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A comparative assessment of the application of ammonium chloride and glycine as lixiviants in the heap leaching of chalcopyritic ores

Michael J. Nicol



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**A Comparative Assessment of the Application of Ammonium Chloride and  
Glycine as Lixiviants in the Heap Leaching of Chalcopyritic Ores**

Michael J Nicol

Murdoch University, Perth, Western Australia

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**Abstract**

A largely electrochemical investigation into the possible use of ammonium chloride or glycine as lixiviants in the heap leaching of chalcopyrite-rich ores has provided good comparative data with which to compare the reagents and also identified several important considerations that need to be taken into account when considering such processes.

The high stability of the copper(II) glycinate complexes results in low reactivity (as measured electrochemically) for the oxidative dissolution of chalcopyrite except at high pH values. The lower stability of the copper(II) ammine complexes results in significantly greater (fifty-fold) rates in the ammonium chloride system under the same conditions. The rates are tenfold higher for the ammonium chloride system at pH 8 compared to glycine at pH 10. Agitated leaching testwork on a chalcopyrite concentrate and column leaching of a chalcopyrite ore have confirmed the electrochemically derived trends.

Loss of copper(II) occurs by precipitation as a basic chloride in the ammonium chloride system at pH values below about 8 depending on the ammonium chloride concentration.

The relatively high cost of glycine and even of ammonium chloride would probably preclude use of these reagents unless the rates of heap leaching can be shown to be significantly greater than those of alternative acidic lixiviant systems.

**Keywords:** Chalcopyrite; heap leaching; ammonia; glycine

## 1. Introduction

The recovery of copper from ores containing chalcopyrite by heap leaching has not to-date been successful using conventional abiotic or bio-processing in sulfate solutions. Recent work has demonstrated some success in the use of chloride at low pH as a lixiviant. In the treatment of ores with a high acid consumption, these processes can become uneconomic and an alternative option requires the use of a high pH. Under these conditions, the iron in chalcopyrite reports to the residue as an hydrated iron(III) oxide while the copper should remain in solution as a soluble complex ion. Possible readily available ligands for stabilization of copper(II) in alkaline solutions are cyanide and ammonia. While the former could act to solubilize copper, complications in the recovery of copper from cyanide solutions and the instability of cyanide in such a system makes this option unattractive.

In the case of ammoniacal systems, copper(II) forms stable ammine complexes that could be extracted using essentially the same solvent extraction process in use in the copper heap leach industry. In addition, the stability of copper(I) in ammoniacal solutions allows for the use of the copper(II)/copper(I) couple as a redox mediator given the rapid homogeneous oxidation of copper(I) by dissolved oxygen (Zuberbuhler, 1967). This eliminates the problem of the low reactivity (and solubility) of dissolved oxygen as the oxidant. However, the volatility of ammonia is a severe drawback and any such process would have to operate at pH values at which the free ammonia concentration is low i.e. well below the  $pK_b$  (9.3) of ammonia.

An alternative to ammonia would be aminoacetic acid (glycine) or other non-volatile amines that have many of the chemical properties of ammonia such as a similar  $pK_b$  and the formation of stable complexes with copper(II) and copper(I). There have been several previous studies of the leaching and electrochemistry of chalcopyrite in the ammoniacal system (Hockings and Freyberger, 1976; Beckstead and Miller, 1977; Dutrizac, 1981; Warren and Wadsworth, 1984; Limpo et al, 1992, 1992a; Bell et al, 1995; Moyo et al, 2015). However, these studies were generally not undertaken with heap leaching in mind i.e. at low (less than 9) pH values at low temperatures. As far as the author is aware, there are no published studies of the electrochemistry of chalcopyrite in the glycine system.

This paper presents selected results from a more detailed study of the electrochemistry and dissolution of chalcopyrite in ammonical solutions at pH values

below 9. Similar limited electrochemical experiments have been conducted with glycine that allow for a direct comparison between the two lixiviants.

## 2. Experimental

The methods used in the leaching and electrochemical experiments are as previously described (Velasques et al, 2010; Nicol, 2017). A rotating chalcopyrite electrode was fabricated as previously described (Nicol, 2017) using a pure sample of natural chalcopyrite from China. Unless otherwise stated, all electrochemical experiments were conducted at 25°C and all potentials shown are versus the standard hydrogen electrode. The copper concentrate was prepared by flotation from Pinto Valley in the USA and contained greater than 90% of the copper as chalcopyrite. The mineralogical analysis (Qemscan) of the sulfide minerals and the chemical and analysis of the -38 um size fraction used are shown in Table 1.

**Table 1. Mineralogy of Sulfide Minerals in the Concentrate**

Mineral	Mass %
Chalcocite	<0.1
Chalcopyrite	45.8
Covellite	<0.1
Bornite	0.1
Enargite	<0.1
Pyrite	20.9
% Cu	18.0
% Fe	30.2

## 3. Results

### 3.1 Thermodynamic Analysis

Given the low reactivity of dissolved oxygen for the oxidation of most sulfide minerals under ambient conditions, the focus should be on alternative oxidants and, in particular, the use of redox mediators such as the iron(III)/iron(II) couple in acid

solutions. In ammoniacal systems, an in-situ suitable mediation system involves the copper(II)/copper(I) system.

Table 2 summarizes the relevant thermodynamic data for the ammonia and glycine copper systems. It is important to note that both ammonia and glycine have similar acid-base properties (one can ignore the protonation of glycine at low pH values).

**Table 2. Thermodynamic Data (Martell and Smith, 2004)**

Reaction	K	Log K
$\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$	2.64E+09	9.42
$\text{Cu}^{2+} + \text{NH}_3 = \text{Cu}(\text{NH}_3)^{2+}$	2.00E+04	4.30
$\text{Cu}^{2+} + 2\text{NH}_3 = \text{Cu}(\text{NH}_3)_2^{2+}$	7.90E+07	7.90
$\text{Cu}^{2+} + 3\text{NH}_3 = \text{Cu}(\text{NH}_3)_3^{2+}$	5.01E+10	10.70
$\text{Cu}^{2+} + 4\text{NH}_3 = \text{Cu}(\text{NH}_3)_4^{2+}$	1.26E+13	13.10
$\text{Cu}^+ + \text{NH}_3 = \text{Cu}(\text{NH}_3)^+$	2.18E+06	6.34
$\text{Cu}^+ + 2\text{NH}_3 = \text{Cu}(\text{NH}_3)_2^+$	6.52E+10	10.81
$2\text{Cu}^{2+} + \text{Cl}^- + 3\text{OH}^- = \text{Cu}_2\text{Cl}(\text{OH})_3(\text{s})$	4.79E-35	-34.32
$\text{Gly}^- + \text{H}^+ = \text{HGly}$	6.46E+09	9.81
$\text{HGly} + \text{H}^+ = \text{H}_2\text{Gly}^+$	2.24E+02	2.35
$\text{Cu}^{2+} + \text{Gly}^- = \text{CuGly}^+$	2.29E+08	8.36
$\text{Cu}^{2+} + 2\text{Gly}^- = \text{CuGly}_2$	2.51E+15	15.4
$\text{CuGly}^+ + \text{H}^+ = \text{CuHGly}^{2+}$	8.32E+02	2.92
$\text{Cu}^+ + 2\text{Gly}^- = \text{CuGly}_2^-$	1.26E+10	10.1
$\text{Cu}(\text{NH}_3)_4^{2+} + \text{e} = \text{Cu}(\text{NH}_3)_2^+ + 2\text{NH}_3$	0.182V	pH 8
$\text{CuGly}_2 + \text{e} = \text{CuGly}_2^-$	-0.159V	pH 8

