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The dissolution of chalcopyrite in chloride solutions. Part 2. Effect of various parameters on the rate.

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Abstract

In Part 1 of this series, which describes the results of a study of the dissolution of chalcopyrite under conditions that could be expected in a heap leaching process for primary copper minerals, it was shown that enhanced leaching of chalcopyrite from several copper concentrates in dilute acidic chloride solutions can be achieved by controlling the potential in a range of 560-600 mV (SHE) in the presence of dissolved oxygen. Based on the results of these experiments, this paper reports on an extensive study of the kinetics of the dissolution of several of chalcopyrite concentrates in chloride solutions under various conditions in specially designed reactors.

It will be demonstrated that the rates of dissolution at constant potential in the range 580-600 mV by control of the oxygen supplied to the reactor are approximately constant for up to 80% dissolution for sized fractions of the concentrates. The rate of dissolution of chalcopyrite under these conditions is largely independent of the pulp density, iron and copper ion concentrations which could be expected in a heap leach operation, the acidity and the chloride ion concentration. Variation of the temperature in the range 25 to 75°C under otherwise constant conditions resulted in an activation energy for dissolution of two different concentrates of 72 kJ mol\(^{-1}\).
Keywords: Chalcopyrite; Heap leaching; Chloride; Kinetics; Controlled potential; Passivation.

1. Introduction

A number of investigations have been conducted to elucidate the reaction kinetics and delineate the important variables for the leaching of chalcopyrite in both chloride and sulfate systems. Although many researchers have reported relevant work, some ambiguities remain. Despite the considerable literature on the kinetics of leaching in ferric and more recently cupric solutions containing chloride ions, there is no general agreement among the various authors about the rate-determining step, activation energy, the form of the leaching curves and the dependence of the rate on the solution composition. Most studies have been conducted at elevated temperatures because of the very low rates of dissolution under ambient conditions which would be appropriate under heap leaching conditions.

Most of the studies agree that rate of leaching of chalcopyrite in chloride media is linear with the time, but some authors have suggested that parabolic or para-linear kinetics are appropriate. In this context Dutrizac (1981), suggested that the para-linear kinetics obtained by Ammou-Chokroum et al. (1981) was due to experimental limitations involving an un-sintered disk containing both very fine and very coarse particles.

According to Dutrizac (1981), the surface area is one of the principal variables and any kinetic study must adequately characterize the area. He suggested that the ideal method for producing a sized feed for kinetics studies is wet cyclo-sizing of small batches, but wet screening is acceptable if carried out thoroughly enough to remove all fines.
Concerning the rate-limiting step, the reported data are very controversial in that some authors have concluded that it is mass transport controlled while others have suggested chemical control. Some of the studies reporting mass transport control are questionable given that the activation energies are too high to be indicative of mass transport control while in other studies the rates are slower and independent of rotation speed. For example, Havlik and Kammel (1995) suggested chemical control at higher temperatures (45-80 °C) and diffusion control at lower temperatures (35-45 °C) based on values of the activation energy.

Another controversial aspect that has appeared in published kinetic studies of the chloride system is the effect of the nature and concentration of the reactants on the rate of dissolution. The presence of ferrous ions even at high concentrations has a negligible effect on the rate at high temperatures (Dutrizac, 1978; Hirato et al., 1986; Jones and Peters, 1976; Majima et al., 1985). The latter authors also found that the presence of ferrous chloride does not affect the mixed potential of chalcopyrite suggesting that the anodic reaction of ferrous ions on the chalcopyrite surface is slow.

Chalcopyrite has been successful leached in presence of cupric ions (Bonan et al., 1981; Dutrizac, 1978; Guy et al., 1983; Hirato et al., 1986; Hirato et al., 1987; Wilson and Fisher, 1981). Jones and Peters (1976) proposed that the fast kinetics for the ferric chloride system were a result of catalysis of the reaction by cupric ions and that ferric chloride leaching is in reality cupric chloride leaching.

Even though temperature is one of the most important parameters in the kinetics of the leaching of chalcopyrite in chloride media, it has been difficult to determine its effect accurately (Dutrizac, 1981). According to this author, the difficulty is due in part to the
presence of even small amounts of secondary copper mineralization that can seriously affect the interpretation of leaching data, especially at low temperatures where the total dissolution of copper is small. However, the agreement among the various authors is that an increase in temperature produces a substantial increase in the rate of dissolution. Researchers claim that the activation energy is dependent on the range of temperature studied and on the value of the ratio of Cu(II)/Cu(I) present in the system (Bonan et al., 1981) and most of the reported values have been obtained under different leaching conditions and in different ranges of temperature.

