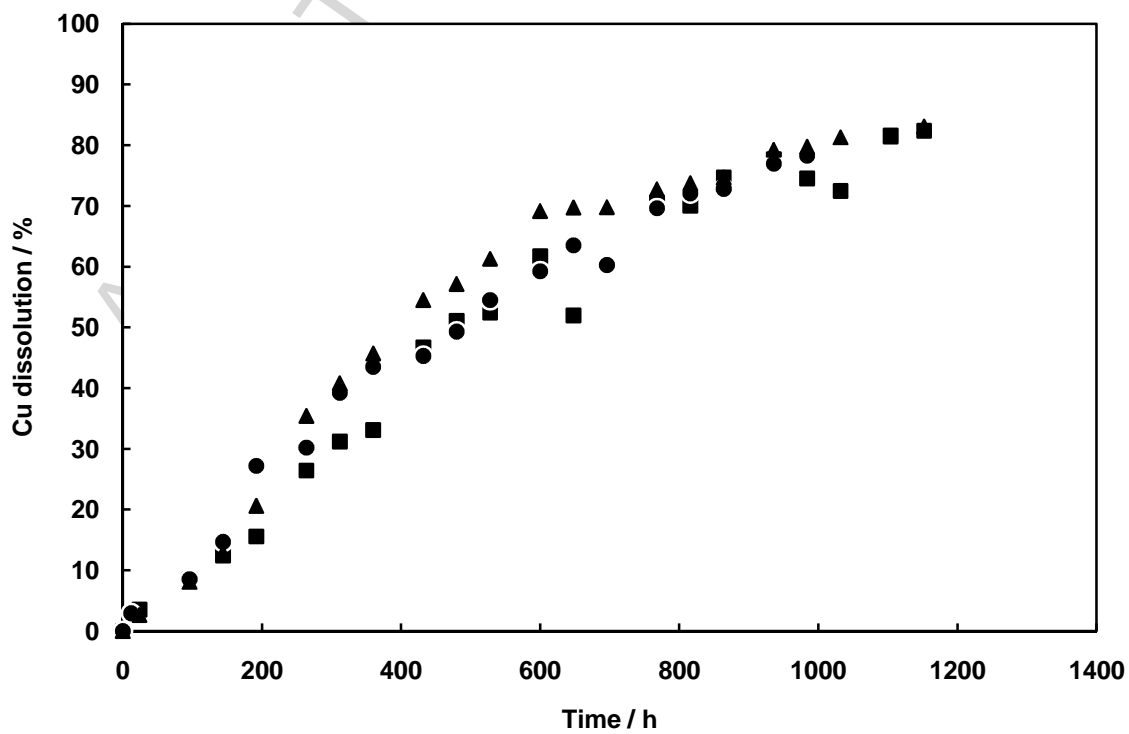


Figure 4

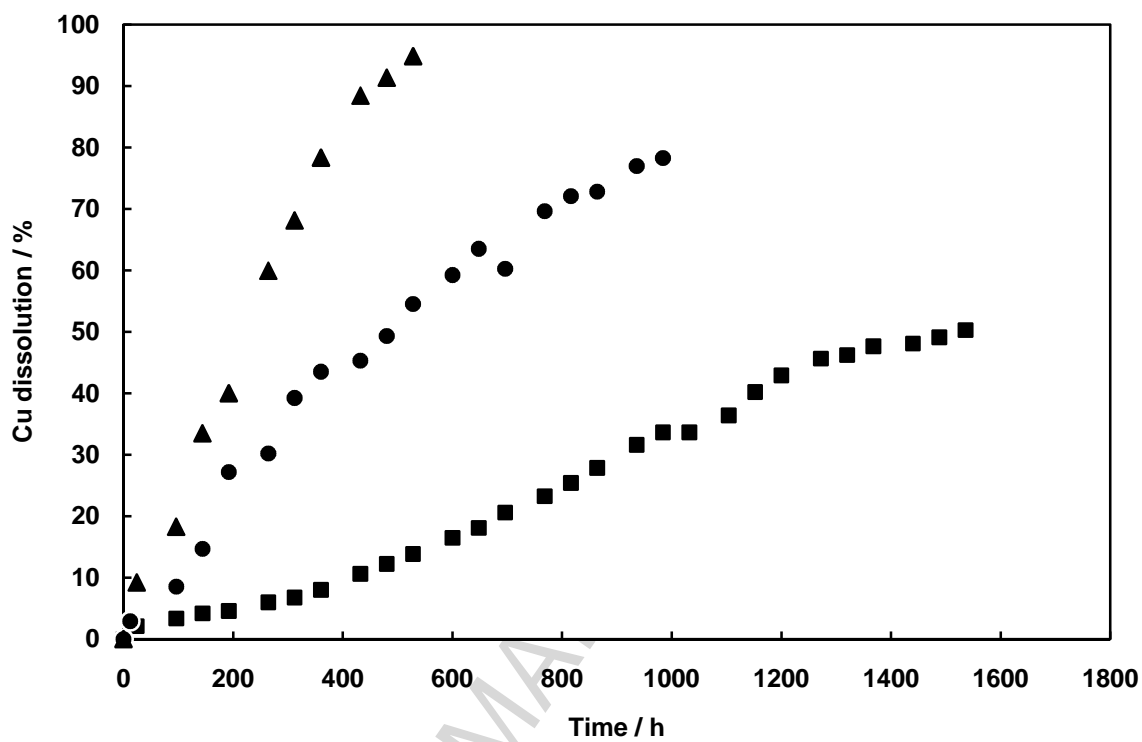


Figure 5

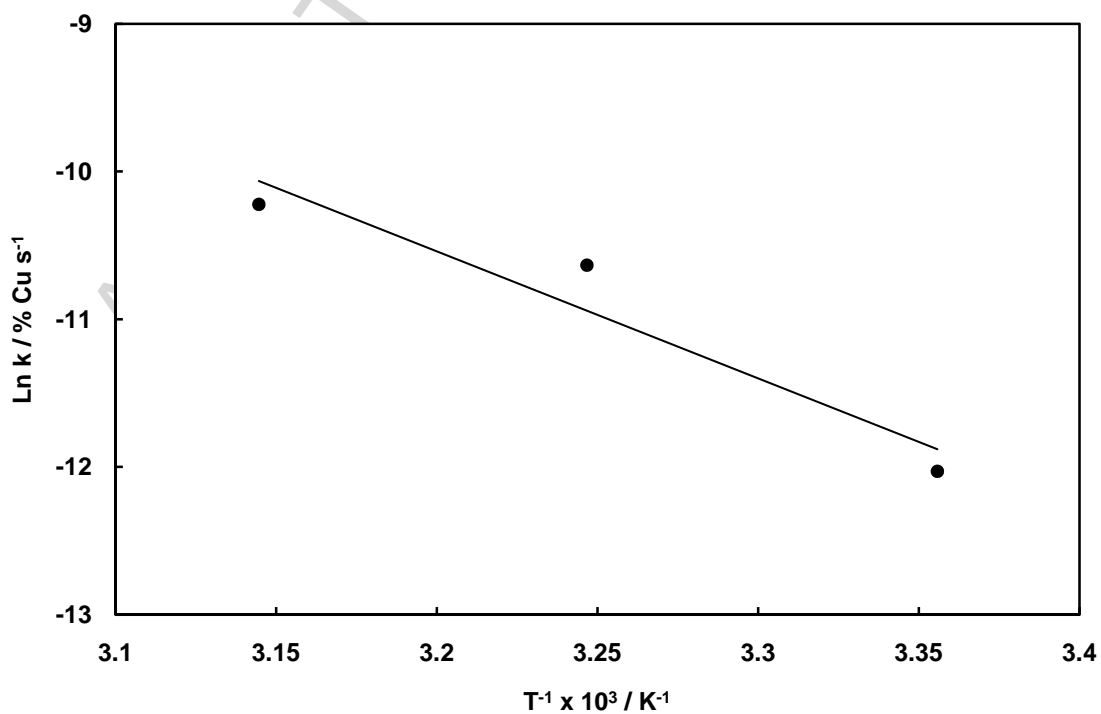


Figure 6

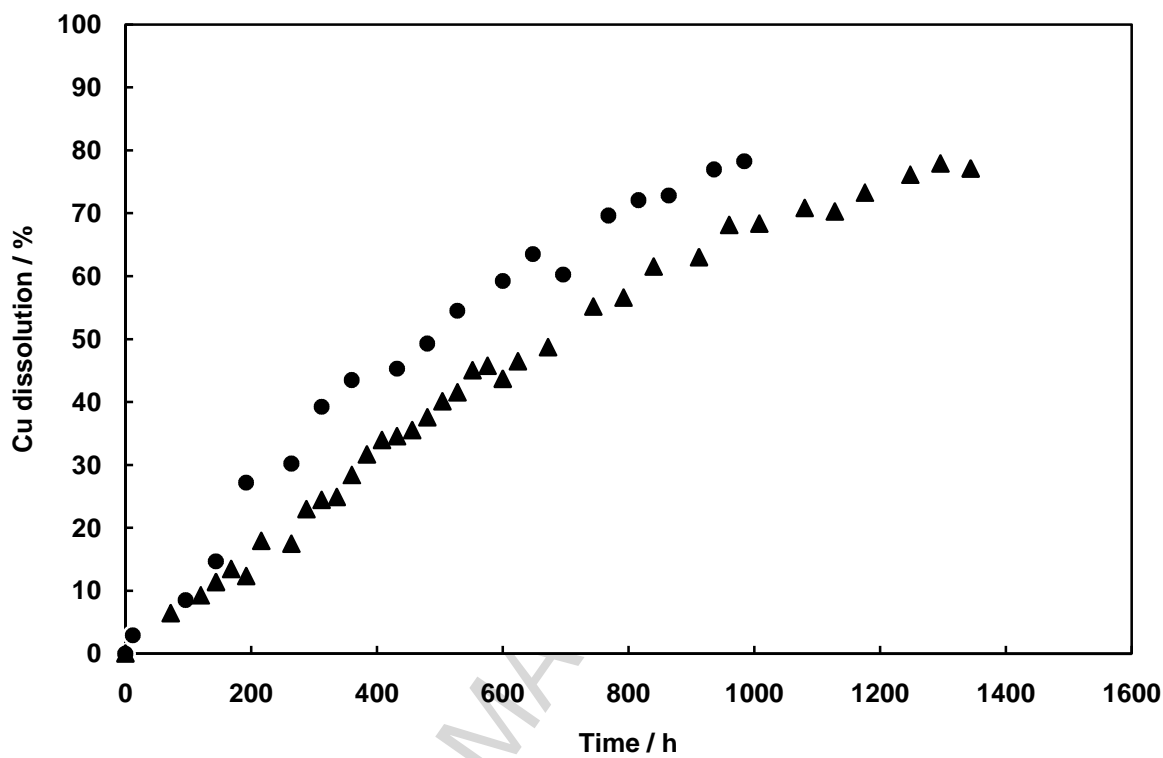


Figure 7

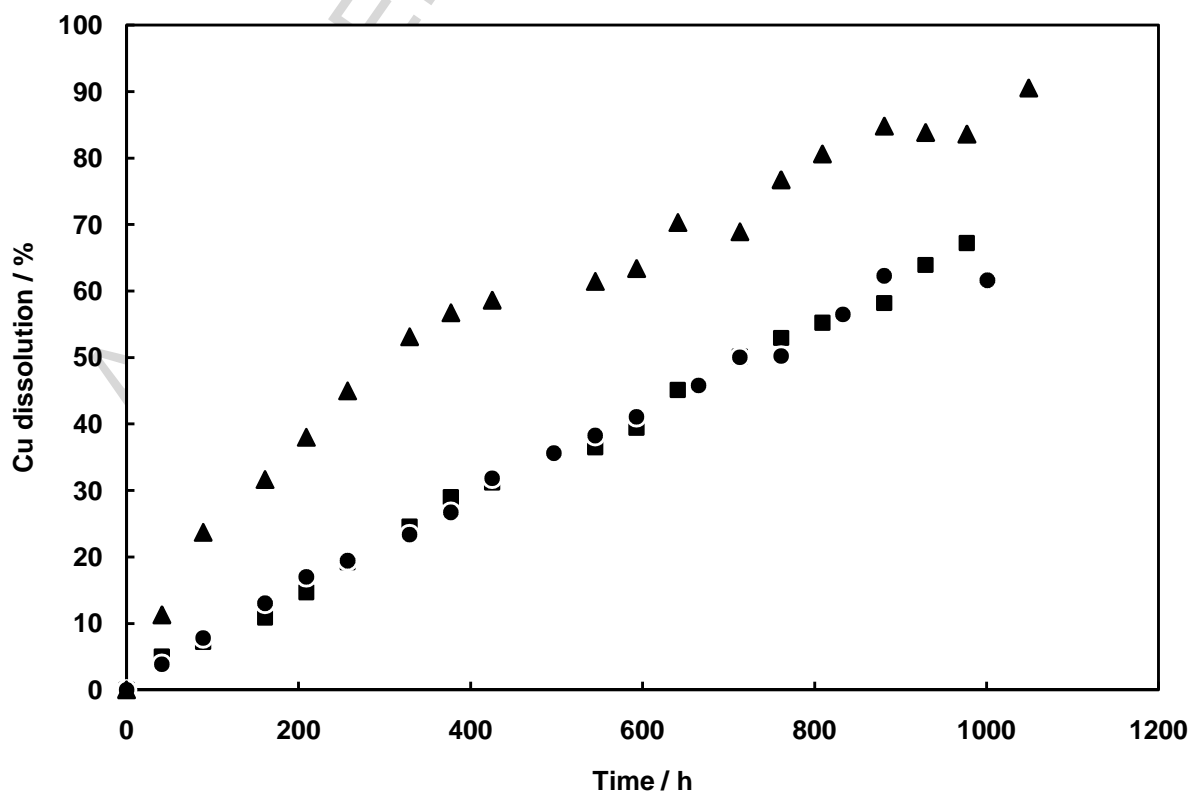


Figure 8