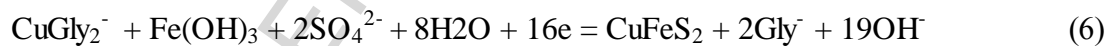
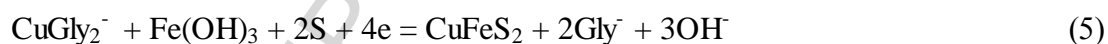
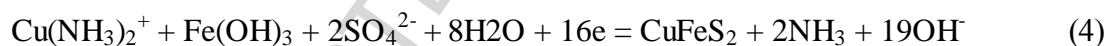
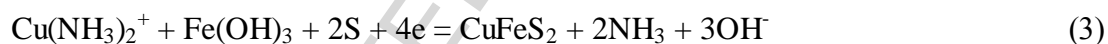
Also, note that copper(I) diammine (most predominant species) is somewhat more stable than that of the diglycinate complex while the copper(II) glycinate complexes are considerably more stable than the ammines due to a chelate effect with the carboxyl group in glycine. The consequence of this is that the potential of the

copper(II)/copper(I) couple is some 0.24V more positive in the ammoniacal compared to the glycine system. This has important consequences for the relative rates of dissolution and possible redox mediation as will be demonstrated below. This problem would apply to the potential use of any  $\alpha$ -aminoacid.

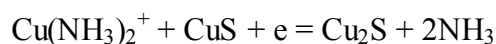
The data in Table 2 together with the standard potentials (HSC Chemistry, V8) for the reactions



were used to derive values for the potentials of the following reactions (Gly<sup>-</sup> is the glycinate ion) as a function of pH using an iterative Excel spreadsheet. Although sulfate ions have generally been postulated as the main product of oxidation of chalcopyrite in ammoniacal systems, elemental sulfur is a minor product. In fact, recent work has shown that thiosulfate is probably the main product of anodic dissolution at low temperatures (Moyo et al, 2015). There is no experimental data for the stoichiometry in the glycine system.



The results of these calculations are shown in Fig. 1 for the ammoniacal system and Fig. 2 for the glycine system. Also shown in the figures are the lines for the oxidation of chalcocite to covellite (7) and covellite to copper(I) and sulphur (8) that were calculated by combining the relevant data in Table 2 with the following standard potentials.



(7)







1.076V

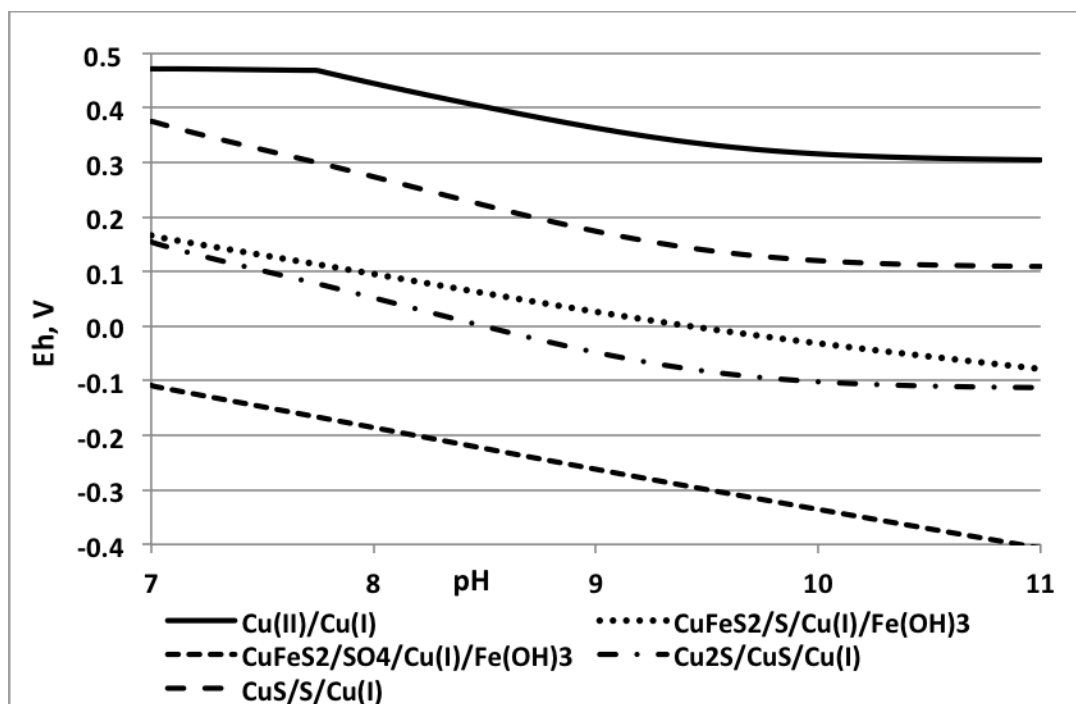


Fig. 1 Partial Eh/pH diagram for the copper/chalcopyrite system in 0.5M total ammonia/ammonium in the presence of 0.5M chloride and 0.5M sulfate. The Cu(II) concentration is 0.5 g/L and Cu(I) is 0.05 mg/L.

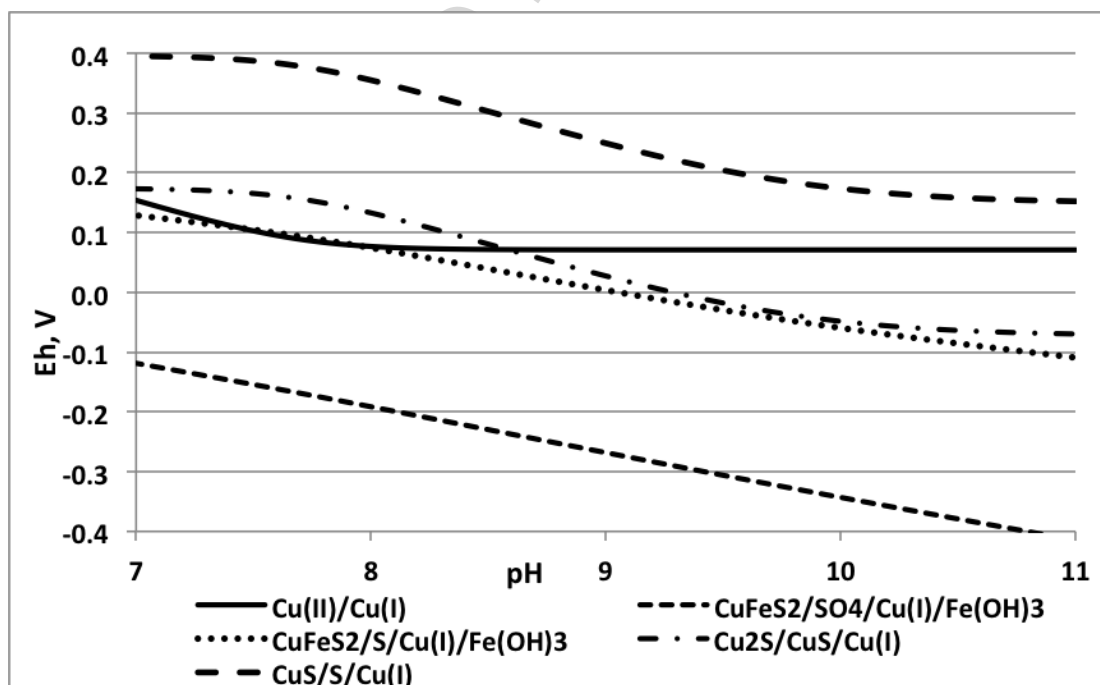


Fig. 2 Partial Eh/pH diagram for the copper/chalcopyrite system in 0.5M total glycine in the presence of 0.5M chloride and 0.5M sulfate. The Cu(II) concentration is 0.5 g/L and Cu(I) is 0.05 mg/L.