This paper presents the results of a study of the dissolution of chalcopyrite under conditions typical of those that could be expected in a heap leach process. Although the leach times are long in order to achieve appreciable extents of dissolution of copper, it has been considered important to ensure that the observed effects are unambiguously due to the dissolution of chalcopyrite and not to the dissolution of small amounts of copper oxides or secondary sulphides. As can be appreciated, control of the leach conditions in an experimental run at constant potential over several months can be difficult and subject to many external constraints. For this reason, the use of a temperature of 35°C was selected as a baseline condition as a compromise between actual heap leach conditions which are unlikely to be above 25°C and the length of the experimental runs.

Part 3 of this series will discuss the experimental results obtained in Parts 1 and 2 and will present additional experimental data relevant to the mechanism of the dissolution process. Finally, alternative mechanisms will be presented which are consistent with the data presented in all three parts.
2. Experimental

2.1. Materials

As described in previous paper of this series chalcopyrite concentrates were obtained by flotation from operations in Chile and the USA. Most experiments were carried out with the -38+25 µm for Concentrate 1 and the -38 µm size fractions for concentrates 3 and 4. The numbering of these materials is consistent with that used in Part 1. The chemical analyses of the screened samples are shown in Table 1 and mineralogical data obtained from mineral liberation analyses (MLA) are presented in Table 2. Concentrate 1 contained chalcopyrite as the major sulfide mineral, with only small amounts of bornite and enargite; while concentrate 3 contained a significant quantity of pyrite and some minor secondary copper sulfides. The mineralogy of Concentrate 4 was not quantitatively determined but a previous sample of concentrate from the same ore had shown that copper was present as chalcopyrite with a very small amount of bornite as the only other copper mineral. Most of the studies were conducted with Concentrate 1.

2.2. Leaching experiments

Leaching experiments were carried out in mechanically agitated instrumented reactors constructed at Murdoch University using the method described in Part 1 of this series. Most experiments were conducted under standard conditions of 35°C using a solution which initially contained 0.2M HCl and 0.5g/L copper(II) ions as these concentrations were considered typical of those that could be expected in the raffinate
from a solvent extraction circuit as part of a heap leach process using chloride on hypogene ore.

3. Results and discussion

3.1. The effect of the dissolution of secondary copper sulfide minerals

In order to establish the extent to which the dissolution of other copper minerals can affect or mask the dissolution of chalcopyrite, Concentrate 3 was leached over an extended period under standard conditions. At intervals of approximately 100 h, solid samples were taken, filtered, washed and dried before being subjected to mineralogical analysis using MLA.

Mineralogical data from the feed and intermediate samples was used to estimate the extent of dissolution of each copper mineral using the quartz content as an indicator of mass loss during leaching and the results are shown in Figure 1. It is apparent that the small amount of chalcocite leaches very rapidly, followed by covellite and bornite, while chalcopyrite leaching is slow, as expected. However, of significance is the observation that chalcopyrite is leaching during the period of dissolution of other minerals with about 50% chalcopyrite dissolved in the time required to leach 90% of the other sulfides.

The results of dissolution of copper and iron obtained using chemical analysis of copper and iron in each solid sample from the MLA data were compared with results of dissolution obtained from AAS analyses of solution samples. The comparative results for copper presented in Figure 2 show that the MLA technique used provides reasonably
accurate estimates of the extent of dissolution of copper as calculated from that of the individual minerals. Results obtained with Concentrate 3 were therefore not used to quantitatively assess chalcopyrite dissolution as the costs of MLA analyses for every experimental run would have been prohibitive.

3.2. The effect of the type of agitation

There is a common agreement (Burkin, 2001) that the rate of dissolution of chalcopyrite in either chloride or sulfate solutions is not promoted by increased agitation. This is expected because the rate of dissolution is not controlled by mass transfer to the mineral surface (Dutrizac, 1981). Simple calculations of the rate of mass transport of typical reagents to suspended chalcopyrite particles show that these rates are several orders of magnitude less than actually observed under ambient conditions. Adequate agitation must simply be provided to keep the particles in suspension and prevent agglomeration and inhomogeneity in solution.