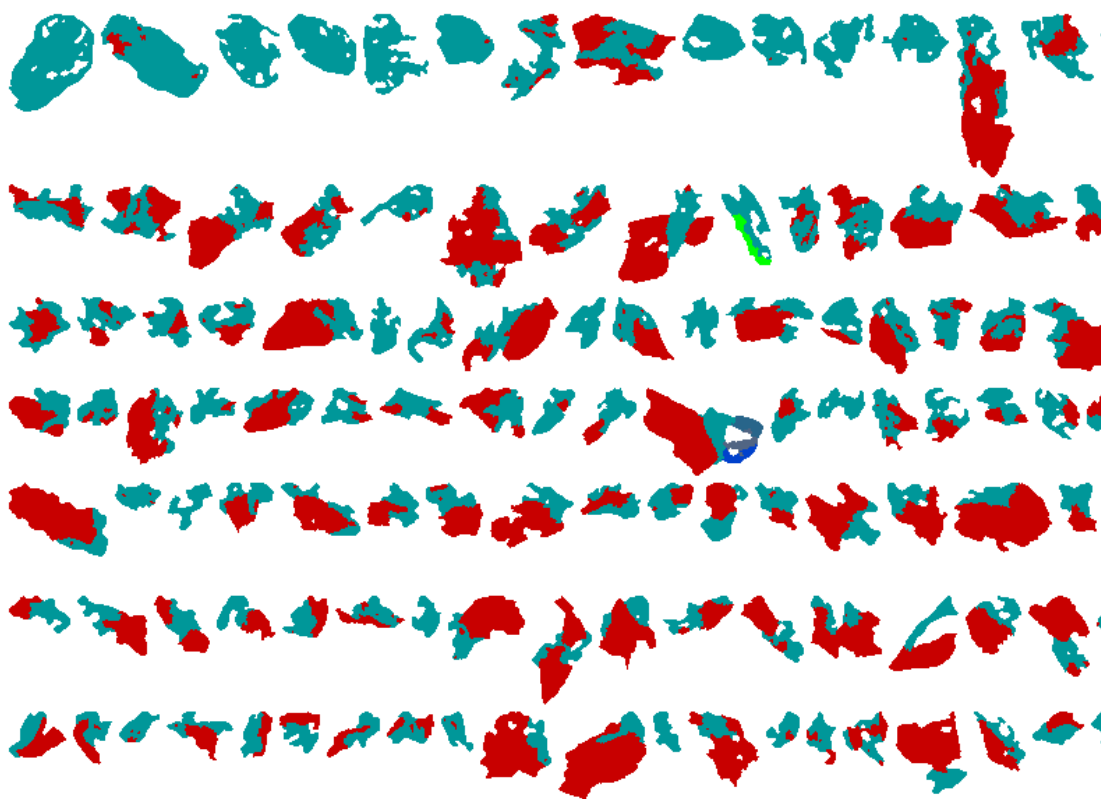


Figure 9

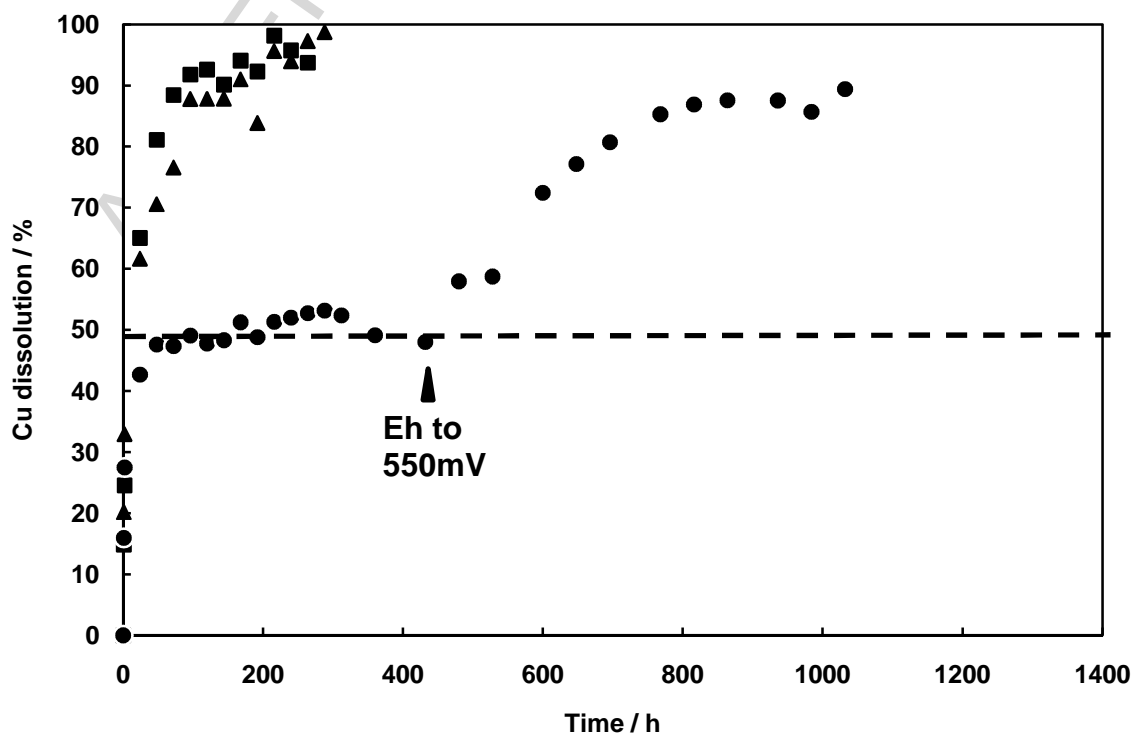


Figure 10

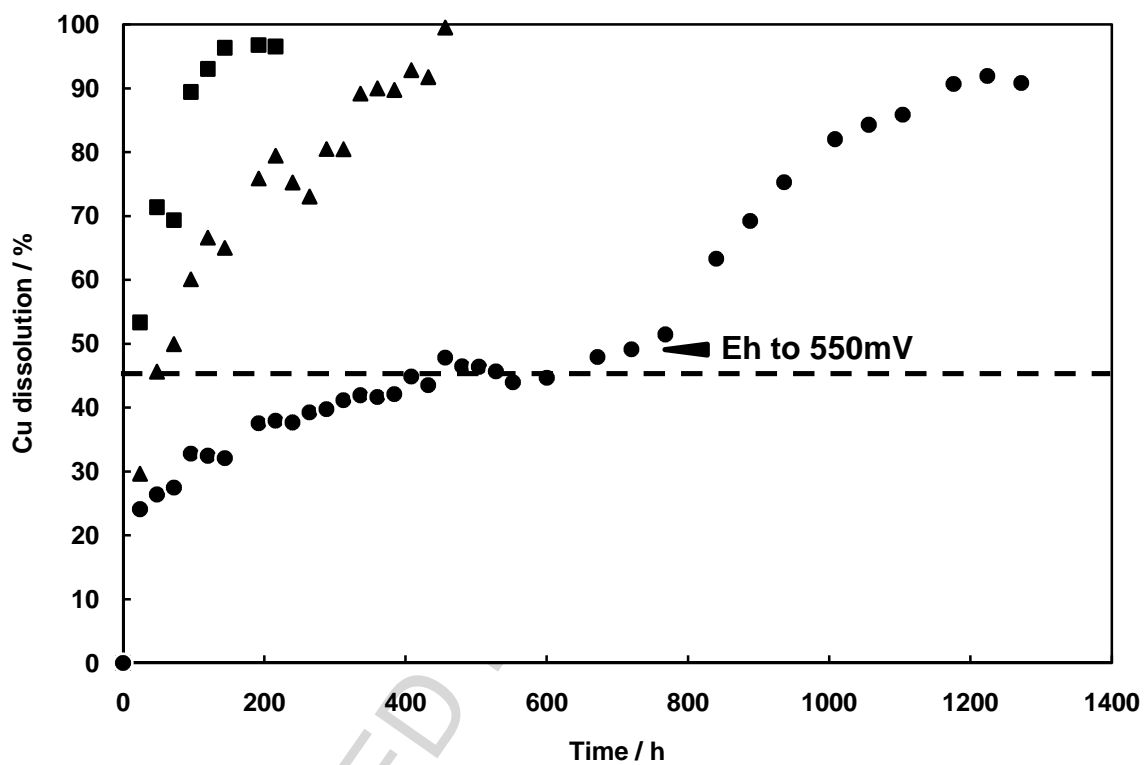


Figure 11

Research Highlights

The rate of dissolution is of covellite similar at potentials of 600 and 650 mV while the rate is noticeably less at a lower potential of 550 mV.

The rate of dissolution of covellite is remarkably similar to that of chalcopyrite under similar conditions.

The rate of dissolution of covellite appears 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 effect of temperature is significant with an activation energy of 71.5 kJ mol^{-1} .

Most of the product sulfur is associated with unreacted covellite and occurs as isolated globules on the surface with over 90% of the unreacted covellite surface free of sulfur.

Dissolution of synthetic chalcocite and digenite is rapid compared with covellite under the same conditions.

At a potential of 500 mV, the relatively rapid initial dissolution of chalcocite and digenite does not proceed beyond 50 % and 45 % copper dissolution respectively.

These results confirm the formation of a covellite-like phase as an intermediate which cannot be dissolved at a potential of 500 mV.

An increase in the potential results in rapid (relative to primary covellite) dissolution of this secondary “covellite”.