The calculated lines for thiosulfate as a product are not shown to simplify the diagrams but they lie almost in the middle of the lines for sulfate and sulfur. The line for reduction of oxygen is also not shown because it lies well above all the lines shown. A high value of 10000 for the copper(II)/copper(I) ratio has been used as copper(I) is rapidly re-oxidised by dissolved oxygen in the ammoniacal system (Zuberbuhler, 1967). No data is available for the kinetics in the glycine system.

There are several important points to note:

1. Copper(II) ions can oxidise chalcopyrite at all pH values in the ammoniacal system because the line for this couple lies well above the lines for the oxidation of chalcopyrite.
2. In the glycine system, it is not possible to oxidise chalcopyrite to sulfur using copper(II) as the oxidant except at high pH values.
3. In the glycine system, oxidation of chalcopyrite to sulfate is possible at all pH values using copper(II) as the oxidant even at lower copper(II)/copper(I) ratios. This equilibrium becomes more favourable at higher pH values.
4. In all cases, the equilibrium involving dissolved oxygen as the oxidant is very favourable.
5. Oxidation of chalcocite to covellite is possible in the ammonia and in the glycine system at high pH values. Oxidative dissolution of covellite would be possible in the ammoniacal system but not in the glycine system using the copper(II) complexes as oxidants.

### 3.1 Electrochemical Measurements

A number of electrochemical experiments were undertaken to establish the main characteristics of the electrochemistry of chalcopyrite in both lixiviant systems using either (or both) copper(II) and dissolved oxygen as the oxidants. These involved mainly mixed potential and slow linear sweep voltammetric measurements. In the case of the ammoniacal system, many additional experiments under different conditions were undertaken using, in addition, potentiostatic measurements that have not been included in this comparative study.

The mixed potentials of chalcopyrite in glycine solutions at pH values of 10 and 8 were measured and the data for pH 10 is shown in Fig. 3. At both pH values the potential is greater with 0.0125 M copper(II) than oxygen suggesting that the rate of

dissolution would be greater with the former as the oxidant. The potential when both oxygen and copper(II) are present is slightly higher than that in the presence of copper(II) alone at pH 10. Also shown is the mixed potential of a covellite electrode under the same conditions. This will be discussed in a later section.

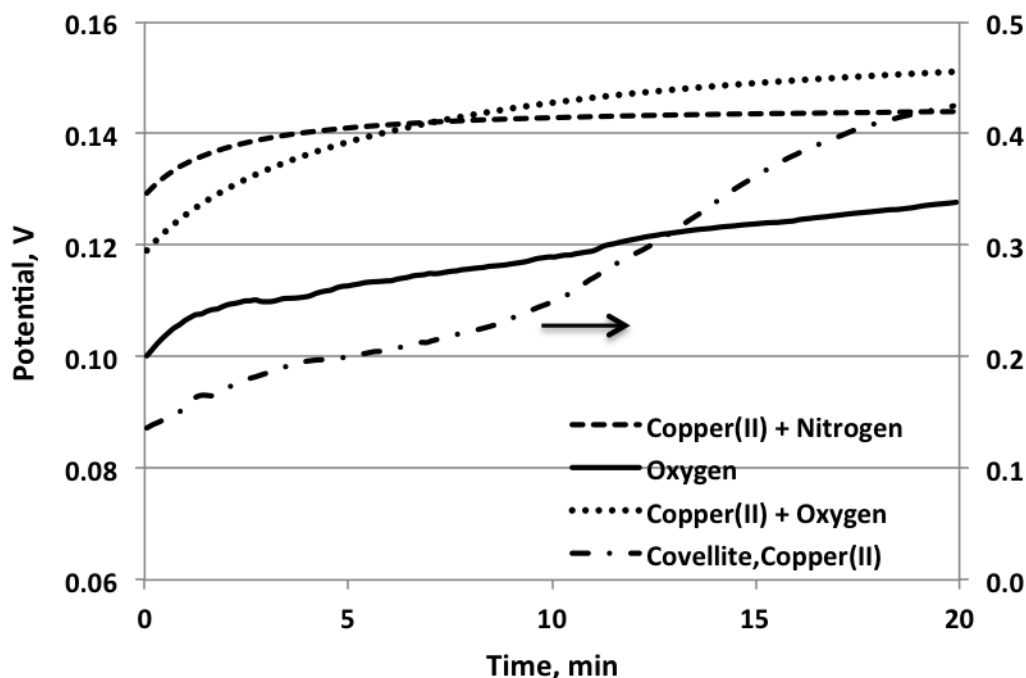


Fig. 3. Effect of copper(II) and dissolved oxygen on the mixed potential of a rotating (200 rev/min) chalcopyrite electrode in a solution of 0.5M glycine at pH 10. The copper concentration was 0.0125M (0.8 g/L). Also shown is data for covellite under the same conditions.

Corresponding data for the ammonium chloride system is shown for pH 8 in Fig. 4. In the case of ammonium chloride solutions, the difference between the mixed potentials in the presence of copper(II) and oxygen are noticeably greater suggesting that the relative rates of dissolution with copper(II) or oxygen as the oxidants will be greater than in the glycine system.

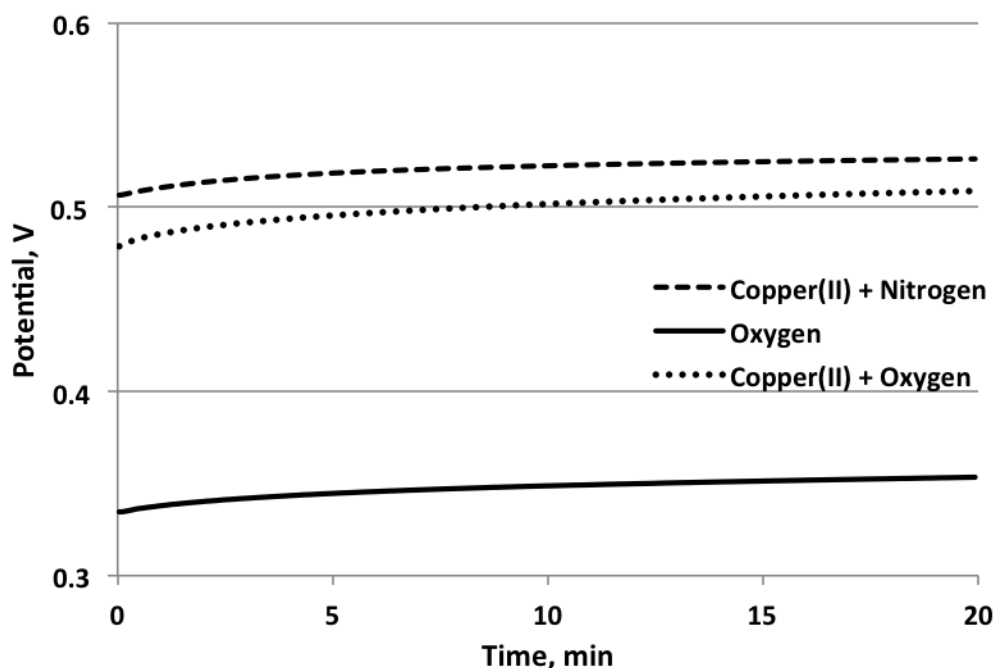


Fig. 4 Effect of copper(II) and dissolved oxygen on the mixed potential of a rotating (200 rev/min) chalcopyrite electrode in a solution of 0.5M ammonium chloride at pH 8. The copper concentration was approximately 0.008M (0.5 g/L).