The type of agitation can affect the kinetics as shown by the data in Figure 3 which summarizes the results obtained with two different types of agitation during the leaching of Concentrate 1. It is obvious that under the same leaching conditions, the rate is noticeably higher when the leach reactor is magnetically agitated than when is it mechanically agitated with a titanium impellor. These results confirm that significant abrasion of the chalcopyrite mineral particles can occur in a magnetically stirred reactor with a resulting greater rate of dissolution. For this reason, all experiments were conducted in mechanically stirred reactors in which this effect is minimal.
3.3. The effect of particle size

It is generally accepted that fine grinding promotes more rapid dissolution of chalcopyrite and that the rate of chalcopyrite leaching increases in direct proportion to the initial surface area. However, as pointed out, (Dutrizac, 1981) problems with obtaining a well characterized surface area have resulted in erroneously reported results that the rate of dissolution is independent of surface area. In order to confirm this effect, two size fractions of the Concentrate 1 were leached under standard conditions at controlled potential. Figure 4 shows clearly that the rate increases as the particle size decreases.

3.4. The effect of pulp density

The effect of pulp density was studied using three different amounts of Concentrate 1 under standard conditions of 0.2 M HCl, 0.5 g L$^{-1}$ Cu(II) at 35 °C under controlled potential using either oxygen or nitrogen sparging for control. Figure 5 summarizes the leaching curves obtained. The curves at all pulp densities studied are essentially linear and there is no clear trend with increasing pulp density. Control of the potential was found to be considerably easier at the higher pulp densities due to the increased rate of consumption of dissolved oxygen.
3.5. The effect of the concentration of chloride

The leaching rate of copper from both Concentrate 1 and Concentrate 3 was studied by using solutions containing 0.2 M HCl, 0.5 g L\(^{-1}\) copper ions and increasing sodium chloride concentrations at 35 °C at controlled potential. Figure 6 and Figure 7 show that the rate of dissolution does not appear to be significantly affected by the total chloride ion concentration under these conditions. These results confirm preliminary observations that the presence of chloride ions is necessary to improve the leaching kinetics, but that high concentrations of chloride are not essential under the conditions studied.

Although a high chloride concentration does not increase the rate of dissolution of chalcopyrite under the present conditions, chloride ions play a very important role in that the rate of oxidation of copper(I) and iron(II) by dissolved oxygen is enhanced at high chloride concentrations (Miki and Nicol, 2008). In the absence of bacterial oxidation, this is a most important component of any possible chloride-based heap leaching operation. It should be noted that much of the published data showing the effect of chloride on the rate of leaching of chalcopyrite were obtained under different conditions of higher temperature, different acid media and in the absence of controlled potential. Therefore, a comparison between many published observations and the present study is difficult. However, most studies agree that higher concentrations of chloride ions do not result in greater rates of copper extraction (Dutrizac, 1978; Hirato et al., 1987; Lu et al., 2000a; Wilson and Fisher, 1981).

Some authors have observed that the presence of sodium chloride during leaching resulted in the precipitation of iron as natrojarosite; and thus a lower iron recovery can be
3.6. The effect of cupric ion concentration

To examine the effect of the initial cupric ion concentration on the rate of leaching, experiments were carried out with Concentrate 1 using 0.2 M HCl solution with various initial concentrations of cupric ions at controlled potential. Figure 8 summarizes the leaching curves obtained at 35 °C. Complete dissolution of the copper under these conditions would result in a final cupric ion concentration of 3 g/L. All the curves are essentially linear and the leaching rate does not increase with increasing initial cupric ion concentration. However, the presence of a small amount of cupric ion is important in order to achieve an acceptable chalcopyrite leaching rate, but concentrations above about 0.1 g/L do not increase the rate of dissolution. These results differ from those found in literature, but again, conditions are very different in the current experiments. At higher temperatures and chloride concentrations the rate could be affected by increasing cupric ion concentrations.
3.7. Effect of iron(II) concentration

The effect of the iron(II) concentration (added as ferrous sulfate) on the leaching rate of copper from Concentrate 1 was examined under otherwise standard conditions under controlled potential at 35 °C. The results obtained are shown in Figure 9. For reference, the result obtained under standard conditions without addition of ferrous ions is included. It is obvious that the addition of ferrous ions apparently causes the rate to fall appreciably. However, it was difficult to control the potential and the higher potentials in the runs with ferrous ions may at least partially explain the lower reactivity in the presence of ferrous ions.