The behaviour of the two lixivants are further compared in Fig. 5 that shows the increase in open-circuit potentials of chalcopyrite in deaerated solutions of either glycine or ammonium chloride on addition of copper(II) at point A. The potential further increases when oxygen replaces the nitrogen at point B and decreases again when oxygen is removed at point C. Variation of agitation (by switching off rotation) at various times showed no effect of mass transport on these potentials in the glycine solution but decreases at about 30 min and 80 min in the ammonium chloride solution in the absence of agitation. Note the significantly higher mixed potential in the ammonia system.

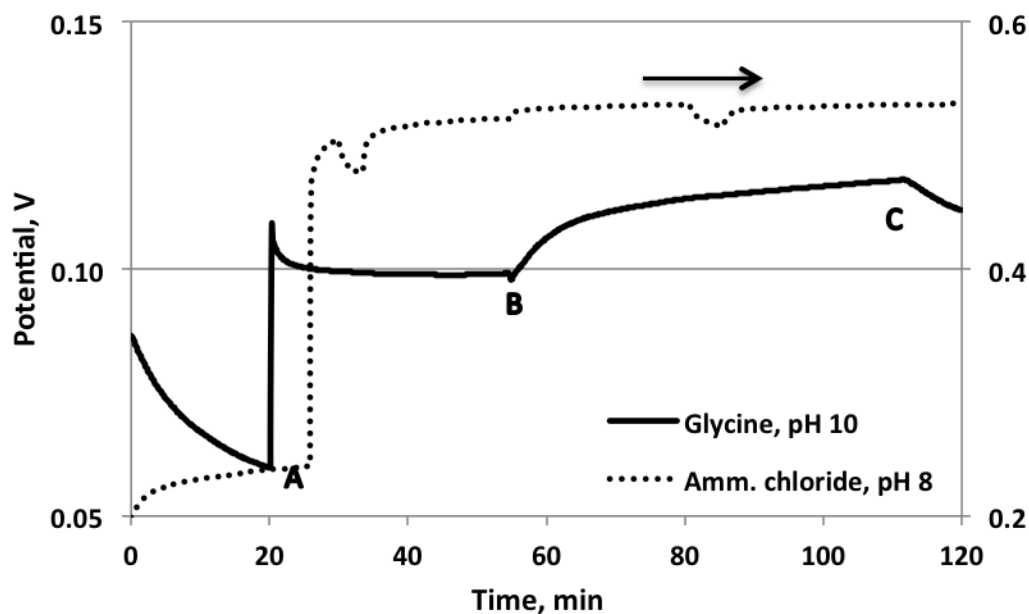


Fig. 5 Effect of copper(II) and dissolved oxygen on the mixed potential of a rotating (200 rev/min) chalcopyrite electrode in a deaerated solutions of 0.5M glycine at pH 10 and 0.5M ammonium chloride at pH 8. Copper was added at point A to give a concentration of 0.0125M (0.8 g/L). At point B, the nitrogen was replaced with oxygen and at point C the oxygen replaced with nitrogen.

The relative rates of dissolution can be further compared by consideration of the mixed potentials shown in Fig. 6. The solutions used were pre-oxidised by the use of oxygen before nitrogen was used to deoxygenate the solutions. This was done to ensure an initial high Cu(II)/Cu(I) ratio. In this case, the potential ( $E_h$ ) of a platinum electrode immersed in the same solution was also monitored. In the case of glycine, the  $E_h$  was significantly higher than the chalcopyrite potential ( $E_m$ ) and remained constant over the hour suggesting that the rate of dissolution is very slow. On the other hand, in the ammonium chloride solution, the  $E_h$  decreased with time while the  $E_m$  increased and converged to the  $E_h$ . The decrease in  $E_h$  is due to copper(I) formed by oxidative dissolution (combination of reactions 1 and 3) and the decay in  $E_h$  can, in theory be used to estimate the initial rate of dissolution.

Some of these conclusions could change depending on the copper(II) concentration and the oxygen partial pressure. Thus, the conditions used of low copper(II) concentration and pure oxygen favoured oxygen over copper(II) as an oxidant. Higher concentrations of copper(II) could not be used for this comparison due to precipitation in the ammonium chloride system (see below).

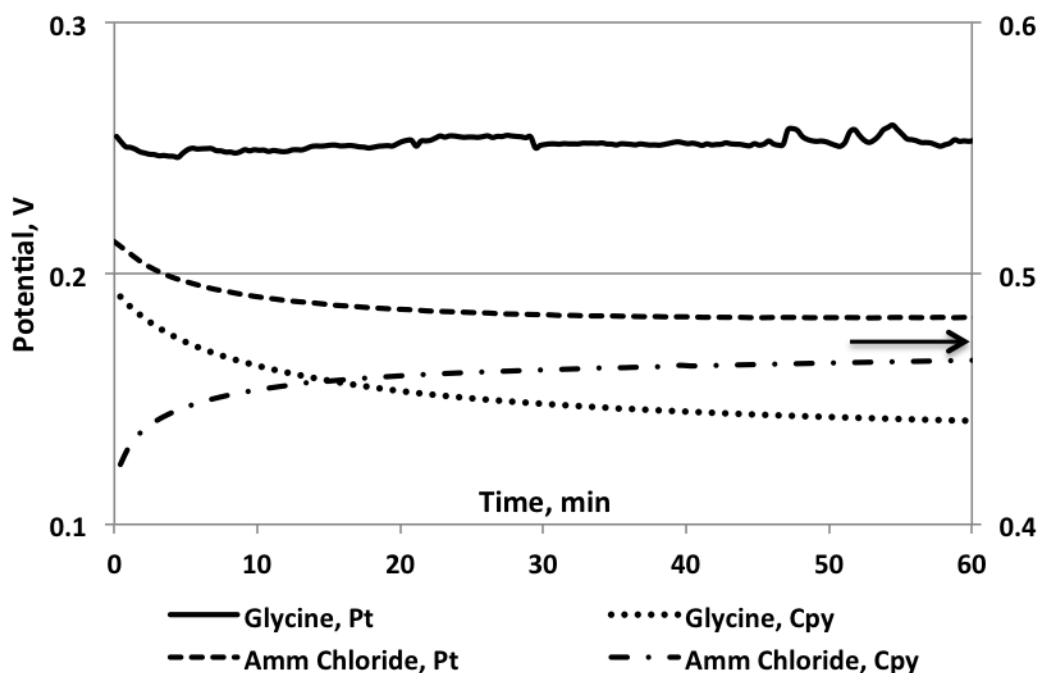


Fig. 6 Comparison of chalcopyrite and Pt potentials in deaerated solutions of either 0.5M ammonium chloride (right axis) at pH 8 or 0.5M glycine (left axis) at pH 10. The copper(II) concentrations were 0.4 g/L and 0.8 g/L respectively.

Linear sweep voltammograms for the oxidation of chalcopyrite are shown in Fig. 7 for solutions containing glycine or ammonium chloride. The curves shown are the negative-going branches of the voltammograms initiated in a positive direction from the open-circuit potentials. It appears that there is little difference in the anodic behaviour in the two solutions at pH 8 while the effect of pH is significant with oxidation in glycine becoming more favourable at the higher pH. This is consistent with the thermodynamic predictions shown in Fig. 2. The same is true for the greater reactivity at pH 9 in the ammoniacal system. Higher pH values were not studied in the case of ammonium chloride given the undesirability of ammonia losses at higher pH values.

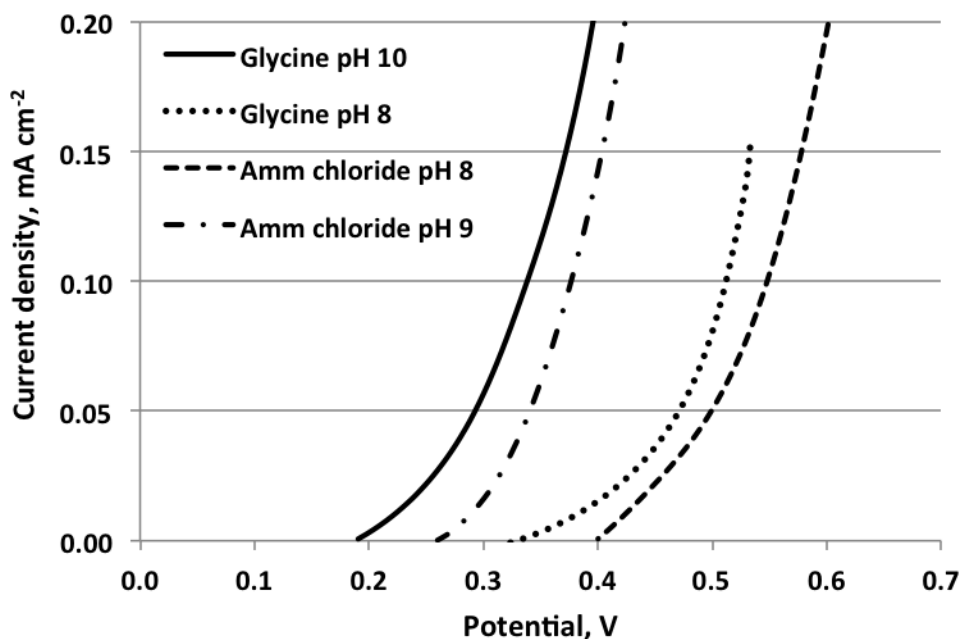


Fig. 7 Linear sweep (0.2mV/s) voltammograms for the oxidation of a rotating (200 rev/min) chalcopyrite electrode in solutions of 0.5M glycine or 0.5M ammonium chloride.

Although in theory, one can estimate the rates of dissolution from the mixed potentials and the anodic dissolution curves (see below), it was considered desirable to also study the rates of the cathodic reduction of copper(II) and/or oxygen. Fig. 8 presents the results of linear sweeps in a negative direction from the mixed potential in glycine solutions containing copper(II) or dissolved oxygen and both at pH 10. The corresponding data for pH 8 is summarized in Fig. 9.

These results confirm the thermodynamic analysis in Fig 2 that reduction of copper(II) becomes more difficult i.e. shifts to more negative potentials at the higher pH. It is also apparent that reduction of copper(II) occurs at a greater rate than that of oxygen in the region of the mixed potential.

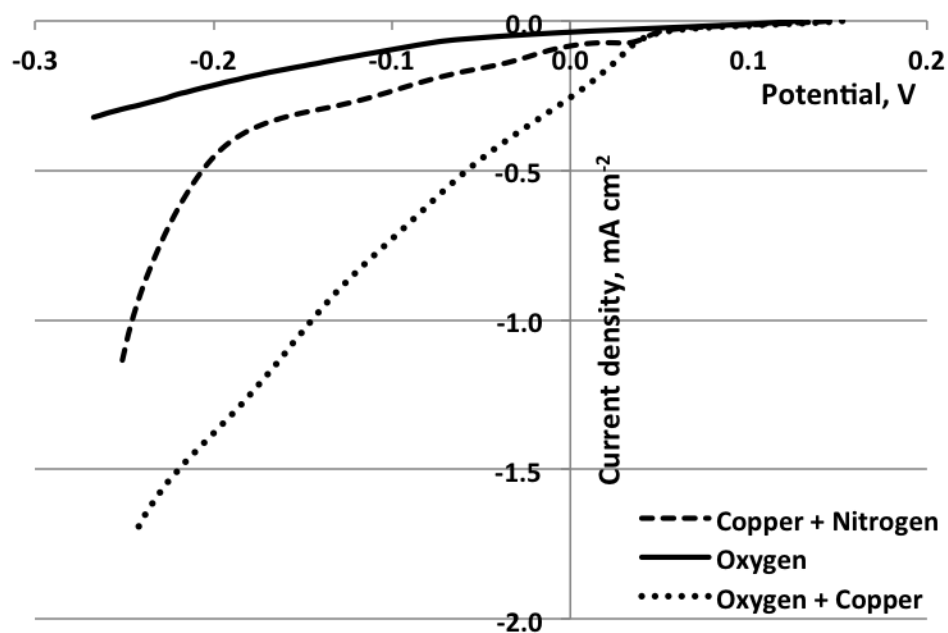


Fig. 8 Linear sweep voltammograms (0.2mV/s) in a negative direction from the rest potential of a rotating (200 rev/min) chalcopyrite electrode in a solution of 0.5M glycine at pH 10.0. The copper(II) concentration was 0.0125M (0.8 g/L).

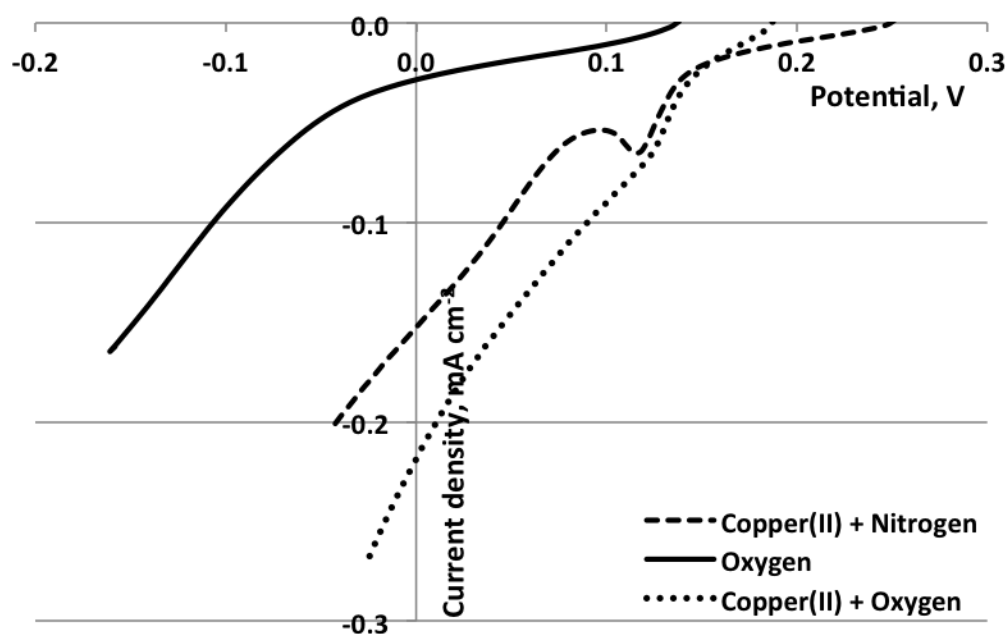


Fig. 9 Linear sweep voltammograms (0.2mV/s) in a negative direction from the rest potential of a rotating (200 rev/min) chalcopyrite electrode in a solution of 0.5M glycine at pH 8.0. The copper(II) concentration was 0.0125M (0.8 g/L).