The present findings support the results of Dutrizac (1978, 1981) and Jones and Peters (1976) in sulfate media but not the results obtained by the same authors in chloride media for which they reported that the rate of leaching of chalcopyrite was unaffected by increasing amounts of ferrous ions at elevated temperatures under more strongly oxidizing conditions. In addition, the present results do not support the Japanese model (Hiroyoshi et al., 2000) in which an intermediate copper sulfide, suggested as Cu$_2$S, is formed in the low potential region by reduction of chalcopyrite by ferrous ions in the presence of copper ions.

\[
\text{CuFeS}_2 + 2\text{Fe}^{2+} + \text{Cu}^{2+} = 2\text{Cu}_2\text{S} + 2\text{Fe}^{3+}
\]

In terms of this mechanism, the intermediate Cu$_2$S is more rapidly oxidized than chalcopyrite and this promotes enhanced copper extraction in the presence of cupric and ferrous ions.
3.8. Effect of pH

To investigate the effect of pH on the rate of dissolution, leaching tests were carried out with both Concentrate 1 and Concentrate 3 at 35 °C at potentials within the potential window. The pH was adjusted with hydrochloric acid and sodium chloride added to maintain an approximately constant chloride concentration. As is obvious from Figures 10 and 11, linear rates were obtained with Concentrate 1 which increase somewhat with increasing pH although the effect is not great. In the early stages of the dissolution at the low pH values it was very difficult to control the potential at the desired value and it was necessary to introduce nitrogen gas into the reactors to reduce the potential. This is shown by a comparison of the potentials for two experiments at high and low pH. Thus, as shown for the data at pH 0.34, the rate decreased during periods of high potential and increased during periods of low potential.

This sensitivity to small changes in dissolved oxygen concentration makes the control of potential more difficult and is due to the enhanced rates of oxidation of copper(I) by dissolved oxygen at low pH (Nicol 1984). On the other hand, according to Dutrizac (1981), low acidity must be avoided due to iron hydrolysis and precipitation which can affect the leaching process. In the current leaching experiments, visible precipitation products were observed at pH 2.1 and the dissolution of iron was considerably lower than that of copper as shown by the results in Figure 12 for the experimental conditions of Figure 11.

Preliminary X-ray diffraction analysis showed that the iron precipitate was a very poorly crystalline akaganite. However, it appears that the dissolution of copper was not
affected by this precipitation which is presumably not occurring on the surface of the mineral even at the highest pH tested.

3.9. Effect of temperature

Figure 12 summarizes the effect of various temperatures on the rate of copper dissolution from Concentrate 1 and Figure 13 shows the data for Concentrate 4 under otherwise standard conditions at controlled potential. Estimates of the rates of dissolution were obtained from the slopes of the linear sections at each temperature. In the case of Concentrate 4, the initial slopes were used because of curvature of the plots due to the fact that a closely sized fraction was not used for this material. The Arrhenius plots obtained using these rates are shown in Figure 14 from which very similar activation energies of 72 kJ mole\(^{-1}\) for Concentrate 1 and 73 kJ mole\(^{-1}\) for Concentrate 4 are obtained. These high values of the activation energy are not unexpected given the very slow rates of dissolution which are due to slow chemical or electrochemical processes occurring on the surface of the mineral. The somewhat higher rates for Concentrate 4 are due to the finer mean particle size used for this material.

4. Conclusions

An increase in concentration of chloride ions in solution does not increase the leaching rate of chalcopyrite concentrates. The presence of chloride ions is fundamental for enhanced leaching kinetics, but high concentrations are not essential. It should be
noted that although an increase in the concentration of chloride ions does not increase the leaching rate, previous paper Part 1 of this series has shown that high chloride concentrations can extend the potential window to higher values.

Arrhenius plots are approximately linear over the range of temperature employed with an apparent activation of energy of 73 kJ mole\(^{-1}\) for Concentrate 1 and 71 kJ mole\(^{-1}\) for the Concentrate 3.

Although the presence of cupric ions is essential for enhanced dissolution rates increased concentrations do not improve the leaching rate in the optimum potential window. Addition of ferrous ions appears to decrease the rate of dissolution but this may be due to the presence of ferric ions and somewhat higher potentials. This observation is in contrast to that claimed in the Japanese model which requires the presence of both ferrous and cupric ions for enhanced leaching rates at low potentials.

It was confirmed that the rate of dissolution of chalcopyrite is proportional to the surface area under the conditions of the present experiments. Attention should be paid to the type of agitation used in leaching experiments in that it was found that magnetically agitated slurries leached at a higher rate due to abrasion/breakdown of the concentrate particles. Although an increase in the pulp density does not increase the leach rate appreciably, it assists in that control of the potential is facilitated in the presence of adequate dissolved oxygen in the system.

The rate is essentially independent of acid concentration in the pH range of 0.5 to 2, but a fairly low pH is necessary to keep iron(III) in solution. There is no obvious evidence that precipitation of iron(III) oxides or jarosite inhibits the rate of dissolution.
Mineralogical studies of samples taken at various times during an experiment have demonstrated that copper dissolves preferentially from chalcocite followed by covellite and bornite. Chalcopyrite appears to dissolve at a slower rate during dissolution of the other secondary sulfide minerals.