This is also observed in the ammonia system and confirms the conclusion that the effective oxidant in these systems is the copper(II) ion and not dissolved oxygen



(Moyo et al, 2015). Note that in a heap leaching environment, air and not oxygen would be used and the above current densities at all potentials for the reduction of oxygen would be reduced by a factor of about 5.

The current densities in the presence of both copper(II) and oxygen are generally greater than the sum of the individual reactions suggesting that some degree of synergism (Miki and Nicol, 2008) is operative in this system. Details are beyond the scope of this paper as are the shapes of these cathodic curves and the appearance of a cathodic peak at about 0.1V in the curves in the presence of copper(II) at pH 8.

Similar plots for the cathodic reactions in the ammonium chloride system at pH 8 are shown in Fig. 10. As predicted from the calculated potentials for the copper(II)/copper(I) couple in Fig. 1 and Fig. 2, the curves in ammonium chloride are shifted by some 0.25V in a positive direction from those in glycine. In addition, the curves in Fig. 10 are “well behaved” in the sense that they exhibit no unusual peaks but as expected show limiting current densities at high overpotentials and no interaction between the processes for oxygen and copper(II) reduction.

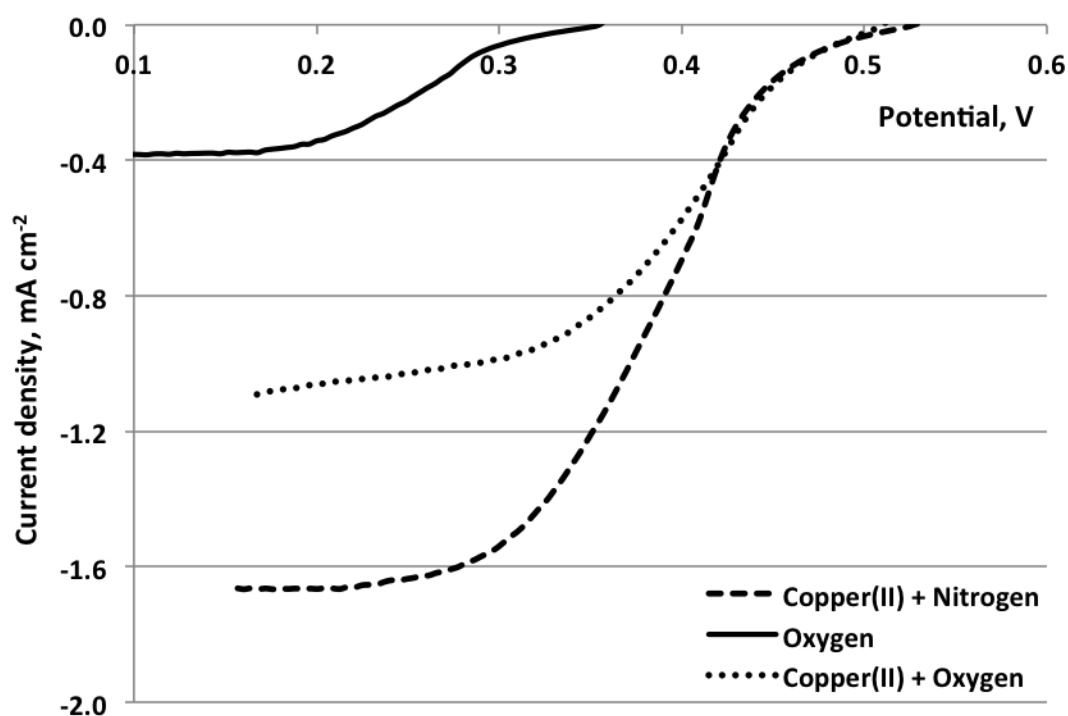


Fig. 10 Linear sweep voltammograms (0.2mV/s) in a negative direction from the rest potential of a rotating (200 rev/min) chalcopyrite electrode in a solution of 0.5M ammonium chloride at pH 8.0. The copper(II) concentration was 0.0125M (0.8 g/L).

The lower limiting current density in the curve for copper(II) + oxygen is due to visible partial precipitation of copper(II) in this solution (see below). In this case, it is more obvious that reduction of copper(II) is preferred to that of oxygen in the mixed potential model for this system.

The anodic dissolution curves shown in Fig. 7 were analysed as Tafel plots (slopes varied from 150 to 165 mV/decade) and the current densities at the mixed potentials in the solutions containing copper(II) or/and oxygen were estimated and are summarized in Table 3. These rates could be expected to increase with increasing concentrations of glycine or ammonium chloride.

**Table 3. Estimated rates of dissolution of chalcopyrite**

Oxidant	Rate of dissolution, mA cm <sup>-2</sup>		
	0.5 M Glycine		0.5M NH <sub>4</sub> Cl
	pH 8	pH 10	pH 8
0.0125M Cu(II)	0.0012	0.0070	0.073
Oxygen	0.00019	0.0050	0.0074
Cu(II) + oxygen	0.0043	0.0063	0.058

Although the anodic dissolution data used to derive these estimates were not obtained under completely steady-state conditions, potentiostatic measurements showed that the current densities on the reverse sweep during slow sweep voltammetry provide reasonable estimates of steady-state behaviour (on average about 20% higher than steady-state that is generally achieved in less than one hour). Thus, at least for comparative purposes, the above results are useful. There are two main conclusions from the above.

1. The rate of dissolution of chalcopyrite in ammonium chloride solutions is at least an order of magnitude greater than that in glycine solutions under the same conditions. This was expected given the lower potential for the copper(II)/copper(I) couple in the glycine system that does not allow sufficient overlap of the anodic and cathodic reactions in the mixed potential system.
2. The rate of dissolution in glycine solutions increases with increasing pH but at pH 10 the rate is still significantly less than that in ammonium chloride at pH 8. It could be expected that the rate would also increase with increasing pH in the ammonium chloride system given the greater reactivity at pH 9 shown in

Fig. 7. This is in agreement with the results of a study (Durizac, 1981) of percolation leaching of a chalcopyrite ore in ammonium carbonate solutions which found that the rate increased from pH 7.5 to pH 10 and was constant at higher pH values. The rate would not be expected to increase significantly at pH values greater than  $pK_b + 1$  above which the speciation would not change to any extent. In the glycine system, this could be predicted for pH values above about 11.

## 2.2 Leaching of Secondary Copper Sulfides

Although not the primary subject of this paper, it is useful to predict the behaviour of secondary copper sulphides such as chalcocite and covellite in these systems. As indicated in Fig. 1 and Fig. 2 the dissolution of chalcocite is marginally possible and that of covellite very unlikely in the copper(II)-mediated glycine system while there are no such restrictions in the ammoniacal system. This was confirmed by the mixed potential measurements shown in Fig. 3 that revealed that the mixed potential of covellite in the glycine system is significantly more positive than that of chalcopyrite as predicted from Fig. 2. At these relatively high potentials, reduction of copper(II) is not possible while that of dissolved oxygen will be very slow. As a consequence, one must conclude that covellite will not dissolve at acceptable rates in the glycine system even under the most favourable conditions. The same is possibly true of chalcocite although no electrochemical measurements have been made. Thus, it could be expected that ores containing chalcocite will yield at most 50% extraction of copper from the chalcocite content (chalcocite dissolves with the formation of covellite as an intermediate).

No such thermodynamic restrictions apply to the ammoniacal system although there are as yet no data to make conclusions about the rates. During the oxidative dissolution of a sulfide mineral hosted in gangue, mass transport of copper(II) and dissolved oxygen to the mineral surface through cracks and pores in the ore particles and the absence of a "redox buffer" in these systems could further limit the potential (and therefore the rate) at the mineral surface i.e. the above data can only apply to the favourable case of exposed mineral surfaces.

## 3.3 Leaching in the ammoniacal system

It is considered desirable to include the results of some limited experiments using ammonium chloride solutions. These results are a small part of a much larger experimental and pilot program, the full details of which are confidential. Nevertheless, the results presented below are important in terms of defining the advantages and limitations of ammoniacal heap leaching.

The results of two leaching experiments using a chalcopyrite concentrate (-38 $\mu$ m) in aerated ammoniacal solutions at low pH are shown in Fig. 11 together with data obtained using acidic dilute chloride solutions at controlled potential (Velasques et al, 2010). The results show relatively rapid dissolution in ammonium chloride solutions but much slower dissolution in ammonium sulfate solution at the same total ammonium ion concentration. This confirms published data (Limpo et al, 1992, 1992a) on the relative rates in the chloride and sulfate systems. Similar comparative results were obtained at higher pH values. The rate in ammonium chloride is also significantly greater than that in the optimized acid chloride system.

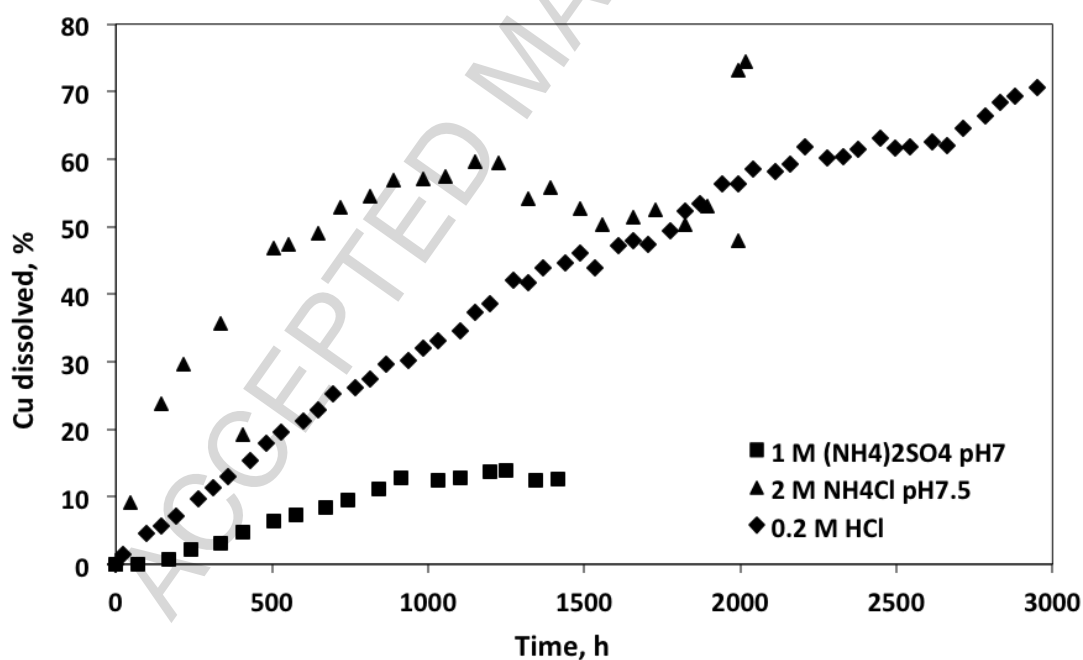


Fig. 11. Dissolution of copper from a chalcopyrite concentrate in ammoniacal solutions containing initially 0.5 g L<sup>-1</sup> copper(II) at 25°C. Also shown for comparison is the data under comparable conditions in acidic chloride solutions.

The rapid rate of oxidation of copper(I) ammine by dissolved oxygen (Zuberbuhler, 1967) allows oxygen to be used as the primary oxidant with the copper(II)/copper(I) couple acting as an efficient redox mediator.

The decrease in recovery after about 1300 hours in the ammonium chloride system is suggested as being due to precipitation of pale green basic copper(II) chloride  $\text{Cu}_2\text{Cl}(\text{OH})_3$  (composition of the mineral atacamite). Addition of acid at 2000 hours to reduce the pH to 2 resulted in a rapid increase of about 25% in copper recovery due to dissolution of the leached but precipitated copper(II).

Fig. 12 shows the calculated solubility of copper(II) in solutions of 0.5 M and 2.0 M ammonium chloride initially containing 0.157 M (10 g/L) copper(II) as a function of pH. The data in Table 2 was used in an iterative Excel procedure for these calculations based on the solid being atacamite.

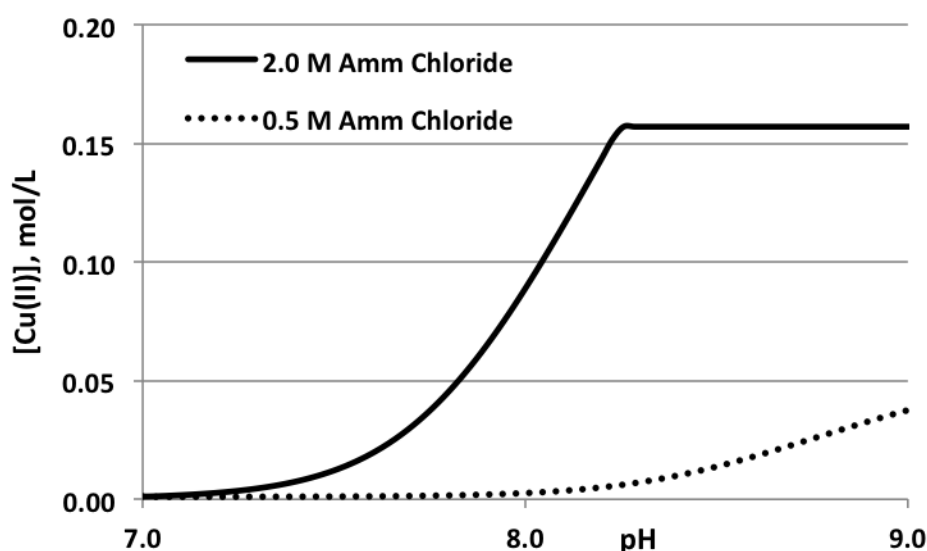


Fig. 12. Calculated solubility of copper(II) in 0.5 M and 2.0 M ammonium chloride at 25°C in solutions containing initially 0.157M (10 g/L) copper(II).

These calculations confirm the observations in Fig. 10 and also visible but slow precipitation of copper in a solution of 0.5M ammonium chloride at pH 8 containing initially 0.5 g/L copper(II). No precipitation was observed in the glycine system due to the greater stability of the copper(II) glycinate complexes that stabilize copper in solution and calculations confirmed that precipitation should not occur even at pH values as low as 6.

Thus, heap leaching of any copper minerals in ammoniacal solutions will need to be conducted at pH values above about 8 in ammonium chloride solutions to avoid precipitation of atacamite. The equivalent diagram for sulfate solutions is similar with brochantite being the solid species that will be expected to precipitate at pH values below about 8. Although the use of high pH is desirable to minimize precipitation and maximize rates, the use of excessively high pH values will result in conversion of most of the ammonium ions to free ammonia that will be lost by vaporization.

Data obtained during 1m column leaching of agglomerated ore from which the concentrate was obtained as used in the experiments shown in Fig. 10 is summarized in Fig. 13 together with data obtained during acid chloride (1 mol/L sodium chloride at pH 1 with 0.5 g/L copper(II)) leaching of the same ore.