Acknowledgements

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5. References


Figure 1  Dissolution of copper sulfide minerals from Concentrate 3 under standard conditions at a controlled potential of 580 mV as obtained by MLA analysis. (■) Cu$_2$S, (▲) Cu$_5$FeS$_4$, (♦) CuS, (●) CuFeS$_2$.

Figure 2  Dissolution of copper from Concentrate 3 as measured by analysis of solution samples by AAS(▲) and intermediate solid samples by MLA(♦). Data from Figure 1.

Figure 3  Effect of the type of agitation on the rate of copper dissolution from Concentrate 1. a) Instrumented reactor with Ti impellor (♦) and b) Magnetically stirred reactor (▲).

Figure 4  Leaching curves for the dissolution of (♦) +25-38 µm and (▲) -25 µm size fractions of Concentrate 1 under standard conditions.

Figure 5  Effect of increasing pulp density on the rate of copper dissolution from Concentrate 1 under standard conditions (■) 1% solids, (▲) 2% solids and (♦) 3% solids.

Figure 6  Effect of chloride concentration (■) 7 g/L, (▲) 20 g/L, (♦) 70 g/L on the rate of copper dissolution from Concentrate 1 under otherwise standard conditions.

Figure 7  Effect of chloride concentration (■) 7 g/L, (▲) 20 g/L, (♦) 50 g/L on the rate of copper dissolution from Concentrate 3 under otherwise standard conditions.

Figure 8  Effect of initial cupric ion concentration (♦) 0.1g/L, (▲) 0.5g/L, (●) 1.0g/L on copper dissolution from Concentrate 1 under otherwise standard conditions.

Figure 9  Effect of initial ferrous ion concentration (♦) zero, (▲) 0.1M, (■) 1.0M on copper dissolution from Concentrate 1 under otherwise standard conditions. Also shown are the solution potentials (open symbols).
Figure 10  Effect of pH ( ■ ) 0.34, ( ✷ ) 0.7, ( ▲ ) 1.3 and ( ● ) 2.1 on copper dissolution from Concentrate 1 in 1 M chloride containing 0.2M HCl. Also shown are the solution potentials (open symbols) for the experiments at pH 0.34 and pH 2.1.

Figure 11  Effect of pH, ( ■ ) 1.2, ( ▲ ) 1.5, ( ● ) 2.0 on the rate of copper dissolution from Concentrate 3 in 0.4M chloride containing 0.2M HCl. Also shown is the rate of iron dissolution ( □ ) at pH 2.0.

Figure 12  Effect of temperature ( ■ ) 25°C ( ✷ ) 35°C ( ▲ ) 50°C ( × ) 65°C ( ● ) 75°C on the dissolution of copper from Concentrate 1 under otherwise standard conditions.

Figure 13  Effect of temperature ( ■ ) 25°C ( ✷ ) 35°C ( ▲ ) 50°C ( ● ) 75°C on the dissolution of copper from Concentrate 4 under otherwise standard conditions.

Figure 14  Arrhenius plots for the dissolution of copper from Concentrate 1 ( ▲ ) and Concentrate 4 ( ■ ) under standard conditions.
Figure 1

Figure 2
Figure 3

Figure 4
Figure 5

Figure 6
Figure 9

Figure 10
Figure 11

Figure 12
Figure 13

Figure 14
Table 1. Chemical composition (element, mass %)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (µm)</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Ag (ppm)</th>
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<tr>
<td>Concentrate 1</td>
<td>+25-38</td>
<td>30.8</td>
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<tr>
<td>Concentrate 3</td>
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<td>13.2</td>
<td>21.8</td>
<td>23.3</td>
<td>30</td>
</tr>
<tr>
<td>Concentrate 4</td>
<td>-38</td>
<td>28.0</td>
<td>27.3</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 2. Mineralogical composition of concentrates (mass, %)

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<thead>
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<th>Mineral</th>
<th>Conc. 1 +25-38 µm</th>
<th>Conc. 3 -38 µm</th>
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</thead>
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<td>Chalcocite</td>
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</tr>
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<td>Chalcopryrite</td>
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<td>Bornite</td>
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<td>Brochantite</td>
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</tr>
<tr>
<td>Chrysocolla</td>
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<td>0.04</td>
</tr>
<tr>
<td>Other Cu</td>
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<td>0.05</td>
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<td>Galena</td>
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<td>Gangue</td>
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