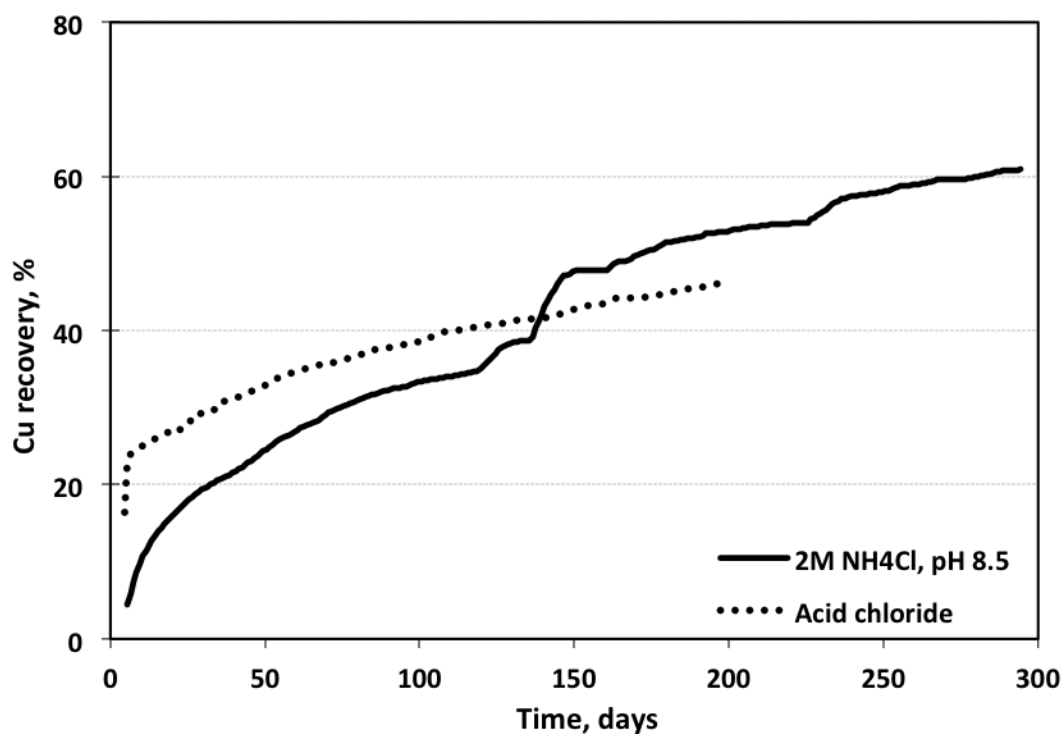


Fig. 13. Dissolution of copper from a chalcopyrite ore in ammoniacal solutions containing initially  $0.5 \text{ g L}^{-1}$  copper(II) at  $25^\circ\text{C}$ . Also shown for comparison is the data under comparable conditions in acidic chloride solutions.

The results show that copper can be initially effectively leached in ammonium chloride solution with about 35% recovery after about 125 days at which time the pH was reduced to 1.5 in the raffinate fed to the column. This resulted in a rapid increase in recovery to about 48% after after 150 days after which the pH was again increased

to 8.5. As in the case of concentrate leaching, this increase is due to acid dissolution of copper precipitated even at pH 8.5 during ammoniacal leaching. At lower ammonium chloride concentrations and lower pH values, the rates achieved were considerably lower than those obtained during acid chloride leaching.

#### 4. Practical considerations and comparison of ammoniacal and glycine systems.

The overall reactions that could be expected to occur during leaching in a heap at pH values below the  $pK_b$  of the lixivants are



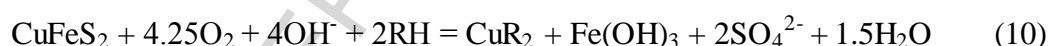
in which Gly<sup>-</sup> is the glycinate ion.

Note that hydroxide ions are consumed in the process and the pH will decrease unless base is added. This could be limestone added to the ore before loading on the heap. Furthermore, during the extraction stage of the copper ammine in solvent extraction, the following reaction can be written,



in which RH is the protonated extraction reagent, recycled from stripping.

The sum of (7) + (9), gives



For the glycine system, the overall equation is similar.

Thus, there is an overall requirement of 4 moles of base per mole of copper leached. Although the results obtained as described above indicate that the leaching of chalcopyrite using ammoniacal or glycine systems could be attractive from a kinetic point of view, there are many important practical and economic considerations that have to be borne in mind.

- a) In addition to the cost of the lixivants, a neutralizing reagent is required.
- b) While addition of a neutralizing agent could maintain the pH at a level appropriate for efficient leaching, a high pH would lead to loss of ammonia in

the ammoniacal system and a low pH to slower leaching using either lixiviant and precipitation of copper(II) in the ammonical system.

- c) The extraction of copper(II) ammines from the pregnant leach solutions by conventional solvent extraction reagents is not well known technology and has not been investigated for the glycine system.

Although the glycine system has the advantages of no losses of lixiviant due to volatilization at any pH and also no precipitation of copper(II) even at low pH values, it suffers from the disadvantages of high reagent costs (US\$1000/t in 100t lots FOB China--Alibaba.com) and relatively low leach rates. On the other hand the ammonium chloride system has the advantages of significantly lower costs (US\$90/t in 100t lots FOB China) and greater rates of extraction even at low pH values. On a mole basis, ammonium chloride is some 16 times less expensive than glycine.

Column testwork in both 1m and 6m columns on the same ore from which the concentrate used above was obtained has shown disappointing results using ammonium chloride even at pH 8.5. (Fig. 12). The results were comparable to an acid chloride leach and significant losses of ammonia were observed as predicted.

The above considerations concur with a previous study (Durizac, 1981) that concluded that “ammonia losses appear to be the most significant technical and economic barrier to commercial adaptation of ammoniacal percolation leaching”. To this could be added that low leach rates, thermodynamic restrictions on the leaching of covellite and cost are the equivalent barriers to the use of glycine.

## 5. Conclusions

The results of this investigation into the possible use of ammonium chloride or glycine as lixiviants in the heap leaching of chalcopyrite-rich ores has provided good comparative data with which to compare the reagents and also identified several important observations that need to be taken into account when considering such processes.

- a) The high stability of the copper(II) glycinate complexes results in low reactivity (as measured electrochemically) for the oxidation of chalcopyrite except perhaps at high pH values.
- b) The lower stability of the copper(II) ammine complexes results in significantly greater (fifty-fold) rates in the ammonium chloride system under the same



conditions. The rates are tenfold higher for the ammonium chloride system at pH 8 compared to glycine at pH 10.

- c) Loss of copper(II) by precipitation as a basic chloride (atacamite) in the ammonium chloride system occurs at pH values below about 8 depending on the ammonium chloride concentration. This could, in theory, be recovered during the latter stages of the life of a heap when the copper(II) concentration in the leach solution is low.
- d) Based on a thermodynamic analysis and mixed potential measurements, it is unlikely that covellite will dissolve in the glycine system and this possibly also applies to chalcocite.
- e) The relatively high cost of glycine and even of ammonium chloride would probably preclude use of these reagents unless the rates of leaching can be made significantly greater than those of alternative lixiviant systems. Even for ores with a high acid consumption the economics of the ammoniacal and glycine systems would have to be carefully evaluated.

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**Highlights**

- The high stability of the copper(II) glycinate complexes results in low reactivity for the oxidation of chalcopyrite
- The lower stability of the copper(II) ammine complexes results in significantly greater (fifty-fold) rates in the ammonium chloride system
- Loss of copper(II) by precipitation as a basic chloride in the ammonium chloride system occurs at pH values below about 8.
- It is unlikely that covellite will dissolve in the glycine system and this possibly also applies to chalcocite.
- The relatively high cost of glycine and even of ammonium chloride would probably preclude use of these reagents.